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A general method for regioselective Heck arylation of electron-rich *N*-acyl-*N*-vinylamine with aryl halides

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Abstract

A highly efficient protocol for the Pd-catalyzed regioselective Heck arylation of the electron-rich olefin *N*-acyl-*N*-vinylamine with aryl halides has been developed. In the presence of hydrogen-bond donor $[H_2NiPr_2][BF_4]$ as an additive, this proceeds smoothly in isopropanol to afford exclusively the branched products in high yields.

The Heck reaction is an important transformation that efficiently functionalizes aromatic halides with olefins in the presence of palladium catalysts. Considerable advances in this reaction have been made through the development of more active catalytic systems, but the synthetic utility is often limited by the poor regioselectivity.[1] In general, the Heck reaction works efficiently with electron-withdrawing olefins to give the terminal products (often referred to as β-products), while the arylation of electron-rich olefins such as enol ethers and enamides almost always generates a mixture of internal α- and terminal β-products.[2] The Heck reaction is believed to proceed via two pathways, one ionic leading to the branched product, and the other neutral producing the linear variant (Scheme 1).[2,3] In the earlier studies, it was found that high α/β regioselectivity could be obtained by employing aryl triflates or by adding stoichiometric halide scavengers when aryl iodides and bromides were used.[1a,2]

In recent publications, we have reported that imidazolium ionic liquids in combination with the readily available $Pd(OAc)_2$ and DPPP (1,3-bis(diphenylphosphino)propane) formed an excellent catalytic system, with which electron-rich olefins could be arylated highly regioselectively by aryl halides without recourse to triflates or halide scavengers.[4,5] Similar results in ionic liquids have also been observed by other groups.[6] More recently, we have found that these regioselective reactions could be greatly accelerated by hydrogen-bond-donating ammonium salts, and the reactions could be carried out not only in imidazolium ionic liquids but also in common organic solvents.[7] As a result, the electron-rich olefins such as vinyl ethers and tertiary *N*-vinylamides could be regioselectively arylated with aryl halides to provide good yields in shorter reaction time. Following our continued interest in regioselective arylation of electron-rich olefins, herein we report that in the presence of hydrogen-bond-donating ammonium salt, the regioselective Heck arylation of electron-rich olefin *N*-acyl-*N*-vinylamine lacking an *N*-alkylsubstituent with aryl halides can be carried out smoothly in isopropanol, exclusively generating the branched products in high yields. These arylated enamides are important precursors in the synthesis of optically active amines by transition-metal catalyzed asymmetric reactions.[8]

Several methods to prepare internally arylated *N*-acyl enamides have been reported in the literature, and they all suffer from either low yields, or low functional group tolerance or both.[9] Recently, an alternative approach involving Pd-catalyzed Heck reaction of aryl triflates with

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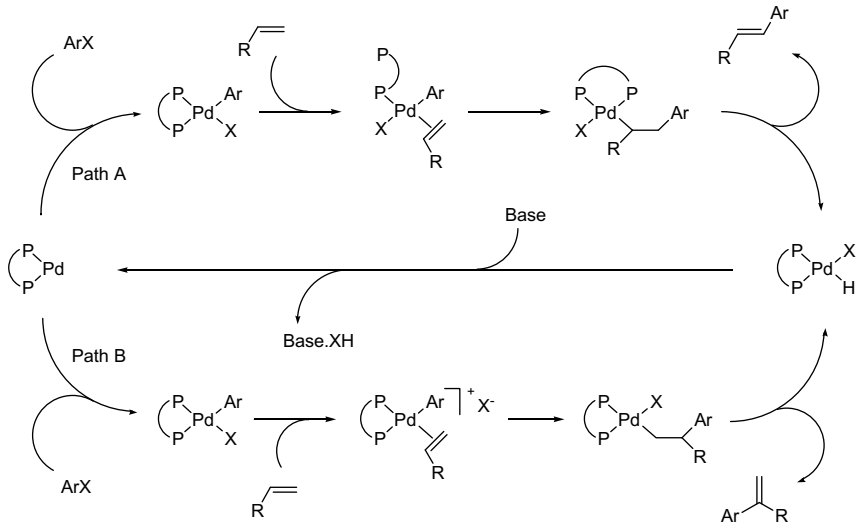


Scheme 1.

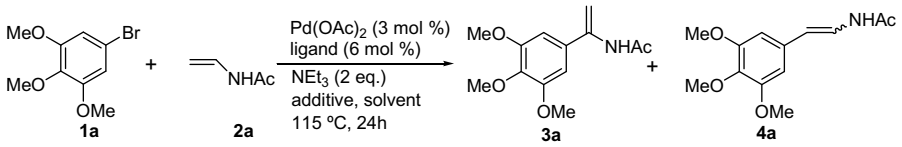
N-acyl enamides has been reported by two groups.[10] With this efficient protocol, highly regioselective α-arylation of *N*-acyl enamides can be accomplished in good yields. It is notable that this method works effectively for the preparation of aryl-*N*-acyl enamides bearing functionality that would not be tolerated by the previous stoichiometric methods. However, a drawback of this chemistry is that it requires the use of base-sensitive, thermally labile and costly triflates. In this context, it is very attractive to develop an additional protocol for the efficient arylation of *N*-acyl enamides with inexpensive and easily accessible aryl halides.

Considering the successful regioselective arylation of various electron-rich olefins in ionic liquids, we first attempted the α-arylation of *N*-vinylacetamide **2a** in [bmim][BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate) with aryl bromide **1a** as the model substrate. The arylation was carried out in the ionic liquid [bmim][BF_4] at 115 °C under the previously employed conditions, where the active catalyst was generated in situ from $Pd(OAc)_2$ and DPPP.[4,5,7] However, no reaction was observed after 24 h. In our early study, it was found that the reaction of aryl bromide with *N*-methyl-*N*-vinylacetamide or *N*-vinyl pyrrolidone generated no desired product in ionic liquid [bmim][BF_4]; but the addition of DMSO as a cosolvent led to the desired product.[4a] With this in mind, we then examined the reaction in [bmim][BF_4]/DMSO. However, still no reaction was observed. Other solvents were screened, and the results are shown in Table 1. Surprisingly, complete conversions were obtained in almost all solvents. No β-substituted **4a** product was detected; however, the yields of the target compound **3a** were different. Although good results were obtained in the reaction of aryl triflates with the enamide in dioxane,[10b] only 24% yield was produced in our case (entry 3). Lower yields were obtained in DMF or toluene (entries 4 and 5). Switching to DMSO led to 29% yield, and the best result was achieved in isopropanol (37% yield, entries 5 and 6). In all the reactions tested, the main side products arose from homo-coupling and debromination.

We have recently disclosed that the regioselective arylation of electron-rich olefins can be accelerated by the potential hydrogen-bond donors such as [H_2NiPr_2][BF_4].[7] The effect of the additive was investigated in this study. Introduction of 1.5 equiv of [H_2NiPr_2][BF_4] to [bmim][BF_4] had no clearly promoting effect on the reaction rate (entry 7). When using [bmim][BF_4]/DMSO mixture, an 80% conversion was observed, but only 10% desired product was obtained. Better results were obtained in DMSO, dioxane, toluene and DMF (entries 10–13). And the best result was observed in isopropanol, in which 50% yield was achieved (entry 14). The addition of non-hydrogen-bonded donor [NBu_4][BF_4] gave rise to only slightly improved results (entry 15). Therefore, in our subsequent study, isopropanol was the choice of solvent and [H_2NiPr_2][BF_4] was chosen as promoter. This study revealed that the amount of [H_2NiPr_2][BF_4] played a crucial role. When increasing the amount of [H_2NiPr_2][BF_4] in isopropanol from 1.5 to 5 equiv, the reaction time could be reduced to 15 h with 78% yield (entry 16). Remarkably increasing the additive to 10 equiv enabled the reaction to go to completion in 8 h with 92% isolated yield (entry 17). However, further increase of the additive had no significant effect on the rate (entry 18). According to Jutand's recent reports,[11] the higher reaction rate is probably due to a higher ionic strength, which favours the formation of cationic Pd(II) intermediate in pathway B, and so the product **3a**. However, hydrogen bonding between the additive and the bromide anion may also contribute to the formation of the Pd(II) species,[7,12] as [NBu_4][BF_4] is less effective.

We then examined various bidentate phosphines aiming to find a more suitable ligand. The results are listed in Table 2. The linear product was not observed regardless of the ligand used. However, the desired product was not

Table 1
Solvent effect on the Heck arylation of *N*-vinylacetamide



Entry	Solvent	Additive (equiv)	Conv.[a] (%)	Yield[b] (%)
1	[bmim][BF_4]	None	nd	
2	[bmim][BF_4]/DMSO	None	nd	
3	1,4-Dioxane	None	100	24
4	DMF	None	100	18
5	Toluene	None	100	17
6	DMSO	None	100	29
7	Isopropanol	None	100	37
8	[bmim][BF_4]	[H_2NiPr_2][BF_4] (1.5)	nd	
9	[bmim][BF_4]/DMSO	[H_2NiPr_2][BF_4] (1.5)	80	10
10	1,4-Dioxane	[H_2NiPr_2][BF_4] (1.5)	100	37
11	DMF	[H_2NiPr_2][BF_4] (1.5)	100	25
12	Toluene	[H_2NiPr_2][BF_4] (1.5)	100	28
13	DMSO	[H_2NiPr_2][BF_4] (1.5)	100	40
14	Isopropanol	[H_2NiPr_2][BF_4] (1.5)	100	50
15	Isopropanol	[NBu_4][BF_4] (1.5)	100	40
16[c]	Isopropanol	[H_2NiPr_2][BF_4] (5)	100	76
17[d]	Isopropanol	[H_2NiPr_2][BF_4] (10)	100	92
18[d]	Isopropanol	[H_2NiPr_2][BF_4] (15)	100	92

[a] Determined by ^{1}H NMR data; >99/1 α/β ratios based on NMR.
[b] Isolated yields.
[c] Reaction time 15 h.
[d] Reaction time 8 h.

Table 2
Ligand effect on the Heck arylation of *N*-vinylacetamide[a]

Entry	Ligand	Time (h)	Conv.[b] (%)	Yield[c] (%)	α/β
1	None	12	20	nd	
2	DPPE[d]	12	25	nd	
3	DPPP	8	100	92	>99/1
4	*rac*-BINAP[d]	10	100	41	>99/1
5	DPPF[d]	8	100	90	>99/1
6	DPPB[d]	12	100	40	>99/1

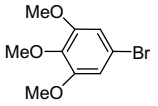
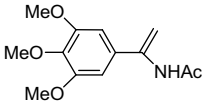
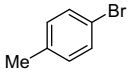
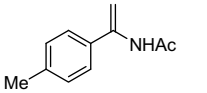
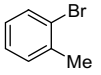
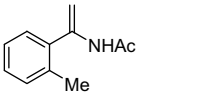
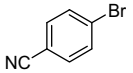
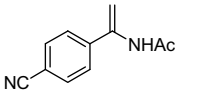
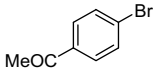
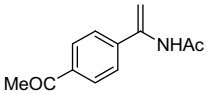
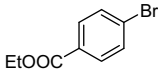
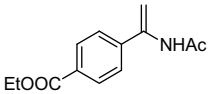
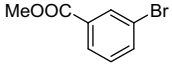
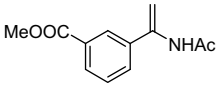
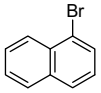
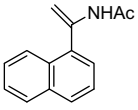
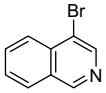
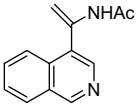
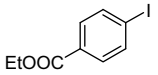
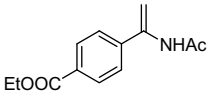
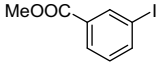
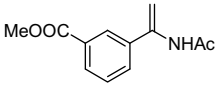
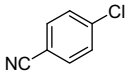
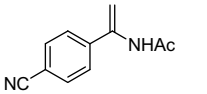
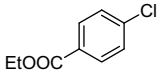
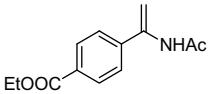
[a] Conditions: **1a** (1.0 equiv), **2a** (3 equiv), $Pd(OAc)_2$ (0.03 equiv), DPPP (0.06 equiv), NEt_3 (2 equiv), [H_2NiPr_2][BF_4] (10 equiv), isopropanol, reflux.
[b] Determined by ^{1}H NMR data. When **4a** was not detected, an α/β ratio of >99/1 was assigned.
[c] Isolated yields.
[d] DPPE: 1,2-bis(diphenylphosphino)ethane; DPPB: 1,4-bis(diphenylphosphino)butane; DPPF: 1,1′-bis(diphenylphosphino)ferrocene; *rac*-BINAP: (±)-2-2′-bis(diphenylphosphino)-1,1′-binaphthalene.

detected with DPPE as the ligand. The combination of DPPP and $Pd(OAc)_2$ led to the best result (entry 3), and reaction with DPPF gave similar results (entry 5). Lower yields were observed when using BINAP and DPPB. Switching the base from NEt_3 to others such as Cy_2NMe and DIPEA (*N*,*N*-diisopropylethylamine) showed no significant promoting effect in terms of yields.

Having established the reliable conditions for the arylation of enamide, we then examined the scope of this reaction with a variety of aryl halides and **2a**, and the results are listed in Table 3.[14] We first focused on the olefination of aryl bromides. As shown in Table 3, bromobenzenes bearing substituents at various positions are all effective coupling partners, providing exclusively the branched products with high isolated yields. For example, olefination of 4-bromobenzonitirle **1d** with enamide **2a** led to the product in 93% yield (entry 4). When the corresponding aryl triflate was employed, only 75% yield was obtained.[10b] However, a lower yield was found in the reaction of *ortho*-substituted bromide **1c** with enamide **2a** (entry 3). It appears that longer reaction time is necessary for the olefination of bromides with electron-withdrawing substituents (entries 4–7). This has been noticed before and may result from a slower olefin insertion process, which can be viewed as an intramolecular nucleophilic attack.[3a] The regioselective reaction was also extended to heteroaromatic bromides. For example, good result was achieved in the reaction of 4-bromoisoquinoline (entry 9). Since the reaction time was not optimized, shorter reaction time may be possible for these cross-coupling processes.

This reaction is not limited to aryl bromides, and aryl iodides participated equally well. For example, the reactions of aryl iodides **1j** and **1k** also afforded good results in shorter reaction times (entries 10 and 11). The utility of this new protocol was further demonstrated by the arylation of enamide with aryl chlorides (entries 12 and 13). However, the reactions were sluggish, furnishing the corresponding products in less than 50% yield after 45 h. It is

Table 3
Heck arylation of *N*-vinylacetamide with aryl halides in isopropanol[a]

Entry	Aryl bromide		Time (h)	Product		Yield (%)
1		**1a**	8		**3a**	92
2		**1b**	8		**3b**	85
3		**1c**	18		**3c**	72
4		**1d**	19		**3d**	93
5		**1e**	15		**3e**	86
6		**1f**	12		**3f**	89
7		**1g**	12		**3g**	82
8		**1h**	8		**3h**	87
9		**1i**	18		**3i**	71
10		**1j**	5		**3f**	83
11		**1k**	5		**3g**	81
12		**1l**	45		**3d**	32
13		**1m**	45		**3f**	41

[a] Conditions: aryl halide (1.0 equiv), olefin (3 equiv), $Pd(OAc)_2$ (0.03 equiv), DPPP (0.06 equiv), NEt_3 (2 equiv), $[H_2NiPr_2][BF_4]$ (10 equiv), isopropanol, reflux.

also notable that no competing amidation reaction was observed in these reactions.[13]

In conclusion, we have developed an efficient method for the highly regioselective Heck arylation of *N*-vinylacetamide with aryl halides, avoiding the use of aryl triflates or halide scavengers. The key to the success of this method lies in the use of an ammonium salt, $[H_2NiPr_2][BF_4]$, as the additive, which is believed to facilitate the formation of charged organopalladium intermediate, thereby promoting the ionic pathway of the Heck reaction.

Acknowledgements

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References and notes

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14. *General procedure for the arylation of* **2a**: An oven-dried, two-necked round-bottom flask containing a stir bar was charged with aryl halide **1** (1.0 mmol), **2a** (170 mg, 2.0 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol), DPPP (25 mg, 0.06 mmol), $[H_2NiPr_2][BF_4]$ (1.89 g, 10 mmol), and dry

isopropanol (2 mL) under nitrogen at room temperature. After degassing three times, NEt_3 (202 mg, 2 mmol) was injected. The flask was placed in an oil bath, and the mixture was stirred and heated under reflux. The reaction was monitored by TLC. After the reaction went to completion, saturated aqueous $NaHCO_3$ was added, and the aqueous phase was extracted with dichloromethane three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified via flash chromatography on silica gel using a mixture of ethyl acetate and hexane (1/1 to 1/5 in volume). *N-Acetyl-1-(3′,4′,5′-trimetoxyphenyl)-ethenamine* (**3a**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.13 (s, 3H), 3.80 (s, 3H), 3.84 (s, 6H), 5.02 (s, 1H), 5.83 (s, 1H), 6.60 (s, 2H), 7.08 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1, 55.8, 60.6, 102.2, 103.7, 128.6, 132.1, 140.7, 153.3, 169.3. HRMS $C_{13}H_{17}NO_4$ calcd: 251.1158; found, 251.1158. *N-Acetyl-1-(4′-methylphenyl)-ethenamine* (**3b**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10 (s, 3H), 2.35 (s, 3H), 5.08 (s, 1H), 5.88 (s, 1H), 6.77 (br s, 1H), 7.30 (d, $J = 7.9$ Hz, 2H), 7.45(d, $J = 7.9$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5, 23.9, 101.2, 125.4, 128.8, 134.9, 137.9, 140.0, 168.5. HRMS $C_{11}H_{13}NO$ calcd: 175.0997; found, 175.0999. *N-Acetyl-1-(2′-methylphenyl)-ethenamine* (**3c**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H), 2.35 (s, 3H), 4.70 (s, 1H), 6.06 (s, 1H), 6.65 (br s, 1H), 7.09–7.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.5, 23.8, 102.2, 126.0, 128.6, 129.2, 130.5, 135.8, 138.9, 140.8, 169.5. HRMS $C_{11}H_{13}NO$ calcd: 175.0997; found, 175.0996. *N-Acetyl-1-(4′-cyanophenyl)-ethenamine* (**3d**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.97 (s, 3H), 5.06 (s, 1H), 5.75 (s, 1H), 6.84 (br s, 1H), 7.45–7.47 (m, 2H), 7.55–7.61 (m, 2H). ^{13}C NMR (75 MHz, CD_3CN): δ 23.9, 106.2, 112.4, 119.6, 127.9, 133.2, 141.7, 143.4, 170.4. HRMS $C_{11}H_{10}N_2O$ calcd: 186.0793; found, 186.0796. *N-Acetyl-1-(4′-acetylphenyl)-ethenamine* (**3e**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12 (s, 3H), 2.53 (s, 3H), 5.05 (s, 1H), 5.80 (s, 1H), 7.03 (br s, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.84 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.3, 28.7, 106.7, 126.2, 128.3, 136.5, 140.8, 141.6, 169.5, 197.6. HRMS $C_{12}H_{13}NO_2$ calcd: 203.0946; found, 203.0949. *Ethyl 4-(1-acetamidovinyl) benzoate* (**3f**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39 (t, $J = 7.2$ Hz, 3H), 2.12 (s, 3H), 4.36 (q, $J = 7.2$ Hz, 2H), 5.18 (s, 1H), 5.85 (s, 1H), 7.01 (br s, 1H), 7.46 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 24.4, 61.1, 104.8, 125.9, 129.9, 130.5, 142.4, 152.6, 166.1, 169.2. HRMS $C_{13}H_{15}NO_3$ calcd: 233.1052; found, 233.1055. *Methyl 3-(1-acetamidovinyl) benzoate* (**3g**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.08 (s, 3H), 3.85 (s, 3H), 5.08 (s, 1H), 5.80 (s, 1H), 6.81 (br s, 1H), 7.43 (t, $J = 7.8$ Hz, 1H), 7.55 (d, $J = 7.7$ Hz, 1H), 7.94 (d, $J = 7.7$ Hz, 1H), 8.06 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.4, 52.2, 103.9, 127.0, 128.6, 128.8, 129.7, 130.6, 138.6, 139.8, 166.7, 169.8. HRMS $C_{12}H_{13}NO_3$ calcd: 219.0895; found, 219.0899. *N-Acetyl-1-(2′-naphthyl)-ethenamine* (**3h**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H), 4.94 (s, 1H), 6.30 (s, 1H), 6.73 (br s, 1H), 7.46–7.54 (m, 4H), 7.86–7.87 (m, 2H), 7.88–7.90 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.4, 103.6, 125.2, 125.4, 126.2, 126.7, 126.8, 128.4, 129.0, 131.0, 133.7, 136.7, 139.5, 169.0. HRMS $C_{14}H_{13}NO$ calcd: 211.0997; found, 211.0999. *N-Acetyl-1-(3′-isoquinolinyl)-ethenamine* (**3i**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.97 (s, 3H), 4.79 (s, 1H), 6.13 (s, 1H), 7.50–7.53 (m, 1H), 7.62–7.68 (m, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.91 (s, 1H), 7.94 (d, $J = 8.5$ Hz, 1H), 8.20 (s, 1H), 8.76 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.3, 104.1, 123.1, 126.9, 127.4, 129.1, 130.8, 131.0, 132.7, 135.5, 141.3, 151.7, 168.2. HRMS $C_{13}H_{12}N_2O$ calcd: 212.0950; found, 212.0955.