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Palladium-Catalyzed Hydrocarbonylative C−N Coupling of Alkenes with Amides

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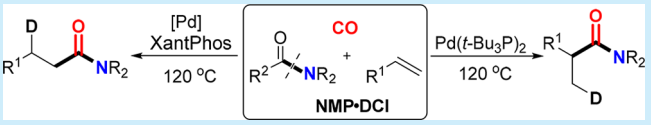
Supporting Information

ABSTRACT: An efficient palladium-catalyzed hydrocarbonylative C−N coupling of alkenes with amides has been developed. The reaction was performed via hydrocarbonylation of alkenes, followed by acyl metathesis with amides. Both intermolecular and intramolecular reactions proceed smoothly to give either branched or linear amides in high turnover number (3500) with NH_4Cl or NMP·HCl as a proton source under the palladium catalysis. This reaction offers a catalytic convenient approach to deuterated amides when inexpensive NMP·DCl served as a deuterium source.



Amide bonds are among the most important linkages for the construction of materials and medicinal molecules.[1] The increasing use of amides in life science and materials science has motivated the development of efficient methodology toward amides.[2,3] Among the numerous strategies for the preparation of amides, transition-metal-catalyzed hydroaminocarbonylation of simple alkenes and alkynes arguably provides the most direct access to these compounds from simple precursors.[4] Although Fe, Co, Ni, and Ru had been utilized as catalyst precursors in this area, these processes required harsh reaction conditions and resulted in poor chemoselectivity.[5] In contrast, recent studies from our group[6] and others[7−9] have demonstrated that the palladium catalytic system, initiated by palladium-hydride species, could address the above synthetic problem for delivering the corresponding target amides with high chemoselectivity and regioselectivity under relative mild reaction conditions. However, because of the fact that palladium hydride only can be produced in the relative acidic conditions,[6a] some special reaction conditions were required for simple aliphatic amines. Moreover, the high coordination abilities of the simple amines to transition metal would inhibit the desired reaction to some extent, via the formation of Werner complexes.[10] Therefore, the substitution of simple aliphatic amines in hydroaminocarbonylation by easier-to-handle synthetic equivalents is of considerable interest.

The catalytic transformation of abundant feedstocks into complex functional molecules is an ongoing challenge that has significant implications for sustainability of process in the chemistry industry. Lower-molecular amides, such as *N*,*N*-dimethylformamide (DMF) or *N*,*N*-diethylformamide (DMA), are abundant chemicals, which not only serve as excellent polar solvents for various reactions, but also act as either electrophilic or nucleophilic agents for some unique reactions.[11−13] In this context, DMF has long-been served as an effective amine source for aminocarbonylation of aromatic halides to complex functional amides in the presence of imidazole.[14] Despite the ease of transferring an amine group from the simple DMF, an interesting question is whether common amides, such as aryl amides and aliphatic amides derived from aliphatic acids with long chains, can be used for the hydroaminocarbonylation of simple alkenes. Inspired by these results and the amide metathesis reactions,[15] as well as our recent results on carbonylation chemistry,[6,16] we have become interested in employing amides as effective amine sources for the hydrocarbonylative C−N coupling of alkenes. We anticipated that the acylpalladium species generated from the hydrocarbonylation would be trapped by amides through acyl metathesis to give the desired amides. Herein, we report an efficient and simple approach to aliphatic amides directly from simple alkenes and amides in the presence of CO (see Scheme 1). Notably, the

Scheme 1. Catalytic Hydrocarbonylative C−N Coupling of Alkenes with Amides

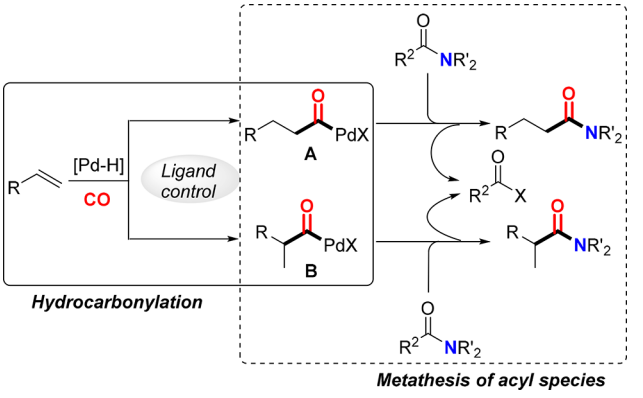


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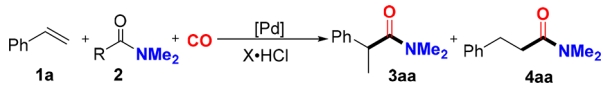
Table 1. Optimization of Reaction Conditions[a]



entry	[Pd]	ligand	X·HCl (mol %)	2 (mL)	yield (%)	3aa:4aa[b]
1	$Pd(CH_3CN)_2Cl_2$	DPPB	NH_4Cl (200)	DMA (2)	<5	
2	$Pd(CH_3CN)_2Cl_2$	DPPH	NH_4Cl (200)	DMA (2)	24	60:40
3	$Pd(CH_3CN)_2Cl_2$	DPEPhos	NH_4Cl (200)	DMA (2)	30	40:60
4	$Pd(CH_3CN)_2Cl_2$	Xantphos	NH_4Cl (200)	DMA (2)	96	12:88
5	$Pd(CH_3CN)_2Cl_2$	Xantphos	NH_4Cl (200)	DMA (3)	98	11:89
6	$Pd(CH_3CN)_2Cl_2$	Xantphos	NH_4Cl (200)	DMF (3)	98	12:88
7	$Pd(CH_3CN)_2Cl_2$	Xantphos	NH_4Cl (5)	DMF (3)	62	16:84
8	$Pd(CH_3CN)_2Cl_2$	Xantphos	$NH_2OH·HCl$ (5)	DMF (3)	53	15:85
9	$Pd(CH_3CN)_2Cl_2$	Xantphos	NMP·HCl (5)	DMF (3)	98	15:85
10	$Pd(CH_3CN)_2Cl_2$	Xantphos	NMP·HCl (5)	DMA (3)	7	8:92
11	$PdCl_2$	Xantphos	NMP·HCl (5)	DMF (3)	87	15:85
12	$PdOAc_2$	Xantphos	NMP·HCl (5)	DMF (3)	82	14:86
13[c]	$Pd(t\text{-}Bu_3P)_2$		NMP·HCl (5)	DMF (3)	43	95:5
14[c]	$Pd(t\text{-}Bu_3P)_2$		NMP·HCl (20)	DMF (3)	98	96:4
15[c]	$Pd(t\text{-}Bu_3P)_2$			DMF (3)	0	
16[c]	$Pd(t\text{-}Bu_3P)_2$		NH_4Cl (200)	DMA (3)	92	91:9

[a]Reaction conditions: **1a** (1.0 mmol), [Pd] (0.02 mmol), ligand (0.025 mmol), CO (10 atm), 120 °C, 24 h. Yields were determined by GC analysis using *n*-cetane as the internal standard. [b]The ratios (**3aa**:**4aa**) were determined by GC-MS and GC analysis of crude product. [c]CO (30 atm).

regioselectivity can be tuned by the appropriate choice of ligand, and both the linear and branched amides can be constructed in a regiodivergent manner from a single alkene.

Initially, the hydrocarbonylative C−N coupling of styrene (**1a**) with DMA catalyzed by a palladium catalyst was investigated under 10 atm of CO. Based on our experiences with palladium-catalyzed hydroaminocarbonylation reactions,[6] a series of phosphine ligands were first investigated with NH_4Cl as proton source, which could facilitate the formation of palladium hydride.[6d] To our delight, the desired *N*,*N*-dimethylamides was obtained in 96% combined yield with good regioselectivity for exclusively giving the linear amide **4aa** as the main product when XantPhos was used as a ligand (Table 1, entries 1−4). Increasing the amount of DMA to 3 mL could slightly improve the yield of amides to 98% (Table 1, entry 5). As expected, DMF could also deliver the desired amides in 98% yield with good regioselectivity under the same reaction conditions (Table 1, entry 6). We supposed that the H atom contained in the DMF could be transferred to the final product via the formation of palladium-hydride species in the catalytic cycle. Indeed, the reaction could be performed well in the presence of a catalytic amount of NH_4Cl (5 mol % of NH_4Cl; see Table 1, entry 7). Further optimization of the reaction conditions demonstrated that excellent results were obtained when a catalytic amount of *N*-methyl-2-pyrrolidone hydrochloride (NMP·HCl) was utilized as an additive under otherwise identical reaction conditions (Table 1, entry 9). A control experiment demonstrated that only 7% yield was obtained when DMA was used as an amine source in the presence of 5 mol % of NMP·HCl (Table 1, entry 10). Examination of palladium precursors revealed that $Pd(CH_3CN)_2Cl_2$ created the most reactive catalyst for this transformation to give the linear amides, and other palladium precursors showed lower activity (Table 1, entries 10 and 11). To our great delight, using $Pd(t\text{-}Bu_3P)_2$ as the catalyst, the regioselectivity was changed to the opposite direction, favoring the branched amide **3aa** in moderate yield with excellent regioselectivity under 30 atm of CO (Table 1, entry 13). Increasing the loading of NMP·HCl to 20 mol % led to a marked improvement in reactivity, giving the amide products in 98% yield with excellent regioselectivity (Table 1, entry 14). As anticipated, no desired reaction occurred in the absence of acid (Table 1, entry 15). Similarly, with 2 equiv of NH_4Cl, the DMA could also be transferred to the desired amide **3aa** as the main product with excellent regioselectivity, albeit in a slightly lower yield (Table 1, entry 16).

With the optimal reaction conditions identified, investigation into the substrate scope for the present regiodivergent hydrocarbonylative C−N coupling reaction with a variety of amides was pursued. As shown in Table 2, the optimized reaction conditions proved to be effective for treatment of styrene (**1a**) with a series of *N*,*N*-dimethyl- or *N*,*N*-diethyl-substituted amides **2a**−**2f** affording the corresponding branched and linear amides in moderate to good yields with high regioselectivities. The aliphatic amides with long aliphatic chain **2c** or aromatic amide **2d** could be smoothly converted to the desired products in good yields with good to excellent regioselectivities (see Table 2, entries 3 and 4). Amide **2g** derived from piperidine was less reactive to give the desired branched and linear adducts in moderate yields with good to excellent regioselectivities. The reactions with morpholine-substituted amides **2h** and **2i** proceeded smoothly, affording the desired adducts in excellent yields with high regioselectivities, respectively. Although almost no desired reaction occurred with *N*-methyl formamide, **2k** and **2l** derived from benzylamine and aniline proved to be efficient partners for the present reaction and gave the corresponding amides in good yields with good to excellent regioselectivities. Almost no desired reaction occurred under the standard reaction conditions when a primary amide was employed as a coupling partner.

Having confirmed that common amides could be utilized as effective coupling partners for the present coupling reaction, we subsequently explored the use of DMF as a coupling partner for the hydrocarbonylative C−N coupling of a range of alkenes in the presence of catalytic amount of NMP·HCl. First, various branched *N*,*N*-dimethylamides could be prepared in the

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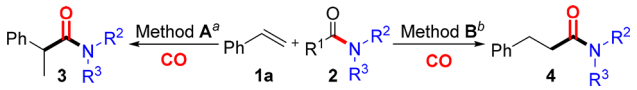
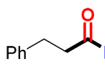
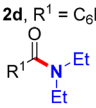
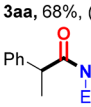
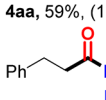
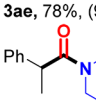
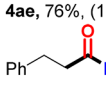
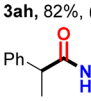
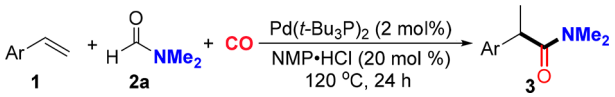
Table 2. Substrate Scope for Amides[a]



entry	2	3[c]	4[c]
			
1	**2a**, R^1 = H	**3aa**, 85%, (98:2)	**4aa**, 81%, (10:90)
2	**2b**, R^1 = CH_3	**3aa**, 81%, (91:9)	**4aa**, 82%, (9:91)
3	**2c**, R^1 = $CH_3(CH_2)_2$	**3aa**, 65%, (96:4)	**4aa**, 60%, (12:88)
4[d]	**2d**, R^1 = C_6H_5	**3aa**, 68%, (97:3)	**4aa**, 59%, (15:85)
			
5	**2e**, R^1 = H	**3ae**, 81%, (96:4)	**4ae**, 80%, (13:87)
6	**2f**, R^1 = CH_3	**3ae**, 78%, (96:4)	**4ae**, 76%, (13:87)
			
7	**2g**	**3ag**, 46%, (97:3)	**4ag**, 50%, (10:90)
			
8	**2h**, R^1 = H	**3ah**, 85%, (97:3)	**4ah**, 76%, (16:84)
9	**2i**, R^1 = CH_3	**3ah**, 82%, (95:5)	**4ah**, 80%, (11:89)
			
10	**2j**, R^1 = H, R^2 = CH_3	**3aj**, <5%	**4aj**, <5%
11[d]	**2k**, R^1 = H, R^2 = $C_6H_5CH_2$	**3ak**, 60%, (98:2)	**4ak**, 58%, (14:86)
12[d]	**2l**, R^1 = CH_3, R^2 = C_6H_5	**3al**, 46%, (96:4)	**4al**, 62%, (16:84)

[a]Method A: **1a** (1.0 mmol), **2** (3.0 mL), Pd(*t*-Bu_3P)$_2$ (0.02 mmol), NH_4Cl (2.0 mmol), CO (30 atm), 120 °C, 24 h. [b]Method B: **1a** (1.0 mmol), **2** (3.0 mL), $Pd(CH_3CN)_2Cl_2$ (0.02 mmol), XantPhos (0.025 mmol), NH_4Cl (2.0 mmol), CO (10 atm), 120 °C, 24 h. [c]Isolated yield. The ratios of **3**/**4**, given within parentheses, were determined by GC-MS and GC analysis of crude product. [d]**2** (10 mmol), anisole (4 mL).

Table 3. Substrate Scope for Branched Amide Synthesis[a]



entry	Ar	3	yield[b] (%)	3:4[c]
1	C_6H_5	**3aa**	89	96:4
2[d]	C_6H_5	**3aa**	70	96:4
3	4-$CH_3C_6H_4$	**3ba**	84	92:8
4	3-$CH_3C_6H_4$	**3ca**	87	90:10
5[e]	2-$CH_3C_6H_4$	**3da**	80	88:12
6[e,f]	2,6-$(CH_3)_2C_6H_3$	**3ea**	55	79:21
7	4-*t*-BuC_6H_4	**3fa**	83	92:8
8	4-$CH_3OC_6H_4$	**3ga**	65	93:7
9	4-$EtOC_6H_4$	**3ha**	74	96:4
10	4-FC_6H_4	**3ia**	82	91:9
11	4-ClC_6H_4	**3ja**	77	90:10
12	4-$CH_3C(O)C_6H_4$	**3ka**	82	98:2
13	4-$H_2N(O)CC_6H_4$	**3la**	58	98:2
14	4-HOC_6H_4	**3ma**	71	95:5
15	4-$MeSC_6H_4$	**3na**	68	96:4
16[e]	2-naphthyl	**3oa**	83	98:2

[a]Reaction conditions: **1** (1.0 mmol), **2a** (3 mL), Pd(*t*-Bu_3P)$_2$ (0.02 mmol), NMP·HCl (0.2 mmol), CO (30 atm), 120 °C, 24 h. [b]Isolated yield. [c]The ratios of **3**/**4**, given within parentheses, were determined by GC-MS and GC analysis of crude product. [d]**1a** (30.0 mmol), **2a** (30 mL), Pd(*t*-Bu_3P)$_2$ (0.006 mmol), 48 h. [e]Pd(*t*-Bu_3P)$_2$ (0.05 mmol). [f]NMP·HCl (0.5 mmol), CO (50 atm), 140 °C, 48 h.

presence of 30 atm of CO with Pd(*t*-Bu_3P)$_2$ as the catalyst together with 20 mol % of NMP·HCl as an additive. As shown in Table 3, in all cases, the present coupling reaction proceeded smoothly to afford their corresponding branched amides in moderate to excellent yields with exellent regioselectivities. In general, both *meta*- and *para*-substituted styrenes were successfully converted into the corresponding amides in good yields with excellent regioselectivities. However, *ortho*-substituted styrenes gave lower yields and regioselectivities, especially for disubstituted **1e**, which was most likely due to the steric environment (**3ca** and **3da**). Pleasingly, the 2-vinylnapthalane (**1o**) can be applied to this protocol, delivering the desired product **3oa** in 83% yield with perfect regioselectivity in the present of 5 mol % of Pd(*t*-Bu_3P)$_2$. Benefiting from the lower coordination ability of DMF, the gram scale reaction for synthesis of **3aa** proceeded smoothly in the presence of 0.02 mol % of Pd(*t*-Bu_3P)$_2$ to give the desired amide in 70% yield (3.74 g, see the Supporting Information (SI)). Notably, this result represents a turnover number (TON) of 3500, which is among the highest reported for hydroaminocarbonylation.[6,7]

Inspired by the above results, we subsequently explored the substrate scope for the synthesis of linear amides with the combination of 2 mol % of $Pd(CH_3CN)_2Cl_2$ with 2.5 mol % of XantPhos and 5 mol % of NMP·HCl in the presence of 10 atm of CO (see Table 4). 2-Vinylnaphthalene and styrenes with various substituents on the *para*-, *meta*-, and *ortho*-position, such as alkyl-, alkoxy-, acyl-, hydroxy-, carboxyl-, and halogens can survive to give the desired linear amides **4ba**−**4pa** in 59%−89% isolated yields with good regioselectivities. The steric hindered substrates **1d** and **1e**, as examples of bulky substrates, favored to transform to the corresponding *N*,*N*-dimethylamides in high yield with excellent regioselectivities. Furthermore, simple unactivated alkenes are also suitable substrates for this reaction to give the corresponding linear amides in good yields and regioselectivities (**4qa**−**4ta**) under the slightly modified reaction conditions. It is worth pointing out that functionalized aliphatic alkenes, bearing chlorine, ether, ester, and phthalimide groups, could be successfully converted to the desired linear amides in 59%−64% isolated yields with good regioselectivities (**4ua**−**4wa**, **4za**). Moreover, (+)-*β*-citronellene (**1x**) was also compatible with this novel reaction, in which the reactions occurred exclusively at the terminal double bond to give the corresponding linear amides **4xa** with partial racemization. It was noted that norbornylene (**1y**) can be smoothly transferred to the amide **4ya** in 87% yield with good selectivity.

To understand the reaction mechanism, many control experiments were conducted. First, the reaction conducted with ^{13}C-labeling DMF disclosed that the CO incorporated into the desired amide came from the CO gas (see Scheme 2, eq 1). In addition, the corresponding ethyl benzoate was detected after treatment of the carbonylation reaction (the carbonylation of styrene with *N*,*N*-dimethylbenzamide) mixture with EtOH (Scheme 2, eq 2), indicating that the transacylation occurred in the catalytic cycle. Inspired by these results, the intramolecular carbonylation of amide-containing alkenes was investigated. As expected, a series of lactams with five- to eight-membered rings were obtained in moderate to good yields (48%−70% yields)

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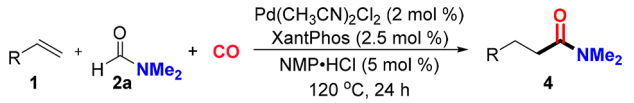
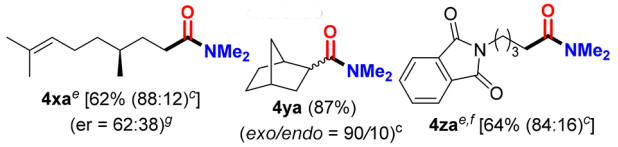
Table 4. Substrate Scope for Linear Amide Synthesis[a]

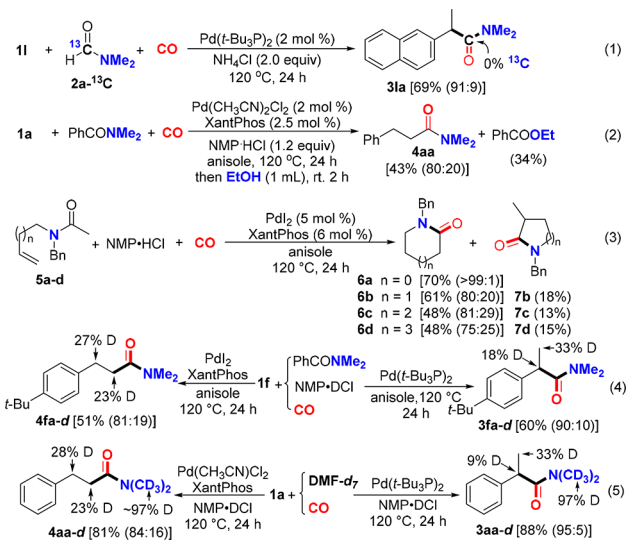


entry	R	4	yield (%)[b]	4:3[c]
1	C_6H_5	**4aa**	81	85:15
2	4-$CH_3C_6H_4$	**4ba**	80	86:14
3	3-$CH_3C_6H_4$	**4ca**	82	85:15
4	2-$CH_3C_6H_4$	**4da**	88	95:5
5	2,6-$(CH_3)_2C_6H_3$	**4ea**	89	99:1
6	4-*t*-BuC_6H_4	**4fa**	73	84:16
7	4-$CH_3OC_6H_4$	**4ga**	73	83:17
8	4-$EtOC_6H_4$	**4ha**	78	83:17
9	4-FC_6H_4	**4ia**	71	85:15
10	4-ClC_6H_4	**4ja**	79	87:13
11	4-$CH_3C(O)C_6H_4$	**4ka**	80	90:10
12	4-$HOOCC_6H_4$	**4pa**	65	84:16
13	4-HOC_6H_4	**4ma**	59	86:14
14[d]	2-naphthyl	**4oa**	79	87:13
15[e]	$CH_3(CH_2)_5$	**4qa**	58	83:17
16[d]	$C_6H_5CH_2$	**4ra**	77	92:8
17[e]	$CyCH_2$	**4sa**	69	90:10
18[e]	*t*-Bu	**4ta**	68	>99:1
19[e,f]	$Cl(CH_2)_4$	**4ua**	61	82:18
20[e,f]	$PhO(CH_2)_2$	**4va**	59	81:19
21[d]	$MeO_2C(CH_2)_8$	**4wa**	62	81:19



[a]Reaction conditions: **1** (1.0 mmol), **2a** (3 mL), $Pd(CH_3CN)_2Cl_2$ (0.02 mmol), Xantphos (0.025 mmol), NMP·HCl (0.05 mmol), CO (10 atm), 120 °C, 24 h. [b]Isolated yield. [c]The ratios of **4**/**3** or dr, given within parentheses, were determined by GC-MS and GC analysis of crude product. [d]48 h. [e]NMP·HCl (0.5 mmol), CO (30 atm). [f]PdI_2 (0.02 mmol), CO (30 atm). [g]Er was determined by HPLC analysis with a chiral stationary phase.

Scheme 2. Control Experiments and Synthetic Applications



by using PdI_2/XantPhos as a catalyst and NMP·HCl as a proton source under slightly modified reaction conditions (Scheme 2, eq 3). Because of the fact that deuterium incorporation can improve the overall therapeutic and metabolic profile of a drug, there is growing interest in selective deuteration.[17] Because of the prevalence of amide in drug molecules,[1] the direct incorporation deuterium into the amide would be an attractive for drug design. Indeed, with inexpensive NMP·DCl as a stoichiometric proton source, the deuterium could be incorporated into the β-position of branched amide and α-position of linear amide in good yields by using the present reaction (Scheme 2, eq 4). Moreover, with DMF-d_7 as a coupling partner, the D-labeled amides could be also prepared in the presence of catalytic amount of NMP·DCl under the standard reaction conditions (Scheme 2, eq 5).

In summary, we have successfully developed a new and efficient protocol for catalytic hydrocarbonylative C−N coupling of alkenes with amides. The reaction proceeded via palladium-catalyzed hydrocarbonylation of alkenes, followed by acyl metathesis. Both linear and branched amides can be obtained in good yields with high regioselectivities by the appropriate choice of ligands. This direct method is an improvement on existing amide-metathesis reactions and can also be employed in the synthesis of deuterated amides with inexpensive NMP·DCl as a deuterium source. The loading of the Pd can be lowered to 0.02 mol %. Further investigations on gaining a detailed mechanistic understanding of this reaction and the application of this strategy in other reactions are currently in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00538.

Experimental details and full spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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