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Combining Transition Metal Catalysis with Radical Chemistry: Dramatic Acceleration of Palladium-Catalyzed C−H Arylation with Diaryliodonium Salts

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Abstract: This paper describes a photoredox palladium/iridium-catalyzed C−H arylation with diaryliodonium reagents. Details of the reaction optimization, substrate scope, and mechanism are presented along with a comparison to a related method in which aryldiazonium salts are used in place of diaryliodonium reagents. The unprecedentedly mild reaction conditions (25 °C in methanol), the requirement for light and a photocatalyst, the inhibitory effect of radical scavengers, and the observed chemoselectivity trends are all consistent with a radical-mediated mechanism for this transformation. This stands in contrast to the analogous thermal reaction with diaryliodonium reagents that is believed to proceed *via* an 'ionic' $2e^-$ pathway and requires a much higher reaction temperature (100 °C).

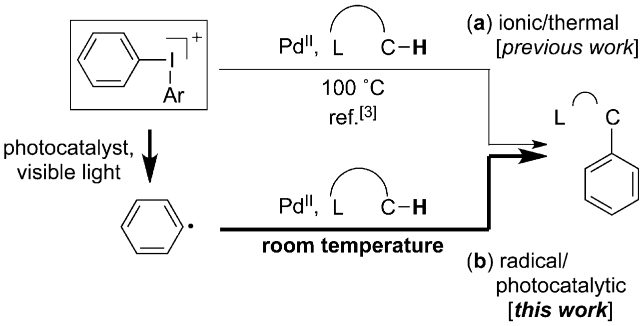
Keywords: C−H activation; diaryliodonium salts; palladium; photochemistry; radicals

Introduction

The merger of transition metal catalysis with radical chemistry has emerged as a powerful strategy for achieving high-yielding transformations under mild conditions.[1] The ability to reroute textbook metal-catalyzed reactions *via* alternative metal/radical-mediated pathways can lead to improvements in rate, functional group tolerance, and/or substrate scope. Manolikakes and Knochel recently reported a striking example of this strategy in the context of the Pd-catalyzed Kumada coupling.[2] They showed that the addition of *i*-PrI led to a remarkable rate acceleration in the coupling of aryl bromides with aryl-Grignard reagents.[2a] This rate enhancement was rationalized based on a new 'radical-catalyzed' mechanistic manifold involving *in situ* generated alkyl and aryl radicals as key intermediates.

We hypothesized that a similar strategy could be used to accelerate Pd-catalyzed C−H arylation reactions with diaryliodonium reagents. As shown in Scheme 1, (a) $Pd(OAc)_2$ is known to catalyze ligand-directed C−H arylation *via* an 'ionic' mechanism involving $2e^-$ oxidation of a palladacycle intermediate by Ar_2I^+.[3–5] However, these transformations are extremely sluggish, typically requiring high temperatures (80–110 °C) over extended periods of time (8–24 h) in acetic acid.[6] We reasoned that the rates of these reactions could potentially be enhanced by rerouting them through radical pathways in which Ar_2I^+ is converted into $Ar^{\bullet}$ *in situ* [Scheme 1, (b)].

Tentative support for the feasibility of this approach is provided by recent reports showing Pd-catalyzed C−H arylation using $Ar^{\bullet}$ generated from aroyl peroxides[7a] or aryldiazonium salts.[7b] We report herein that this strategy enables C−H arylation with Ar_2I^+ under extremely mild conditions (room temperature in MeOH). We also present evidence supporting the proposal that two fundamentally different mechanisms are operating in the ionic [Scheme 1, (a)] versus



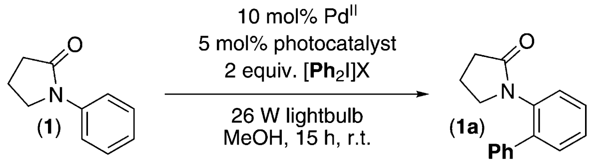
Scheme 1. Two different pathways for Pd-catalyzed C−H arylation with Ph_2I^+.

radical [Scheme 1, (b)] systems. Finally, we compare this new transformation to a related method that uses aryl-N_2^+ as the arylating reagent.[7b]

Results and Discussion

Ph_2I^+ can be converted to $Ph^\bullet$ under mild conditions using visible light and a photocatalyst [$Ru(bpy)_3Cl_2$ or $Ir(ppy)_3$; bpy = 2,2′-bipyridine, ppy = cyclometalated 2-phenylpyridine].[8,9] Thus, we initiated investigations of Pd-catalyzed C–H phenylation of **1** with $[Ph_2I]BF_4$ in combination with a photocatalyst. Visible light irradiation was provided by a 26 W household fluorescent lightbulb, and the reactions were set up on the bench top with no precautions to exclude moisture or air. Remarkably, the use of $Ru(bpy)_3Cl_2$ resulted in a modest yield (18%) of the desired arylated product **1a** after 15 h in MeOH at room temperature (Table 1, entry 1). Evaluation of several different Pd^{II} catalysts revealed that $Pd(NO_3)_2$ provides the best results, generating **1a** in 23% yield (entry 2). $Ru(bpy)_3Cl_2$ and $Ir(ppy)_3$ afforded comparable results (entries 2 and 3), but the cationic photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine)[10] provided a significant improvement (57% yield, entry 4). Replacing $[Ph_2I]BF_4$ with the corresponding triflate salt led to a further enhancement (66% yield, entry 5). Finally, briefly sparging the mixture with N_2 prior to the start of the reaction resulted in 94% yield of **1a** (entry 6).[11] Importantly, both of the metal catalysts, as well as visible light, are critical for efficient room temperature C–H phenylation.[12] Without any one of these three components, only traces of product **1a** were formed (0–2%, entries 7–9).

Table 1. Optimization of the room-temperature C–H phenylation reaction of **1** with Ph_2I^+.[a]



Entry	Pd^{II}	Photocatalyst	X	Yield [%][b]
1	$Pd(OAc)_2$	$Ru(bpy)_3Cl_2$	BF_4^-	18
2	$Pd(NO_3)_2$	$Ru(bpy)_3Cl_2$	BF_4^-	23
3	$Pd(NO_3)_2$	$Ir(ppy)_3$	BF_4^-	17
4	$Pd(NO_3)_2$	$Ir(ppy)_2(dtbbpy)PF_6$	BF_4^-	57
5	$Pd(NO_3)_2$	$Ir(ppy)_2(dtbbpy)PF_6$	OTf^-	66
6[c]	$Pd(NO_3)_2$	$Ir(ppy)_2(dtbbpy)PF_6$	OTf^-	94
7[c]	*none*	$Ir(ppy)_2(dtbbpy)PF_6$	OTf^-	2
8[c]	$Pd(NO_3)_2$	*none*	OTf^-	2
9[c,d]	$Pd(NO_3)_2$	$Ir(ppy)_2(dtbbpy)PF_6$	OTf^-	0

[a] *General conditions:* **1** (1 equiv.), Pd^{II} (0.10 equiv), photocatalyst (0.05 equiv.), $[Ph_2I]X$ (2 equiv.), MeOH (0.2 M in **1**), 26 W lightbulb, 15 h, room temperature.

[b] Yields determined by GC.

[c] Reaction mixture was degassed by sparging with N_2 for 1 min.

[d] General conditions, but with no light.

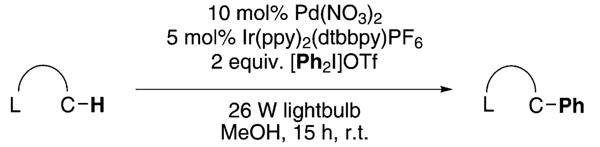
A variety of aromatic substrates underwent room temperature C–H phenylation under these conditions (Table 2). In addition to pyrrolidinones **1** and **2**, other *N*-aryl amides were effective directing groups (entries 3 and 4). *C*-Aryl amides, such as benzamides **5** and **6**, also underwent room temperature C–H phenylation, albeit in moderate yields (40% and 54%). The *N*,*N*-disubstituted analog **7** provided phenylated product **7a** in poor yield (9%), suggesting that C–H arylation is facilitated by the presence at least one N–H bond in this substrate class. 2-Arylpyridines **8** and **9** as well as ketoxime and aldoxime ethers **10** and **11** were also good substrates. The ability to use oxime ethers as directing groups is particularly notable, as these do not undergo C–H arylation with diaryliodonium reagents under the previously reported thermal reaction conditions.[3]

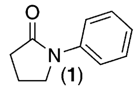
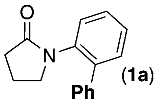
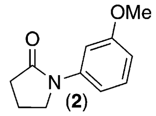
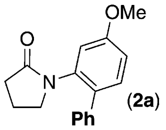
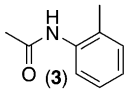
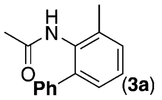
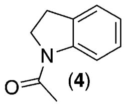
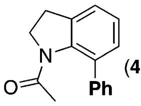
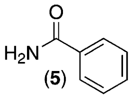
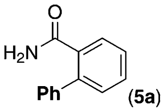
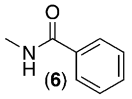
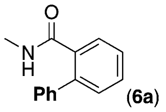
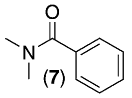
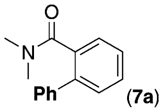
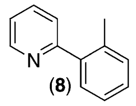
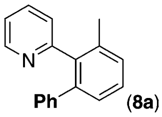
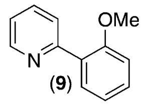
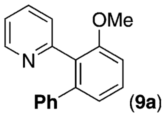
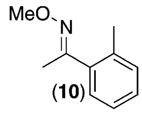
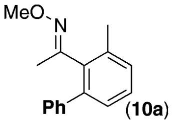
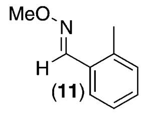
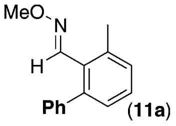
Diaryliodonium salts containing diverse arene substituents were evaluated in this photocatalytic C–H arylation. As shown in Table 3, the highest yields were obtained with those bearing relatively electron neutral substituents (e.g., *p*-Cl, *p*-Br, *p*-CH_3, *o*-CH_3, entries 4–7). Nonetheless, oxidants possessing more strongly electron-donating and electron-withdrawing substituents were also effective. For example, C–H arylation with *p*-methoxyphenyl (entry 9) as well as *para*-, *meta*-, and *ortho*-trifluoromethylphenyl (entries 1–3) reagents proceeded in moderate to good yields. Remarkably, even the highly sterically hindered mesityl group could be transferred, albeit in low yield (11%, entry 8). Notably, the analogous thermal reaction of $[Mes_2I]OTf$ with **1** did not provide detectable quantities of **1i** (as determined by GC).

We propose that the Ir/Pd-catalyzed photocatalytic C–H arylation proceeds *via* a fundamentally different mechanism than the analogous thermal reaction, despite the fact that the reagents and products are the same in both processes. A first piece of evidence to support this proposal is the reaction outcome in the presence of free radical scavengers. As shown in Table 4, the thermal C–H arylation reaction is not inhibited by the addition of 25 mol% galvinoxyl or 100 mol% of TEMPO. With both radical scavengers, the reactions proceed to complete conversion and afford comparable yield (entries 1–3). In contrast, the % conversion and the % yield of the photocatalytic reaction are suppressed in a dose-dependent manner by galvinoxyl and TEMPO (entries 4–8). These results are consistent with the intermediacy of radicals in the latter but not the former reaction.

In addition, the chemoselectivity of the reaction between **1** and unsymmetrical iodonium reagent **12** is

Table 2. Substrate scope for the Pd/Ir-catalyzed C–H phenylation reaction with Ph_2I^+.[a]



Entry	Substrate	Product	Isolated yield [%]
1	 (1)	 (1a)	81
2	 (2)	 (2a)	94
3[b]	 (3)	 (3a)	72
4[b,c,d]	 (4)	 (4a)	44
5	 (5)	 (5a)	40
6	 (6)	 (6a)	54
7	 (7)	 (7a)	9
8	 (8)	 (8a)	62
9	 (9)	 (9a)	67
10	 (10)	 (10a)	60
11	 (11)	 (11a)	57

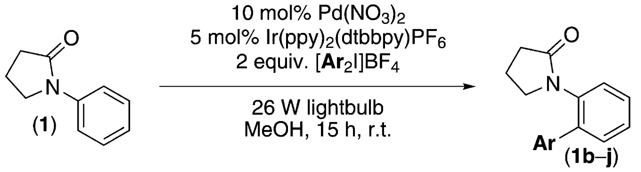
[a] *General conditions:* substrate (1 equiv.), $[Ph_2I]OTf$ (2 equiv.), $Pd(NO_3)_2$ (0.10 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (0.05 equiv.), MeOH (0.2 M in substrate), 26 W lightbulb, 15 h, room temperature, degassed by sparging with N_2.

[b] $[Ph_2I]BF_4$ was the oxidant.

[c] With 1 equiv. MgO.

[d] 0.20 equiv. $Pd(NO_3)_2$.

Table 3. Scope of Ar_2I^+ salts for Pd/Ir-catalyzed C–H arylation of **1**.[a]

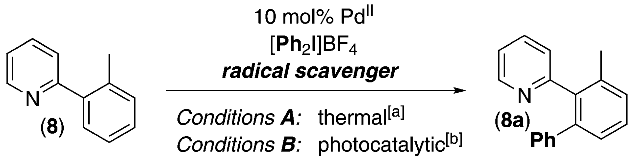


Entry	Ar	Product	Isolated yield [%]
1	p-$CF_3C_6H_4$	**1b**	69
2	m-$CF_3C_6H_4$	**1c**	56
3	o-$CF_3C_6H_4$	**1d**	46
4	p-ClC_6H_4	**1e**	77
5	p-BrC_6H_4	**1f**	79
6	p-$CH_3C_6H_4$	**1g**	87
7	o-$CH_3C_6H_4$	**1h**	85
8[b]	Mes	**1i**	11
9	p-$CH_3OC_6H_4$	**1j**	41

[a] *General conditions:* **1** (1 equiv.), $[Ar_2I]BF_4$ (2 equiv.), $Pd(NO_3)_2$ (0.10 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (0.05 equiv.), MeOH (0.2 M in **1**), 26 W lightbulb, 15 h, room temperature, degassed by sparging with N_2.

[b] OTf salt of oxidant.

Table 4. Effect of radical scavengers on the Pd/Ir-catalyzed C–H arylation of **8**.



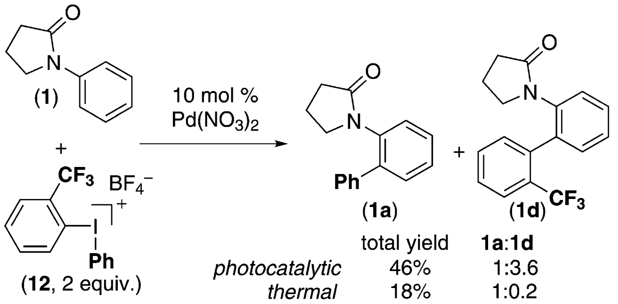
Entry	Scavenger	Mol%	Conditions	Yield [%][c]
1	none	–	**A**	79 ± 7
2	galvinoxyl	25	**A**	81 ± 1
3	galvinoxyl	100	**A**	74 ± 8
4	none	–	**B**	52 ± 4
5	galvinoxyl	10	**B**	42 ± 2
6	galvinoxyl	25	**B**	20 ± 9
7	TEMPO	50	**B**	34 ± 14
8	TEMPO	100	**B**	6 ± 2

[a] *Thermal conditions **A**:* **8** (1 equiv.), $[Ph_2I]BF_4$ (1.1 equiv.), $Pd(OAc)_2$ (0.10 equiv.), AcOH (0.12 M in **8**), 15 h, 100 °C.

[b] *Photocatalytic conditions **B**:* **8** (1 equiv.), $[Ph_2I]BF_4$ (2 equiv.), $Pd(NO_3)_2$ (0.10 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (0.05 equiv.), MeOH (0.2 M in **8**), 26 W lightbulb, 15 h, room temperature, degassed by sparging with N_2.

[c] GC calibrated yield reported as % yield ± standard deviation.

highly dependent on the reaction conditions [Eq. (1)]. Under the thermal conditions, the less hindered phenyl group is transferred selectively, providing a 1:0.2 ratio of **1a**:**1d**. In contrast, selective transfer of the o-$CF_3C_6H_4$ group occurs under the photocatalytic



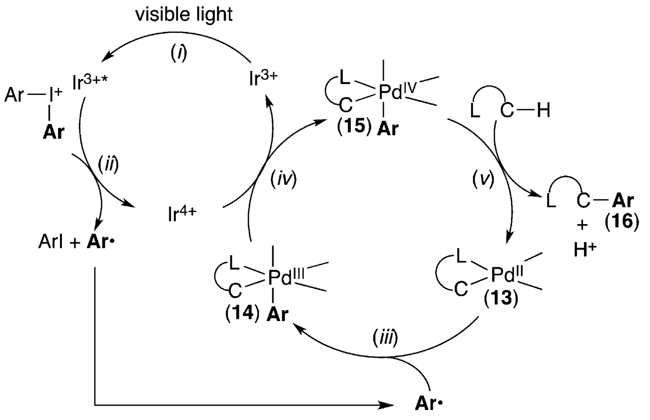
(1)

conditions, affording a 1:3.6 ratio of **1a**:**1d**. These differences in chemoselectivity provide further support for divergent mechanistic pathways.

We preliminarily propose a reaction pathway that merges $\mathrm{Pd^{II/IV}}$ and $\mathrm{Ir^{III/IV}}$ catalytic cycles. As shown in Scheme 2, ground state $\mathrm{Ir^{3+}}$ undergoes photoexcitation by visible light (step *i*), and the resultant $\mathrm{Ir^{3+*}}$ complex can reduce $\mathrm{Ar_2I^+}$ to generate Ar$^\bullet$, ArI, and $\mathrm{Ir^{4+}}$ (step *ii*).[8,9] Ar· could then enter the Pd catalytic cycle by oxidizing cyclopalladated complex **13** (step *iii*). Complex **14** could then be further oxidized to **15** by $\mathrm{Ir^{4+}}$ (step *iv*), regenerating $\mathrm{Ir^{3+}}$. Finally, C–Ar bond-forming reductive elimination from **15** would afford product **16** and regenerate $\mathrm{Pd^{2+}}$ (step *v*). Importantly, a number of other pathways are also possible (for example, $\mathrm{Pd^{I/III}}$ catalysis) and cannot be distinguished based on the current data.

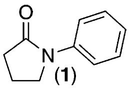
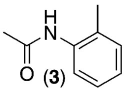
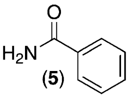
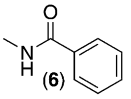
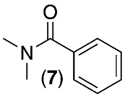
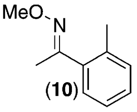
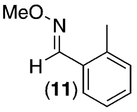
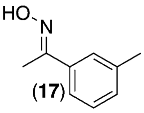
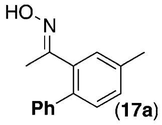
We have recently reported a related room temperature photocatalytic C–H arylation reaction that was proposed to proceed *via* a mechanism similar to that shown in Scheme 1.[7b] However, this previously reported transformation used a different Ar$^\bullet$ precursor (aryl diazonium salts), a different photocatalyst [$\mathrm{Ru(bpy)_3Cl_2}$], a different Pd catalyst [$\mathrm{Pd(OAc)_2}$] and slightly different optimized reaction conditions. Thus, a final set of studies was conducted to compare these two processes.

As illustrated in Table 5, the performance of the two systems is often comparable (e.g., for substrates **1** and **11**). However, for benzamide substrates **5**–**7** and ketoxime ether **10**, the Pd/Ir/$\mathrm{Ph_2I^+}$ system provided better yields of C–H phenylation. Conversely, the Pd/Ru/$\mathrm{PhN_2^+}$ system performed better for acetanilide **3**, and it is effective for hydroxyl oxime **17**, a substrate class that undergoes decomposition in the Pd/Ir/$\mathrm{Ph_2I^+}$ system. Overall, the room-temperature Pd/photocatalyzed C–H arylation methods using $\mathrm{Ar_2I^+}$ and $\mathrm{ArN_2^+}$ reagents are often complementary in terms of substrate scope.[13]



Scheme 2. Possible mechanism for the Pd/Ir-catalyzed C–H arylation with $\mathrm{Ar_2I^+}$.

Table 5. Comparison of Pd/Ir-catalyzed C–H phenylation with $\mathrm{Ph_2I^+}$ *vs.* Pd/Ru-catalyzed C–H phenylation with $\mathrm{PhN_2^+}$.

Substrate	Product	Yield [%] with $\mathrm{Ph_2I^+}$[a,b]	Yield [%] with $\mathrm{PhN_2^+}$[a,c]
 (1)	**1a**	89	91
 (3)	**3a**	69[d]	89
 (5)	**5a**	54	25
 (6)	**6a**	52	38
 (7)	**7a**	11	8
 (10)	**10a**	52	23
 (11)	**11a**	63	68
 (17)	 (17a)	<1[e]	66

[a] GC calibrated yield.

[b] *General conditions:* substrate (1 equiv.), [$\mathrm{Ph_2I}$]OTf (2 equiv.), $\mathrm{Pd(NO_3)_2}$ (0.10 equiv.), $\mathrm{Ir(ppy)_2(dtbbpy)PF_6}$ (0.05 equiv.), MeOH (0.2 M in substrate), 26 W lightbulb, 15 h, room temperature, degassed by sparging with $\mathrm{N_2}$.

[c] *General conditions:* substrate (1 equiv.), [$\mathrm{PhN_2}$]$\mathrm{BF_4}$ (4 equiv.), $\mathrm{Pd(OAc)_2}$ (0.10 equiv.), $\mathrm{Ru(bpy)_3Cl_2 \cdot 6H_2O}$ (0.025 equiv.), MeOH (0.1 M in substrate), 26 W lightbulb, room temperature, 15 h, degassed by sparging with $\mathrm{N_2}$.

[d] [$\mathrm{Ph_2I}$]$\mathrm{BF_4}$ was the oxidant.

[e] Product **17a** was not detected by GC, and only trace amounts of **17** and 3′-methylacetophenone were detected.

Conclusions

In summary, this paper describes a photoredox Pd/Ir-catalyzed C–H arylation with diaryliodonium reagents. The unusually low reaction temperature, the requirement for light and a photocatalyst, the inhibitory effect of radical scavengers, and the observed chemoselectivity trends are all consistent with a radical mechanism for this transformation. This stands in contrast to the analogous thermal reaction that requires dramatically higher temperature (100 °C) and is believed to proceed *via* an 'ionic' $2e^-$ pathway. This example adds to a growing body of work suggesting that re-routing traditional metal-catalyzed transformations *via* radical pathways can offer major advantages in terms of reaction rates, substrate scope, and functional group tolerance.[1,2,14]

Experimental Section

Representative Procedure for C–H Phenylation of Substrate 1

N-Phenylpyrrolidinone **1** (80.6 mg, 0.50 mmol, 1.0 equiv.), $[Ph_2I]OTf$ (430 mg, 1.00 mmol, 2.0 equiv.), $Ir(ppy)_2(dtbbpy)PF_6$ (22.8 mg, 0.025 mmol, 0.05 equiv.), and $Pd(NO_3)_2·2H_2O$ (13.3 mg, 0.05 mmol, 0.10 equiv.) were combined in MeOH (2.5 mL) in a 4 mL scintillation vial. The reaction mixture was cooled in an ice bath (to prevent solvent evaporation) and sparged with N_2 using a submerged needle for 10 min, and the vial was then immediately sealed with a Teflon-lined cap. The vial was placed on a stir plate with two 26 W compact fluorescent lightbulbs (one on either side of the vial about 5–8 cm away), and the reaction mixture was allowed to stir at room temperature for 15 h. The reaction mixture was diluted with EtOAc (50 mL) and washed with 10% aqueous Na_2SO_3 (2×25 mL) and brine (1×25 mL). The combined aqueous layers were extracted with EtOAc (3×10 mL), and the organic layers were then combined, dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography on silica gel ($R_f = 0.17$ in 20% hexanes/80% Et_2O). Product **1a** was obtained as a pale yellow oil; yield: 96.3 mg (81%). ^1H and ^{13}C NMR data matched those reported in the literature.[7b]

Acknowledgements

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