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Ligand-Free Pd-Catalyzed and Copper-Assisted C−H Arylation of Quinazolin-4-ones with Aryl Iodides under Microwave Heating

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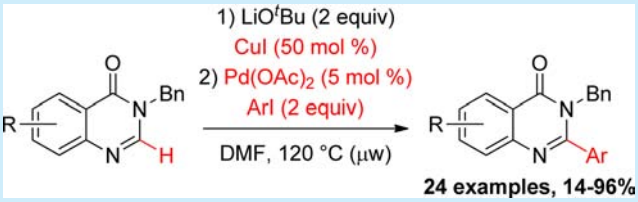
Supporting Information

ABSTRACT: A microwave-assisted method for the palladium-catalyzed direct arylation of quinazolin-4-one has been developed under copper-assistance. This method is applicable to a wide range of aryl iodides and substituted (2*H*)-quinazolin-4-ones. This protocol provides a simple and efficient way to synthesize biologically relevant 2-arylquinazolin-4-one backbones.



Quinazolin-4-one derivatives are usually key core motifs in many natural products, pharmaceuticals, and biologically active compounds.[1] Thus, development of efficient functionalization methodologies of these heterocycles is required and their C-2 arylation remains a challenging goal for organic chemists.[2] Traditional strategies to synthesize such molecules involve the construction of the heterocycle part, starting from anthranilic acid derivatives, by a ring-closure condensation[2,3] or C−H amidation,[4] or by palladium-catalyzed carbonylation of 2-halogenoaniline derivatives or *N*-arylamidines.[5] Copper-catalyzed coupling reactions of 2-halogenobenzoic acid derivatives with amidines are also described.[6] Radical approaches have been recently developed as a strategy to assemble 2-arylquinazolinone structures.[7] Among these methodologies, transition-metal-catalyzed intermolecular C−C coupling of quinazolin-4-ones through C−H functionalization represents an extremely attractive approach. During the past decade, palladium-catalyzed C−H functionalization of heteroarenes has been intensively developed as an efficient and versatile approach in complex molecule syntheses.[8] Direct arylation or heteroarylation of heteroarenes is increasingly attractive as a C−C bond formation methodology, offering a powerful alternative to standard cross-coupling reactions. Examples of direct Pd-catalyzed C−H arylation involving nonaromatic nitrogen heterocycles are sparsely reported in the literature[9] and appear to be limited to the synthesis of some natural products and analogues in the case of quinazolin-4-ones.[10] Following our effort for the construction of a broad range of substituted quinazoline derivatives as potential inhibitors of kinases,[11] we report herein the first extensive study of palladium-catalyzed direct C-2-H arylation of N^3-benzylated quinazolin-4-ones with aryl iodides.

The direct arylation of N^3-benzylated quinazolin-4-one **1a** was initially explored using CuI (1 equiv), LiO^{t}Bu (2 equiv), and iodobenzene (PhI, 2 equiv) in DMF at 120 °C for 12 h, according to the conditions reported by Daugulis[12] allowing the C−H arylation of various heteroarenes. Unfortunately, under these conditions no arylated compound was isolated. However, we were pleased to observe that the addition of a catalytic amount of Pd(OAc)$_2$ in the reaction mixture, provided the C-2 phenylated quinazolin-4-one **2a** with a complete conversion. Nevertheless, this palladium/copper cooperative catalysis was not reproducible and provided the desired phenylated product **2a** in erratic conversions. This phenomenon was previously reported in the literature for the C−H arylation of purines and oxazoles.[13] The problem was overcome by applying a premixing step.[13a] In our case, the copper source was first mixed with the base and the quinazolin-4-one substrate for 10 min before adding the rest of the reactants. Microwave irradiation[14] was also used to shorten reaction times, and complete conversion was observed within 30 min at 120 °C (Table 1, entry 1). Initial experiments were aimed at screening the copper source and catalyst loading. The desired product **2a** was isolated in 91% yield using a substoichiometric amount of CuI (50 mol %, entry 2). Even if both Cu(I) and Cu(II) catalysts could be employed in the transformation, Cu(I) provided better results (entries 2−5). Addition of TEMPO to the reaction mixture did not affect the conversion rate, providing strong support to rule out a radical mechanism. Decreasing the amount of CuI source resulted in lower yields (entries 6−7), and no reaction occurred without copper (entry 8).

Evaluation of solvent and base was then performed to optimize the reaction conditions. As reported in Table 2, the screened conditions revealed that the choice of the solvent drastically affected the yields of desired product **2a** (entries 1−5).

Either no reaction or low conversion was observed with common solvent such as DMPU, DMSO, or dioxane used for copper-catalyzed arylation reaction. Moderate to good conversions were only obtained with DMA and DMF as solvent. This could be explained by the ability of these solvents to reduce Pd(II) to Pd(0).[15a] Indeed, this high reactivity could be a result of

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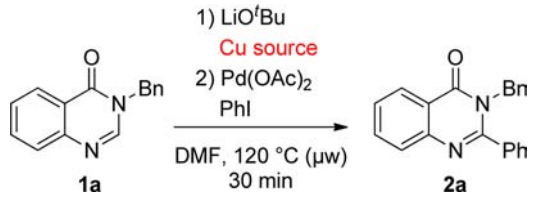
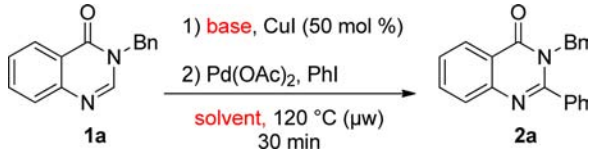
Table 1. Effect of Copper Source[a]



entry	copper source	Cu catalyst loading	yield[b] (%)
1	CuI	1 equiv	96
2	CuI	50%	91
3	CuBr	50%	54
4	CuOAc	50%	0
5	$CuCl_2$	50%	56
6	CuI	30%	78
7	CuI	10%	66
8	none		0

[a]Conditions: Reactions were performed in a sealed tube at 0.4 M with premixing **1a** (1 equiv), LiO^{t}Bu (2 equiv), and the copper source in a microwave reactor for 10 min at 120 °C, before adding PhI (2 equiv) and Pd(OAc)$_2$ (5 mol %). [b]Reported yields are isolated yields.

Table 2. Effect of Solvent and Base[a]



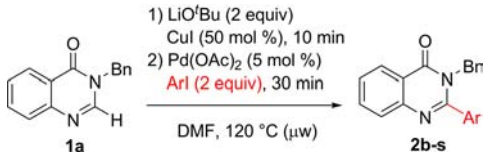
entry	solvent	base	yield[b] (%)
1	DMF	LiO^{t}Bu	91 (90)[c]
2	DMA	LiO^{t}Bu	43
3	DMPU	LiO^{t}Bu	0
4	DMSO	LiO^{t}Bu	0
5	dioxane	LiO^{t}Bu	0
6	DMF	KO^{t}Bu	14
7	DMF	K_3PO_4	0

[a]Conditions: Reactions were performed in a sealed tube at 0.4 M with premixing **1a** (1 equiv), base (2 equiv), and CuI (50 mol %) in a microwave reactor for 10 min at 120 °C, before adding PhI (2 equiv) and Pd(OAc)$_2$ (5 mol %). [b]Reported yields are isolated yields. [c]Scale up, 8.5 mmol of **1a** under optimized conditions.

the rapid microwave degradation of DMF, affording *in situ* generated dimethylamine.[16] Whereas stronger base such as KO^{t}Bu provided poor yield (entry 6), no conversion was observed with weaker base such as K_3PO_4 (entry 7). Upon examining various bases and solvents, LiO^{t}Bu and DMF were found to give optimal results (entry 1). Interestingly, the optimized protocol was also easily scaled up from 0.8 to 8.5 mmol without a decrease in yield (entry 1).

With the optimized conditions in hand, the scope of the reaction was undertaken by using N^3-benzylated quinazolin-4-one **1a** with a broad range of aryl iodides, bearing electron-donating or -withdrawing groups (Table 3). We were pleased to observe the formation of the desired C2-arylated products, **2b−s** in good yields. The present strategy was tolerant to various functional groups including fluoro (**2h**), cyano (**2i**), trifluoromethyl (**2j**), and nitro (**2k**) (entries 7−10). We assume that electronic effects may influence the performance of the direct coupling of **1a** with ortho-substituted aryl iodides: the 2-methyliodobenzene has been revealed as an excellent coupling

Table 3. Direct Arylation of N^3-Benzylated Quinazolin-4-one 1a with Aryl Iodides[a]



entry	Ar-	2	yield[b] (%)
1	4-MeO-Ph-	**2b**	96
2	4-PhO-Ph-	**2c**	95
3	4-Me-Ph-	**2d**	94
4	4-nBu-Ph-	**2e**	76
5	4-Br-Ph	**2f**	0 (43)[c]
6	4-Cl-Ph-	**2g**	94
7	4-F-Ph-	**2h**	93
8	4-CN-Ph	**2i**	90
9	4-CF_3-Ph	**2j**	89
10	4-NO_2-Ph	**2k**	65
11	3-Me-Ph	**2l**	92
12	3-MeO-Ph	**2m**	91
13	2-MeO-Ph	**2n**	14
14	2-Me-Ph	**2o**	90
15	1-naphthyl	**2p**	68
16	2-naphthyl	**2q**	93
17	9-phenanthryl	**2r**	80
18	3-pyridyl	**2s**	76

[a]Conditions: Reactions were performed in a sealed tube at 0.4 M with premixing **1a** (1 equiv), LiO^{t}Bu (2 equiv), and CuI (50 mol %) in a microwave reactor, before adding ArI (2 equiv) and Pd(OAc)$_2$ (5 mol %). [b]Reported yields are isolated yields. [c]C−H arylation proceed at both halogen atoms.

partner (entry 11) and the 2-methoxyiodobenzene has given a low yield of expected product (entry 13), while further experiments involving 2-fluorophenyl iodide, 2-iodopyridine, and 2-iodo-pyrazine, were unsuccessful.

To further examine the versatility of this methodology, the arylation was attempted with pyrido-pyrimidin-4-ones **1b−e** and substituted N^3-benzylated quinazolin-4-ones **1f−g** (Scheme 1). We were pleased to observe that N^3-benzylated quinazolin-4-ones bearing chloro or methyl groups on the aromatic nucleus led to the corresponding C-2 phenylated compounds **2x** and **2y** in good yields. Likewise, the C-2 arylation could be applied to the four isomers of pyrido-pyrimidin-4-ones **1b−e** affording compounds **2t−w** in good yields ranging from 62 to 87%.

A plausible reaction mechanism for the C-2 arylation of quinazolin-4-ones is depicted in Scheme 2 on the basis of previously reported investigations.[12a,15]

It could be expected that the metalation step may be facilitated by coordination of copper species to nitrogen of quinazolin-4-one (Scheme 2). In addition, without ligand, the in situ generated dimethylamine (resulting from the microwave degradation of DMF at 120 °C) may stabilize the Cu(I)-amide type complex. Interestingly, during the activation step with 1 equiv of CuI, LiO^{t}Bu, and quinazolinone **1a**, we were able to observe the [(Cu-**1a**) + H]$^+$ cation (m/z 299) using ESI-MS/MS analysis, which upon MS/MS gave the same fragmentation as that of the product **1a** alone (m/z 91).[17] It was proposed that exchange of the most acidic proton at C-2 with Cu results in an organocopper intermediate. The latter is enabled to undergo cross-coupling with iodoarylpalladium species to form C-2 arylated product **2**.

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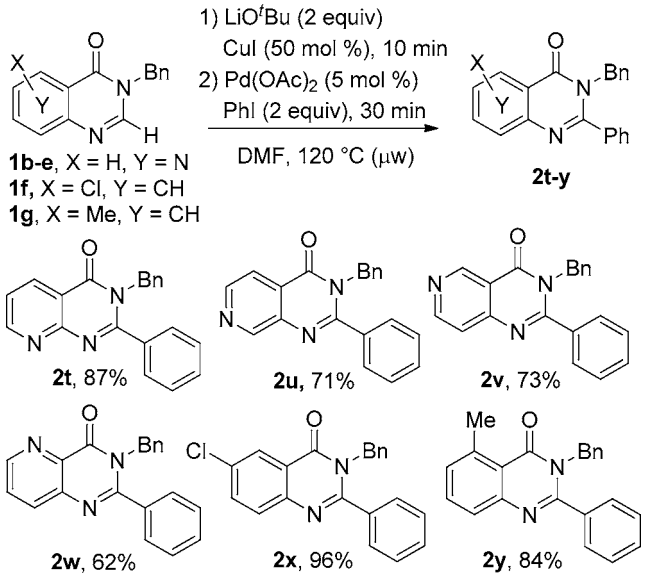
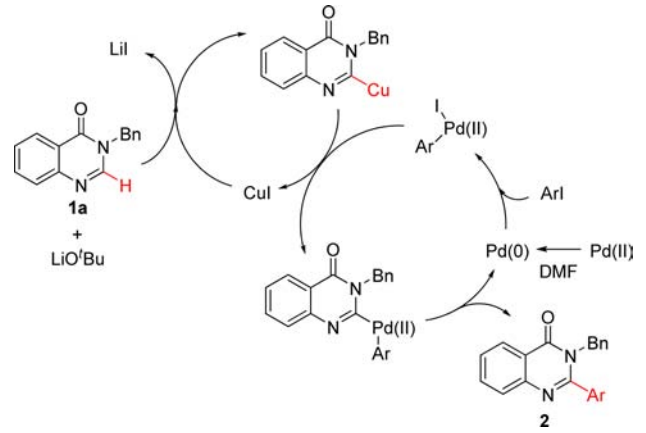
Scheme 1. Arylation of N^3-Benzylated Pyrido-Pyrimidin-4-ones 1b−e and Quinazolin-4-ones 1f−g with Phenyl Iodide[a]



[a]Conditions: Reactions were performed in a sealed tube at 0.4 M with premixing **1b−g** (1 equiv), LiO^{t}Bu (2 equiv), and CuI (50 mol %) in a microwave reactor for 10 min at 120 °C, before adding PhI (2 equiv) and Pd(OAc)$_2$ (5 mol %).

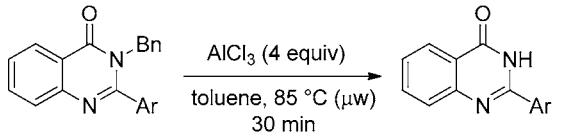
Scheme 2. Plausible Mechanism for the C-2 Arylation of Quinazolin-4-one 1



To obtain easy access to N^3-H 2-aryl-quinazolin-4-ones, we have focused our attention on the cleavage of benzyl protecting group. Indeed, N^3-H 2-aryl-quinazolin-4-ones are key intermediates for the synthesis of more challenging and complex 4-amino-2-aryl-quinazoline derivatives as potential inhibitors of kinases.[11a] The deprotection was achieved using conditions developed in our laboratory with $AlCl_3$ under microwave heating[18] (Scheme 3), and compounds **3a−c** were isolated in high yields. Under these reaction conditions, the aromatic methoxy group of quinazolin-4-one **2b** was also cleaved, providing the corresponding phenol **3b**. Since the two-step synthesis of N^3-H 2-aryl-quinazolin-4-ones **3a−c** was achieved in 85% overall yield from **1a**, our method could be employed as a convenient tool for molecular diversity.

Notably, compounds **3** are well-known key intermediates in the classical synthesis of 4-amino-2-aryl-quinazoline derivatives via a two-step synthesis (chlorination/SNAr procedure).

Scheme 3. Deprotection of Arylated Quinazolinones 2a−b,g



2a, Ar = Ph	**3a**, Ar = Ph	94%
2b, Ar = 4-MeOC$_6$H$_4$	**3b**, Ar = 4-HOC$_6$H$_4$	88%
2g, Ar = 4-ClC$_6$H$_4$	**3c**, Ar = 4-ClC$_6$H$_4$	92%

In conclusion, we have developed the first ligand-free Cu/Pd-catalyzed microwave-enhanced C−H (hetero)arylation of quinazolin-4-ones with aryl iodides in high yields. This innovative methodology tolerates a broad range of aryl iodides substituted by electronically different groups. The scope of substrate model was also successfully extended to pyridinopyrimidin-4-ones. This method provides an efficient, versatile, and rapid access to important 2-arylquinazolin-4-ones, which are potentially active compounds or key intermediates for the synthesis of molecules of therapeutic interest. Efforts are now underway to extend this methodology to other classes of fused pyrimidin-4-one derivatives. Similarly, mechanistic investigations are currently in progress in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

T.B. and C.F. conceived the project and designed the experiments with S.L., M.H., and J.G., who executed the chemical synthesis. MS analyses were realized by I.S.-A. The manuscript was written through contributions of all authors who have given approval to the final version.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Kahn, I.; Ibrar, A.; Abbas, N.; Saeed, A. *Eur. J. Med. Chem.* **2015**, *90*, 124. (b) Kahn, I.; Ibrar, A.; Abbas, N.; Saeed, A. *Eur. J. Med. Chem.* **2014**, *76*, 193. (c) Padithem, M.; Annapurnapadmavathi, D.; Prasunamba, P. L.; Saraladevi, C. H. *Int. J. Pharm. Pharm. Sci.* **2013**, *5*, 179.

(2) For recent examples of bioactive C2-arylated quinazolin-4-ones, see (a) Kahn, K. M.; Saad, S. M.; Shaikh, N. N.; Hussain, S.; Fakhri, M.;

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Org. Lett. 2015, 17, 1700−1703

Perveen, S.; Taha, M.; Choudhary, M. I. *Bioorg. Med. Chem.* **2014**, *22*, 3449. (b) Nathubhai, A.; Wood, M. D.; Thompson, A. S.; Threadgill, M. D. *ACS Med. Chem. Lett.* **2013**, *4*, 1173.

(3) (a) Yang, W.; Qiao, R.; Chen, J.; Huang, X.; Liu, M.; Gao, W.; Ding, J.; Wu, H. *J. Org. Chem.* **2015**, *80*, 482. (b) Yang, W.; Chen, J.; Huang, X.; Ding, J.; Liu, M.; Wu, H. *Org. Lett.* **2014**, *16*, 5418. (c) Kim, N. Y.; Cheon, C.-H. *Tetrahedron Lett.* **2014**, *55*, 2340. (d) Shakhidoyatov, K. M.; Elmuradov, B. Z. *Chem. Nat. Compd.* **2014**, *50*, 781. (e) Huang, G.; Roos, D.; Stadtmüller, P.; Decker, M. *Tetrahedron Lett.* **2014**, *55*, 3607. (f) Aikawa, S.; Sekiguchi, C.; Yamazaki, Y.; Hattori, M.; Isaka, T.; Yoshida, Y.; Ihara, S. *J. Heterocycl. Chem.* **2014**, *51*, 343. (g) Sneddon, H. F.; Lynn, S. M. *Synlett* **2011**, *4*, 573. (h) Patil, A.; Patil, O.; Patil, B.; Surana, J. *Mini-Rev. Med. Chem.* **2011**, *11*, 633. (i) Giri, R.; Lam, J. K.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 686. (j) Giri, R. S.; Thaker, H. M.; Giordano, T.; Williams, J.; Rogers, D.; Sudersanam, V.; Vasu, K. K. *Eur. J. Med. Chem.* **2009**, *44*, 2184.

(4) (a) Wang, L.-X.; Xiang, J.-F.; Tang, Y.-L. *Eur. J. Org. Chem.* **2014**, 2682. (b) Hikawa, H.; Ino, Y.; Suzuki, H.; Yokoyama, Y. *J. Org. Chem.* **2012**, *77*, 7046. (c) Xu, W.; Jin, Y.; Liu, H.; Jiang, Y.; Fu, H. *Org. Lett.* **2011**, *13*, 1272.

(5) (a) Wu, X.-F.; Schranck, J.; Neumann, H.; Beller, M. *Chem.—Eur. J.* **2011**, *17*, 12246. (b) Ma, B.; Wang, Y.; Peng, J.; Zhu, Q. *J. Org. Chem.* **2011**, *76*, 6362. (c) Zheng, Z.; Alper, H. *Org. Lett.* **2008**, *10*, 829.

(6) (a) Xu, L.; Jiang, Y.; Ma, D. *Org. Lett.* **2012**, *14*, 1150. (b) Liu, X.; Fu, H.; Jiang, Y.; Zhao, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 348.

(7) (a) Wang, Y.-F.; Zhang, F.-L.; Chiba, S. *Org. Lett.* **2013**, *15*, 2842. (b) Servais, A.; Azzouz, M.; Lopes, D.; Courillon, C.; Malacria, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 576.

(8) For recent general reviews on direct C−H arylation of heterocycles, see (a) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C. *Adv. Synth. Catal.* **2014**, *356*, 17. (b) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C.; Perego, L. A. *Synthesis* **2014**, *46*, 2833. (c) Kapdi, A. R. *Dalton Trans.* **2014**, *43*, 3021. (d) Shibahara, F.; Murai, T. *Asian J. Org. Chem.* **2013**, *2*, 624. (e) Wencel-Delord, J.; Glorius, F. *Nat. Chem.* **2013**, *5*, 369. (f) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (g) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. (h) Hirano, K.; Miura, M. *Synlett* **2011**, *3*, 294. (i) Roger, J.; Gottumukkala, A. L.; Doucet, H. *ChemCatChem* **2010**, *2*, 20. (j) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269.

(9) (a) Muselli, M.; Baudequin, C.; Hoarau, C.; Bischoff, L. *Chem. Commun.* **2015**, *51*, 745. (b) Carrër, A.; Brion, J.-D.; Alami, M.; Messaoudi, S. *Adv. Synth. Catal.* **2014**, *356*, 3821. (c) Carrër, A.; Brion, J.-D.; Messaoudi, S.; Alami, M. *Org. Lett.* **2013**, *15*, 5606. (d) Demory, E.; Farran, D.; Baptiste, B.; Chavant, P. Y.; Blandin, V. *J. Org. Chem.* **2012**, *77*, 7901. (e) Zhao, H.; Wang, R.; Chen, P.; Gregg, B. T.; Hsia, M. M.; Zhang, W. *Org. Lett.* **2012**, *14*, 1872. (f) Gigant, N.; Gillaizeau, I. *Org. Lett.* **2012**, *14*, 3304. (g) Ackermann, L.; Barfüsser, S.; Kornhaass, C.; Kapdi, A. R. *Org. Lett.* **2011**, *13*, 3082. (h) Yotphan, S.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2009**, *11*, 1511. (i) Lewis, J. C.; Berman, A. M.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 2493. (j) Majumdar, K. C.; Pal, A. K.; Taher, A.; Debnath, P. *Synthesis* **2007**, 1707.

(10) For a unique example of intermolecular palladium-catalyzed direct C−H arylation of quinazolinone, see (a) Naik, N. H.; Urmode, T. D.; Sikder, A. K.; Kusurkar, R. S. *Aust. J. Chem.* **2013**, *66*, 1112. For examples of intramolecular direct C−H arylation of quinazolin-4-one, see (b) Golubev, A. S.; Bogomolov, V. O.; Shidlovskii, A. F.; Dezhenkova, L. G.; Peregudov, A. S.; Shtil, A. A.; Chkanikova, N. D. *Russ. Chem. Bull.* **2010**, *59*, 209. (c) Nacro, K.; Zha, C.; Guzzo, P. R.; Herr, R. J.; Peace, D.; Friedrich, T. D. *Bioorg. Med. Chem.* **2007**, *15*, 4237. (d) Harayama, T.; Hori, A.; Serban, G.; Morikami, Y.; Matsumoto, T.; Abe, H.; Takeuchi, Y. *Tetrahedron* **2004**, *60*, 10645. (e) Harayama, T.; Morikami, Y.; Shigeta, Y.; Abe, H.; Takeuchi, Y. *Synlett* **2003**, 847. For other transition metal-catalyzed direct C−H alkylation of quinazolinones, see (f) Tamura, R.; Yamada, Y.; Nakao, Y.; Hiyama, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 5679. (g) Yoshiaki Nakao, Y.; Idei, H.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2009**, *131*, 15996. (h) Gary, A.; Molander, G. A.; Virginie Colombel, V.; Braz, V. A. *Org. Lett.* **2011**, *13*, 1852.

(11) (a) Foucourt, A.; Hédou, D.; Dubouilh-Benard, C.; Girard, A.; Taverne, T.; Casagrande, A.-S.; Désiré, L.; Leblond, B.; Besson, T. *Molecules* **2014**, *19*, 15411. (b) Hédou, D.; Deau, E.; Dubouilh-Benard, C.; Sanselme, M.; Martinet, A.; Chosson, E.; Levacher, V.; Besson, T. *Eur. J. Org. Chem.* **2013**, 7533. (c) Deau, E.; Hédou, D.; Chosson, E.; Levacher, V.; Besson, T. *Tetrahedron Lett.* **2013**, *54*, 3518.

(12) (a) Do, H.-Q.; Kashif Kahn, R. M.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 15185. (b) Do, H.-Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128. (c) Do, H.-Q.; Daugulis, O. *J. Am. Chem. Soc.* **2007**, *129*, 12404.

(13) (a) Vabre, R.; Chevot, F.; Legraverend, M.; Piguel, S. *J. Org. Chem.* **2011**, *76*, 9542. (b) Besselièvre, F.; Piguel, S.; Mahuteau-Betzer, F.; Grierson, D. *Org. Lett.* **2008**, *10*, 4029.

(14) For recent relevant reviews on microwave-assisted C−H arylation and C−C coupling, see (a) Sharma, A.; Vacchhani, D.; Van der Eycken, E. *Chem.—Eur. J.* **2013**, *19*, 1158. (b) Mehtaa, V. P.; Van der Eycken, E. *Chem. Soc. Rev.* **2011**, *40*, 4925.

(15) (a) Lesieur, M.; Lazreg, F.; Cazin, C. S. J. *Chem. Commun.* **2014**, *50*, 8927. (b) Gorelsky, S. I. *Organometallics* **2012**, *31*, 794. (c) Huang, J.; Chan, J.; Chen, Y.; Borths, C. J.; Baucom, K. D.; Larsen, R. D.; Faul, M. M. *J. Am. Chem. Soc.* **2010**, *132*, 3674−3675. (d) Storr, T. E.; Baumann, C. G.; Thatcher, R. J.; De Ornellas, S.; Whitwood, A. C.; Fairlamb, I. J. S. *J. Org. Chem.* **2009**, *74*, 5810.

(16) (a) Loidreau, Y.; Besson, T. *Tetrahedron* **2011**, *67*, 4852. (b) Nouira, I.; Kostakis, I. K.; Dubouilh, C.; Chosson, E.; Iannelli, M.; Besson, T. *Tetrahedron Lett.* **2008**, *49*, 7033. (c) Kostakis, I. K.; Elomri, A.; Seguin, E.; Iannelli, M.; Besson, T. *Tetrahedron Lett.* **2007**, *48*, 6609.

(17) See the Supporting Information.

(18) Hédou, D.; Guillon, R.; Lecointe, C.; Logé, C.; Chosson, E.; Besson, T. *Tetrahedron* **2013**, *69*, 3182.

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