OL Organic Letters

Letter

Cite This: Org. Lett. 2019, 21, 6830–6834

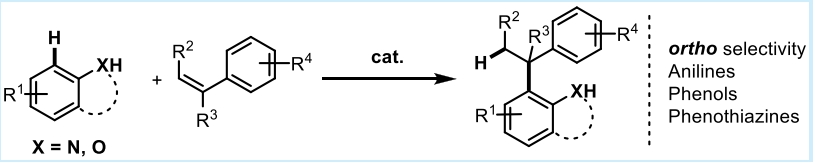
pubs.acs.org/OrgLett

HBF_4- and $AgBF_4$-Catalyzed *ortho*-Alkylation of Diarylamines and Phenols

Christian K. Rank, Bünyamin Özkaya, and Frederic W. Patureau*

Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

Supporting Information

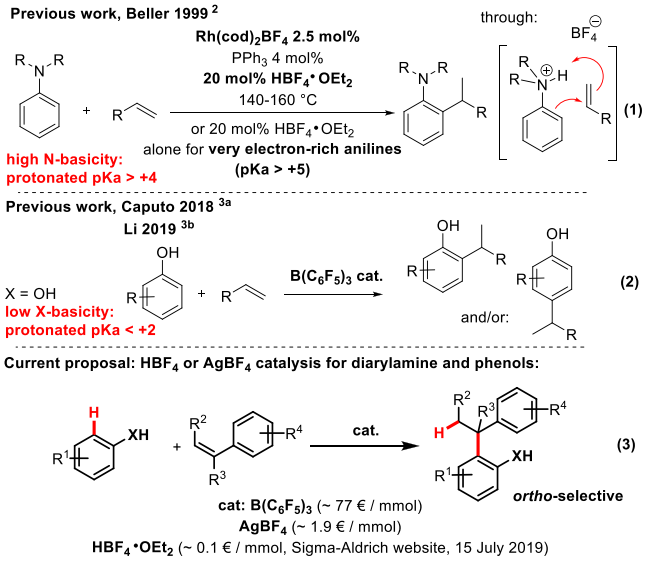


ABSTRACT: A silver-tetrafluoroborate- or HBF_4-catalyzed *ortho*-alkylation reaction of phenols and diarylamines with styrenes has been explored. A broad substrate scope is presented as well as mechanistic experiments and discussion.

Modern hydroarylation methods are increasingly popular for the construction of C−C bonds. Indeed, some elegant strategies have recently appeared that allow excellent Markovnikov or anti-Markovnikov regioselectivity and broad functional group tolerance.[1] In 1999, Beller et al. reported the case of a Rh(I)/HBF_4 cocatalyzed system for the *ortho*-alkylation of primary electron-rich anilines with styrene. For the most electron-rich anilines (pK_a of the corresponding ammonium >5), it was even found that the reaction could proceed without the Rh catalyst (Scheme 1, eq 1).[2] This brought us to wonder what it would take to bring this very simple HBF_4-catalyzed hydroarylation system to both lower reaction temperatures and especially to broader and less reactive substrate classes (lower basicity of the substrate; pK_a of the corresponding ammonium <2). With phenols, for example,[3a−c] elegant methods were very recently reported by Caputo[3a] and independently by Li,[3b] which demonstrate the use of a powerful and increasingly popular Lewis acid catalyst, tris(perfluorophenyl)borane (Scheme 1, eq 2). We therefore contemplated whether a redox approach might provide a superior strategy, in particular, in terms of the ortho selectivity, a persistent problem. We thus turned our attention to Ag(I) salts as prospective catalysts.[4] We considered, in particular, $AgBF_4$[4] for poorly O- or N-basic phenol and diarylamine substrates. Indeed, we anticipated that radical mechanisms[5] might improve the reactivity and regioselectivity while providing a cheaper and operationally simpler synthetic method compared with perfluoro organo-boron Lewis acidic catalysts (Scheme 1, eq 3). In parallel, we also re-explored Beller's control HBF_4-catalyzed approach, without the rhodium catalyst, to evaluate the impact of the redox-active Ag(I) component. To our surprise, and in contrast with the literature,[2a] we found that the considerably cheaper HBF_4 catalyst (Scheme 1, eq 3) also performs admirably well in the catalytic alkylation of anilines and phenols, with only small differences. This study is therefore focused on both $AgBF_4$ and HBF_4 catalysts and on related mechanistic considerations.

Phenothiazine was selected as a first convenient nonbasic diarylamine test substrate, a compound known to easily undergo radical oxidation.[6] Phenothiazines are, moreover, interesting scaffolds in some fields of organic materials[7] as well as essential bioactive compounds.[8] Some optimization elements are shown in Table 1. (See the SI for other parameters such as solvent and temperature.) Importantly, it was found that the reaction proceeds well in a number of very diverse conditions, whether potentially radical (Table 1, entry 1), Brønsted-acid-catalyzed (entry 23), or Lewis-acid-catalyzed (entry 24). For the phenothiazine test substrate, the $AgBF_4$ catalyst (entry 1) delivered the highest yield of desired

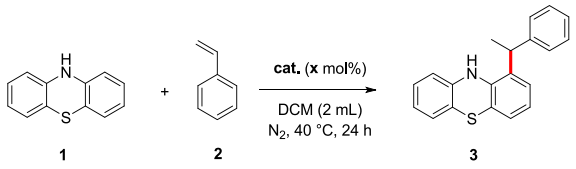
Scheme 1. Introduction



Received: July 16, 2019
Published: August 20, 2019

DOI: 10.1021/acs.orglett.9b02470
Org. Lett. 2019, 21, 6830–6834

Table 1. Reaction Optimization[a]



	catalyst	loading	**1a**/**2a** (mmol)	yield (%)[a]
1[b]	**$AgBF_4$**	**10 mol %**	**0.5/0.75**	**90 (84)**
2	$AgBF_4$	5 mol %	0.5/0.75	77
3	$NaBF_4$	10 mol %	0.5/0.75	0
4	Ag_2O	10 mol %	0.5/0.75	0
5	$AgNO_3$	10 mol %	0.5/0.75	trace
6	AgOAc	10 mol %	0.5/0.75	0
7	AgF	10 mol %	0.5/0.75	trace
8	AgCl	10 mol %	0.5/0.75	0
9	AgBr	10 mol %	0.5/0.75	0
10	AgI	10 mol %	0.5/0.75	0
11	AgOTf	10 mol %	0.5/0.75	54
12	$AgSbF_6$	10 mol %	0.5/0.75	64 (63)
13	$AgSbF_6$	5 mol %	0.5/0.75	57
14	$AgSbF_6$	10 mol %	0.5/1.00	54
15	$CuCl_2$	10 mol %	0.5/1.00	0
16	$AuCl_3$	10 mol %	0.5/1.00	8
17	PPh_3AuCl	10 mol %	0.5/1.00	0
18	$AgBF_4$	10 mol %	0.5/0.5	46
19	$AgBF_4$	10 mol %	0.5/1	70
20	$AgBF_4$	10 mol %	0.75/0.5	55
21	$AgBF_4$	10 mol %	1/0.5	80
22	$AgBF_4$	10 mol %	3/0.5	82
23[c]	HBF_4Et_2O	20 mol %	0.5/0.75	65
24[d]	PPh_3AuX	10 mol %	0.5/0.75	48

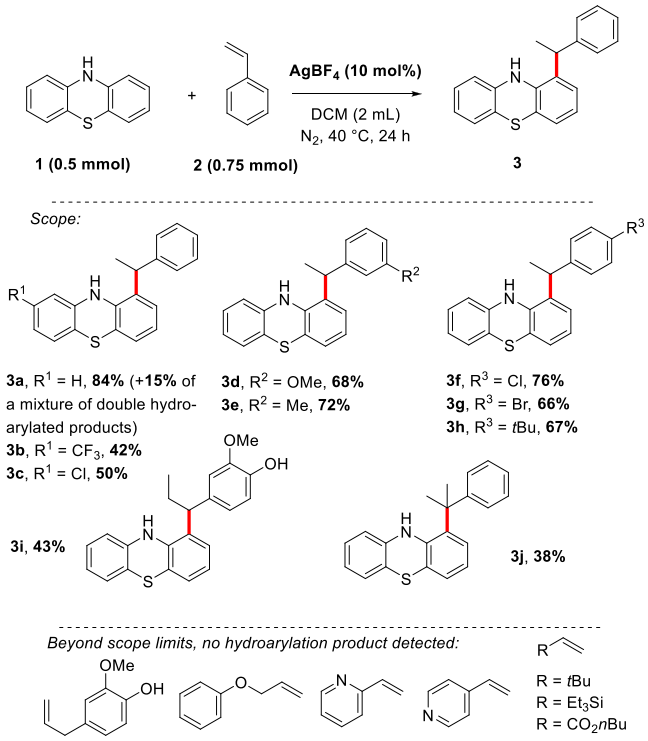
[a]Yields were determined by GC using *n*-dodecane as the standard (isolated yield in parentheses). [b]+15% of a mixture of bis-alkylated products. [c]+31% of a mixture of bis-alkylated products. [d]X = $[N(CF_3SO_2)_2]$.

(monoalkylated) product. We moreover screened numerous counterions (Table 1, entries 4−14), thereby demonstrating the clear superiority of the tetrafluoroborate anion.

With the $AgBF_4$-catalyzed optimized conditions in hand (Table 1, entry 1), we then screened a number of phenothiazines and styrenes (Scheme 2). Interestingly, the branched (Markovnikov) *ortho* (C1) alkylated product is typically by far the major product. In some cases, small amounts of bis-alkylated products can be observed (i.e., Table 1, entry 1); however, the first alkylation step seems to consistently occur in the ortho position to the X−H functional group (Scheme 2). This is moreover a synthetically interesting regioselectivity outcome in light of the usual preference of phenothiazine for C3-(*para*-) electrophilic aromatic substitution.[9] This strong preference for the ortho-branched alkylated product is in good agreement with the concerted mechanism of Scheme 1. Even 1,1-and 1,2-disubstituted styrenes were found to be competent hydroarylation substrates, albeit in lower yields (**3i**, 43%; **3j**, 38%). Acrylates, however, or heterocyclic olefins such as vinylpyridines, did not afford any hydroarylation product (Scheme 2).

With this first set of phenothiazine examples in hand, we wondered whether noncyclic diarylamines and phenols (all with lower basicity than the primary anilines of Beller)[2] would also be applicable. Diarylamines and phenols are less easily

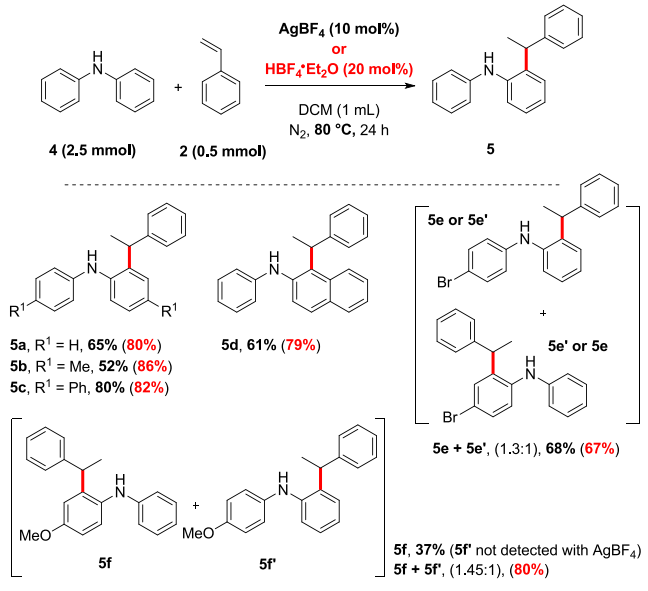
Scheme 2. Phenothiazine Scope, Isolated Yields



protonated or oxidized than phenothiazines, however, necessarily implying higher activation energies and potentially shorter-lived radical intermediates. Fortunately, simply increasing the reaction temperature to, respectively, 80 and 100 °C allowed the hydroarylation reaction to proceed under otherwise altered starting material ratios. Elements of the substrate scope are presented in Schemes 3 and 4, again with very high *ortho*-alkylation selectivity.

There, too, we could not find or identify any *para*-monoalkylated byproducts. In the case of product **5a**, much

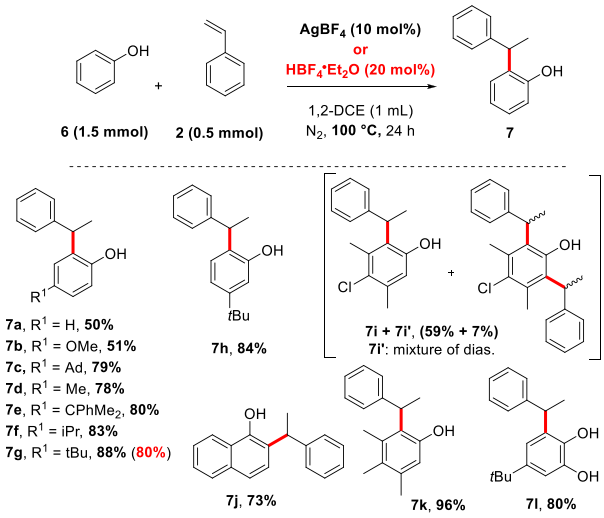
Scheme 3. Diarylamine Scope, Isolated Yields[a]



[a]Numbers in black are the yields with 10 mol % $AgBF_4$; numbers in red are the yields with 20 mol % HBF_4.

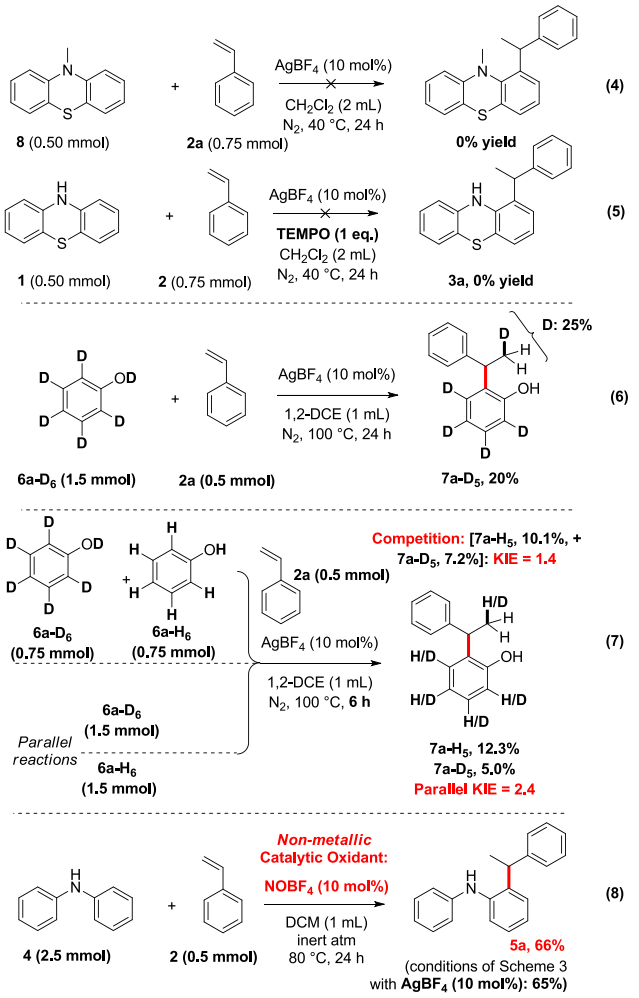
DOI: 10.1021/acs.orglett.9b02470
Org. Lett. 2019, 21, 6830−6834

Scheme 4. Phenol Scope, Isolated Yields[a]



[a]Numbers in black are the yields with 10 mol % $AgBF_4$; numbers in red are the yields with 20 mol % HBF_4.

Scheme 5. Mechanistic Experiments, Isolated Yields



of the excess of the diarylamine substrate **4a** could be recovered and reisolated (1.97 mmol; see the SI), which seems to be a general trend when examining the various crude products presented herein. In contrast, none of the limiting coupling partners is ever reisolated, indicating the full conversion and probable decomposition of the missing mass balance. Importantly, we noted a superior isolated yield with the simple Brønsted HBF_4 catalyst in almost all diarylamine cases (Scheme 3, red yields in parentheses).

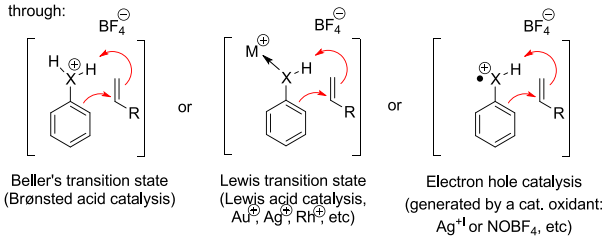
We then performed a series of mechanistic experiments to probe some of the possible scenarios, in particular, with the ambiguous $AgBF_4$ catalyst. First, *N*-methyl-phenothiazine does not provide any hydroarylated product (Scheme 5, eq 4), thus confirming the requirement for a heteroproton ortho to the functionalized C−H bond. This is strong evidence that the concerted protonation/C−C bond-formation hypothesis postulated by Beller (Scheme 1) is probably also important with the $AgBF_4$ catalyst. Second, the presence of TEMPO, a typical radical scavenger, does not allow the reaction to proceed (eq 5). TEMPO might either inhibit radical chains or alternatively reduce the Ag(I) catalyst toward the piperidinium-2,2,6,6-tetramethyl-1-oxo-tetrafluoroborate salt, which would, in turn, no longer be a competent oxidant for initiating the catalytic cycle. Furthermore, labeled phenol-d_6 was engaged in the hydroarylation reaction, yielding a 25% D-enriched branched methyl group in the coupling product (eq 6). This corresponds to a 76% deuteron transfer efficiency and therefore also supports the ortho-concerted mechanism of Scheme 1. It could be noted that the deviation from the theoretical 33% deuterium content at the methyl group (full deuteron transfer efficiency) may come from either the integration approximation of the corresponding ^{1}H NMR experimental profile or traces of water contamination in some of the components, which might lead to rapid OD/OH scrambling. We then compared the initial reaction rate between labeled phenol-d_6 and natural abundance phenol in a competition experiment, yielding an initial kinetic isotope effect (KIE) of 1.4 (eq 7). This may indicate that C−H bond cleavage is not rate-limiting, in contrast with the prior concerted C−C bond-formation step. Moreover, interestingly, when measuring the initial KIE between phenol and phenol-d_6 in two parallel reactions, a somewhat higher KIE of 2.4 was observed under otherwise identical conditions. This suggests that the cyclic concerted C−C bond-forming step and proton/deuteron oxygen-to-carbon transfer may indeed be rate-significant. Finally, to probe the suspected radical character of the $AgBF_4$-catalyzed reaction, we performed a final control experiment in which the speculated catalytic electron hole is generated by a nonmetallic single electron oxidant (eq 8). For this purpose, we selected the $NOBF_4$ salt as the nonmetallic catalytic electron hole generator because it possesses the same counterion as our $AgBF_4$ precatalyst and because it is reputed to possess a similar (slightly superior) redox potential as well.[10]

To our surprise, when we indeed replaced the catalytic $AgBF_4$ salt with the same catalytic amount of $NOBF_4$ salt (10 mol %) in the alkylation of diphenylamine under otherwise unaltered reaction conditions (Scheme 3), we isolated almost exactly the same amount of hydroarylated product **5a** (65 vs 66%, respectively, eq 8). This result, in combination with the TEMPO poisoning experiment of eq 5, indicates that an electron-hole-catalyzed pathway is possible in the case of $AgBF_4$. This is moreover in line with the usual observation of shiny Ag^0 particles in suspension in the crude product mixtures. The fact that HBF_4 and a cationic gold species are also competent catalysts (Table 1, entries 23 and 24) nevertheless suggests that the various mechanistic scenarios

DOI: 10.1021/acs.orglett.9b02470
Org. Lett. 2019, 21, 6830−6834

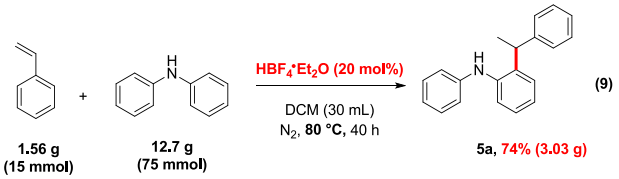
considered herein are not necessarily mutually exclusive,[11] especially if partial in situ hydrolysis of the $AgBF_4$ would take place to generate active HBF_4. These scenarios are summarized in Scheme 6.

Scheme 6. Possible ortho-Selective Transition States



Finally, to demonstrate the utility of the reaction with the cheapest herein studied catalyst, HBF_4, we scaled up the synthesis of new compound **5a** on a multigram level. We were satisfied to obtain 3.03 g of product **5a** in a single batch (74%, Scheme 7).

Scheme 7. Scale-Up of 5a, Isolated Yield



In conclusion, we have developed a $AgBF_4$- and HBF_4-catalyzed alkylation method of phenothiazines, diarylamines, and phenols. These methods allow the alkylation of considerably less basic anilines and phenols compared with previous methods,[2] with moreover excellent ortho-selectivity. Several mechanistic pathways were identified depending on the reaction conditions: Brønsted acid catalysis, Lewis acid catalysis, and also electron hole catalysis. The proximal XH functional group was found to be essential for reactivity and ortho regioselectivity through a characteristic concerted protonation/C−C bond-formation pathway. The herein presented reactivity elements are expected to complement the hydroarylation/alkylation toolbox.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02470.

Experimental procedures and characterization of new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Frederic.Patureau@rwth-aachen.de.

ORCID

Frederic W. Patureau: 0000-0002-4693-7240

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The DFG-funded transregional collaborative research center SFB/TRR 88 "Cooperative effects in homo and heterometallic complexes" (http://3MET.de), DFG-funded project PA 2395/2-1, and ERC project 716136: "2O2ACTIVATION" are acknowledged for financial support. We also thank Philipp Kramer and Prof. G. Manolikakes for technical help. This work was started at the Technische Universität Kaiserslautern and finished at the RWTH Aachen University.

■ REFERENCES

(1) (a) Rueping, M.; Nachtsheim, B. J. A Review of New Developments in the Friedel-Crafts Alkylation - From Green Chemistry to Asymmetric Catalysis. *Beilstein J. Org. Chem.* **2010**, *6*, 6. (b) Green, S. A.; Matos, J. L. M.; Yagi, A.; Shenvi, R. A. Branch-Selective Hydroarylation: Iodoarene−Olefin Cross-Coupling. *J. Am. Chem. Soc.* **2016**, *138*, 12779. (c) Yan, M.; Lo, J. C.; Edwards, J. T.; Baran, P. S. Radicals: Reactive Intermediates with Translational Potential. *J. Am. Chem. Soc.* **2016**, *138*, 12692. (d) Boyington, A. J.; Riu, M.-L. Y.; Jui, N. T. Anti-Markovnikov Hydroarylation of Unactivated Olefins via Pyridyl Radical Intermediates. *J. Am. Chem. Soc.* **2017**, *139*, 6582. (e) Ma, X.; Dang, H.; Rose, J. A.; Rablen, P.; Herzon, S. B. Hydroheteroarylation of Unactivated Alkenes Using *N*-Methoxyheteroarenium Salts. *J. Am. Chem. Soc.* **2017**, *139*, 5998. (f) Lo, J. C.; Kim, D.; Pan, C.-M.; Edwards, J. T.; Yabe, Y.; Gui, J.; Qin, T.; Gutierrez, S.; Giacoboni, J.; Smith, M. W.; Holland, P. L.; Baran, P. S. Fe-Catalyzed C−C Bond Construction from Olefins via Radicals. *J. Am. Chem. Soc.* **2017**, *139*, 2484. (g) He, Y.; Cai, Y.; Zhu, S. Mild and Regioselective Benzylic C−H Functionalization: Ni-Catalyzed Reductive Arylation of Remote and Proximal Olefins. *J. Am. Chem. Soc.* **2017**, *139*, 1061. (h) Seath, C. P.; Vogt, D. B.; Xu, Z.; Boyington, A. J.; Jui, N. T. Radical Hydroarylation of Functionalized Olefins and Mechanistic Investigation of Photocatalytic Pyridyl Radical Reactions. *J. Am. Chem. Soc.* **2018**, *140*, 15525. (i) Matsuura, R.; Jankins, T. C.; Hill, D. E.; Yang, K. S.; Gallego, G. M.; Yang, S.; He, M.; Wang, F.1.; Marsters, R. P.; McAlpine, I.; Engle, K. M. Palladium(II)-catalyzed γ-selective hydroarylation of alkenyl carbonyl compounds with arylboronic acids. *Chem. Sci.* **2018**, *9*, 8363. (j) Shevick, S. L.; Obradors, C.; Shenvi, R. A. Mechanistic Interrogation of Co/Ni-Dual Catalyzed Hydroarylation. *J. Am. Chem. Soc.* **2018**, *140*, 12056. (k) Gurak, J. A.; Engle, K. M. Practical Intermolecular Hydroarylation of Diverse Alkenes via Reductive Heck Coupling. *ACS Catal.* **2018**, *8*, 8987. (l) Green, S. A.; Vasquez-Cespedes, S.; Shenvi, R. A. Iron−Nickel Dual-Catalysis: A New Engine for Olefin Functionalization and the Formation of Quaternary Centers. *J. Am. Chem. Soc.* **2018**, *140*, 11317. (m) Lv, H.; Xiao, L.-J.; Zhao, D.; Zhou, Q.-L. Nickel(0)-catalyzed linear-selective hydroarylation of unactivated alkenes and styrenes with aryl boronic acids. *Chem. Sci.* **2018**, *9*, 6839. (n) Lehnherr, D.; Wang, X.; Peng, F.; Reibarkh, M.; Weisel, M.; Maloney, K. M. Mechanistic Study of a Re-Catalyzed Monoalkylation of Phenols. *Organometallics* **2019**, *38*, 103.

(2) (a) Beller, M.; Thiel, O. R.; Trauthwein, H. Catalytic Alkylation of Aromatic Amines with Cationic Rhodium Complexes and Acid. *Synlett* **1999**, *1999*, 243. On related topics, see also: (b) Vaughan, B. A.; Webster-Gardiner, M. S.; Cundari, T. R.; Gunnoe, T. B. A rhodium catalyst for single-step styrene production from benzene and ethylene. *Science* **2015**, *348*, 421. (c) Vaughan, B. A.; Khani, S. K.; Gary, J. B.; Kammert, J. D.; Webster-Gardiner, M. S.; McKeown, B. A.; Davis, R. J.; Cundari, T. R.; Gunnoe, T. B. Mechanistic Studies of Single-Step Styrene Production Using a Rhodium(I) Catalyst. *J. Am. Chem. Soc.* **2017**, *139*, 1485. (d) Webster-Gardiner, M. S.; Chen, J.; Vaughan, B. A.; McKeown, B. A.; Schinski, W.; Gunnoe, T. B. Catalytic Synthesis of "Super" Linear Alkenyl Arenes Using an Easily Prepared Rh(I) Catalyst. *J. Am. Chem. Soc.* **2017**, *139*, 5474.

(3) (a) Bentley, J. N.; Caputo, C. B. Catalytic Hydroarylation of Alkenes with Phenols using $B(C_6F_5)_3$. *Organometallics* **2018**, *37*, 3654. (b) Wang, G.; Gao, L.; Chen, H.; Liu, X.; Cao, J.; Chen, S.; Cheng,

DOI: 10.1021/acs.orglett.9b02470
Org. Lett. 2019, 21, 6830−6834

X.; Li, S. Chemoselective Borane-Catalyzed Hydroarylation of 1,3-Dienes with Phenols. *Angew. Chem., Int. Ed.* **2019**, *58*, 1694. For a review, see also: (c) Huang, Z.; Lumb, J.-P. Phenol-Directed C−H Functionalization. *ACS Catal.* **2019**, *9*, 521.

(4) (a) Weibel, J.-M.; Blanc, A.; Pale, P. Ag-Mediated Reactions: Coupling and Heterocyclization Reactions. *Chem. Rev.* **2008**, *108*, 3149. (b) Alvarez-Corral, M.; Munoz-Dorado, M.; Rodriguez-Garcia, I. Silver-Mediated Synthesis of Heterocycles. *Chem. Rev.* **2008**, *108*, 3174. (c) Fang, G.; Bi, X. Silver-catalysed reactions of alkynes: recent advances. *Chem. Soc. Rev.* **2015**, *44*, 8124. (d) Zheng, Q.-Z.; Jiao, N. Ag-catalyzed C−H/C−C bond functionalization. *Chem. Soc. Rev.* **2016**, *45*, 4590. (e) Fang, G.; Cong, X.; Zanoni, G.; Liu, Q.; Bi, X. Silver-Based Radical Reactions: Development and Insights. *Adv. Synth. Catal.* **2017**, *359*, 1422.

(5) (a) Fischer, H. The Persistent Radical Effect: A Principle for Selective Radical Reactions and Living Radical Polymerizations. *Chem. Rev.* **2001**, *101*, 3581. (b) Studer, A.; Curran, D. P. The electron is a catalyst. *Nat. Chem.* **2014**, *6*, 765. (c) Luca, O. R.; Gustafson, J. L.; Maddox, S. M.; Fenwick, A. Q.; Smith, D. C. Catalysis by electrons and holes: formal potential scales and preparative organic electrochemistry. *Org. Chem. Front.* **2015**, *2*, 823. (d) Studer, A.; Curran, D. P. Catalysis of Radical Reactions: A Radical Chemistry Perspective. *Angew. Chem., Int. Ed.* **2016**, *55*, 58.

(6) (a) Lucarini, M.; Pedrielli, P.; Pedulli, G. F.; Valgimigli, L.; Gigmes, D.; Tordo, P. Bond Dissociation Energies of the N−H Bond and Rate Constants for the Reaction with Alkyl, Alkoxyl, and Peroxyl Radicals of Phenothiazines and Related Compounds. *J. Am. Chem. Soc.* **1999**, *121*, 11546. (b) Louillat-Habermeyer, M.-L.; Jin, R.; Patureau, F. W. O_2-mediated dehydrogenative amination of phenols. *Angew. Chem., Int. Ed.* **2015**, *54*, 4102. (c) Zhao, Y.; Huang, B.; Yang, C.; Xia, W. Visible-Light-Promoted Direct Amination of Phenols via Oxidative Cross-Dehydrogenative Coupling Reaction. *Org. Lett.* **2016**, *18*, 3326. (d) Zhao, Y.; Huang, B.; Yang, C.; Li, B.; Gou, B.; Xia, W. Photocatalytic Cross-Dehydrogenative Amination Reactions between Phenols and Diarylamines. *ACS Catal.* **2017**, *7*, 2446. (e) Tang, S.; Wang, S.; Liu, Y.; Cong, H.; Lei, A. Electrochemical Oxidative C-H Amination of Phenols: Access to Triarylamine Derivatives. *Angew. Chem., Int. Ed.* **2018**, *57*, 4737. (f) Bering, L.; D'Ottavio, L.; Sirvinskaite, G.; Antonchick, A. P. Nitrosonium ion catalysis: aerobic, metal-free cross-dehydrogenative carbon−heteroatom bond formation. *Chem. Commun.* **2018**, *54*, 13022. (g) Goswami, M.; Konkel, A.; Rahimi, M.; Louillat-Habermeyer, M.-L.; Kelm, H.; Jin, R.; de Bruin, B.; Patureau, F. W. Mechanism of the Dehydrogenative Phenothiazination of Phenols. *Chem. - Eur. J.* **2018**, *24*, 11936. (h) Patureau, F. W. The Phenol-Phenothiazine Coupling: an Oxidative Click Concept. *ChemCatChem* **2019**, DOI: 10.1002/cctc.201900152.

(7) (a) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. Metal-Free Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* **2014**, *136*, 16096. (b) Pan, X.; Lamson, M.; Yan, J.; Matyjaszewski, K. Photoinduced Metal-Free Atom Transfer Radical Polymerization of Acrylonitrile. *ACS Macro Lett.* **2015**, *4*, 192. (c) Pan, X.; Fang, C.; Fantin, M.; Malhotra, N.; So, W. Y.; Peteanu, L. A.; Isse, A. A.; Gennaro, A.; Liu, P.; Matyjaszewski, K. Mechanism of Photoinduced Metal-Free Atom Transfer Radical Polymerization: Experimental and Computational Studies. *J. Am. Chem. Soc.* **2016**, *138*, 2411. (d) Salunke, J. K.; Wong, F. L.; Feron, K.; Manzhos, S.; Lo, M. F.; Shinde, D.; Patil, A.; Lee, C. S.; Roy, V. A. L.; Sonar, P.; Wadgaonkar, P. P. Phenothiazine and carbazole substituted pyrene based electroluminescent organic semiconductors for OLED devices. *J. Mater. Chem. C* **2016**, *4*, 1009. (e) Kumar, S.; Singh, M.; Jou, J.-H.; Ghosh, S. Trend breaking substitution pattern of phenothiazine with acceptors as a rational design platform for blue emitters. *J. Mater. Chem. C* **2016**, *4*, 6769. (f) Grisorio, R.; Roose, B.; Colella, S.; Listorti, A.; Suranna, G. P.; Abate, A. Molecular Tailoring of Phenothiazine-Based Hole-Transporting Materials for High-Performing Perovskite Solar Cells. *ACS Energy Lett.* **2017**, *2*, 1029.

(8) Ohlow, M. J.; Moosmann, B. Phenothiazine: the seven lives of pharmacology's first lead structure. *Drug Discovery Today* **2011**, *16*, 119.

(9) (a) Bernthsen, A. *Ber. Dtsch. Chem. Ges.* **1883**, *16*, 2896. (b) Bernthsen, A. *Annalen* **1885**, *230*, 73. (c) Jin, R.; Bub, C. L.; Patureau, F. W. Phenothiazinimides: Atom-Efficient Electrophilic Amination Reagents. *Org. Lett.* **2018**, *20*, 2884.

(10) See, for example: Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96*, 877.

(11) Youn's hydroarylation reaction sequence of phenols with dienes, under silver triflate catalysis, and suggested mechanism in which catalytic Ag(I) is proposed to act as a Lewis acid: Youn, S. W.; Eom, J. I. Ag(I)-Catalyzed Sequential C−C and C−O Bond Formations between Phenols and Dienes with Atom Economy. *J. Org. Chem.* **2006**, *71*, 6705.

DOI: 10.1021/acs.orglett.9b02470
Org. Lett. 2019, 21, 6830−6834