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A Bifunctional Ligand Enables Gold-Catalyzed Hydroarylation of Terminal Alkynes under Soft Reaction Conditions

Ting Li,* Yuhan Yang, Baomin Luo, Bo Li, Luyi Zong, Weiguang Kong, Hao Yang, Xinpeng Cheng, and Liming Zhang*

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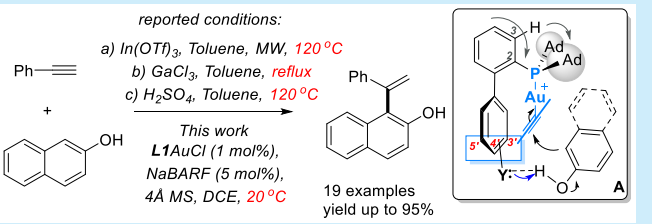
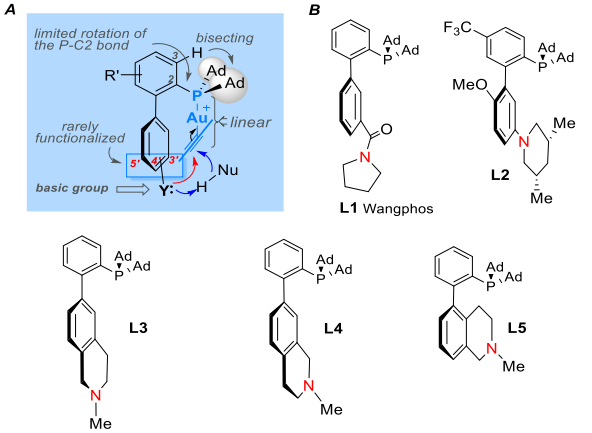
ABSTRACT: An efficient gold-catalyzed hydroarylation of alkynes under soft reaction conditions is developed by utilizing a bifunctional ligand. This transformation features a broad substrate scope and thus exhibits moderate to excellent efficiency.

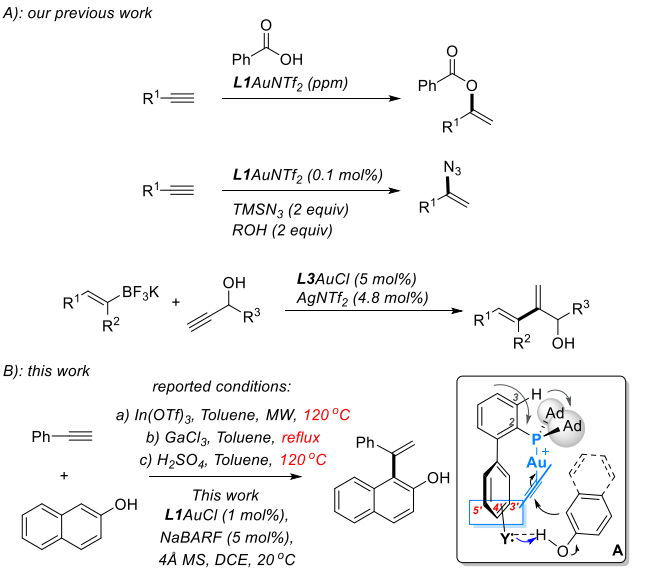


Over the past few years one of our groups has developed a range of new bifunctional phosphine ligands[1] in gold catalysis.[2] These ligands, as revealed in Scheme 1B, despite possessing the traditional biphenyl-2-ylphosphine skeleton similar to Johnphos,[3] are unique and extraordinary by a remote basic group on the other benzene ring. With this kind of bifunctional ligands, cooperative interactions between the ligand and either the external nucleophiles or substrates by overcoming the solid linear character of the centroid in the gold(I) intermediate could be achieved. Meanwhile, rotation of the P−C2 bond in the ligand would also be restricted with the help of Ad groups (Scheme 1A). This metal−ligand cooperation[4] has permitted the development of novel gold catalysis.[1] For example, the ligands **L2**−**L5** (Scheme 1B) featuring a remote amino group enable soft propargylic deprotonations, which is the key transformation in several of our recent work.[1a,b,f] Especially,

Scheme 1. Biphenyl-2-ylphosphine Ligands for Homogeneous Gold Catalysis



Scheme 2. Previous Work and Our Design



the WangPhos (**L1**) ligand, which is installed with a remote amide group, could promote the gold-catalyzed transformations of terminal or interminal alkynes with the aid of the weak hydrogen bonding between the external nucleophiles and the ligand.[1b,d] With such a ligand, facile addition of carboxylic acids

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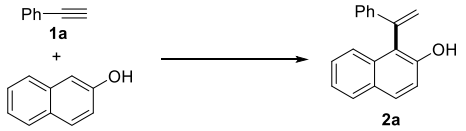
Table 1. Reaction Conditions Study[a]



entry	conditions[a]	yield[b]
1	**L1**AuCl (1 mol %), NaBARF (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	92
2	**L2**AuCl (1 mol %), NaBARF (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	<5
3	**L3**AuCl (1 mol %), NaBARF (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	<5
4	**L4**AuCl (1 mol %), NaBARF (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	<5
5	**L5**AuCl (1 mol %), NaBARF (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	<5
6	PPh_3, IPr or JohnPhos as Au ligand (1 mol %), NaBARF (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	0
7	PPh_3, IPr or JohnPhos as Au ligand (1 mol %), NaBARF (5 mol %), Et_3N (1.0 equiv), DCE, 4 Å MS, 20 °C, 4 h	0
8	**L1**AuCl (1 mol %), DCE, 4 Å MS, 20 °C, 4 h	0
9	NaBARF (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	0
10	**L1**AuCl (1 mol %), AgOTf (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	55
11	**L1**AuCl (1 mol %), $AgNTf_2$ (5 mol %), DCE, 4 Å MS, 20 °C, 4 h	72
12	**L1**AuCl (1 mol %), NaBARF (5 mol %), PhF, 4 Å MS, 20 °C, 2 h	77
13	**L1**AuCl (1 mol %), NaBARF (5 mol %), $PhCF_3$, 4 Å MS, 20 °C, 2 h	82

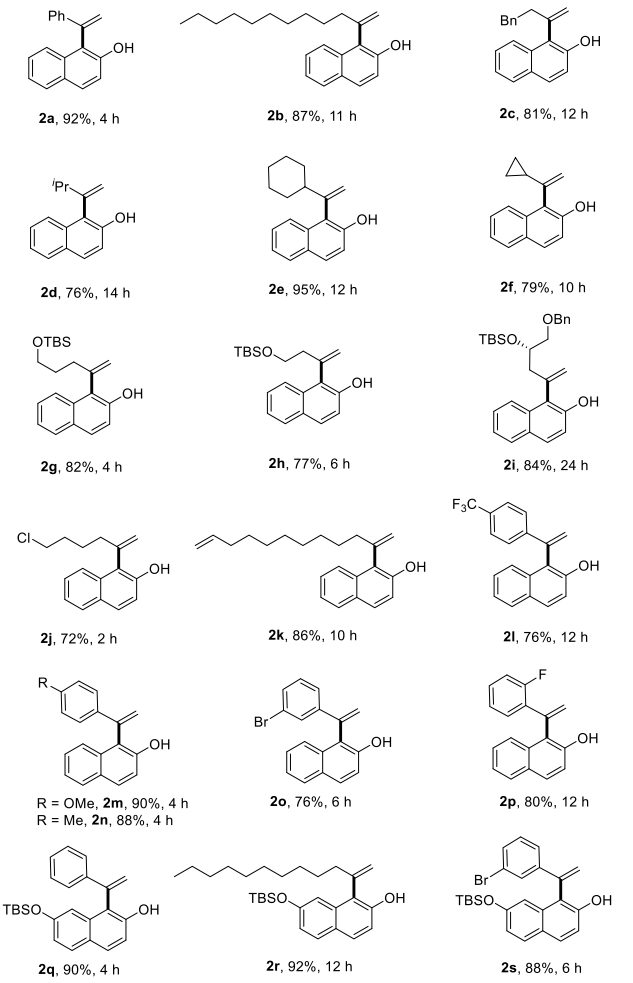
[a]General reaction conditions: reactions run in vials, alkyne (0.2 mmol), naphthol (0.3 mmol), 4 Å MS (50 mg), 0.1 m. [b]Isolated yields.

as well as in situ-generated hydrazoic acid to alkynes was achieved. This rate-accelerating phenomenon has also been harnessed to achieve highly enantioselective allenol cyclizations.[1e] Very recently, an intermolecular propargylic alcohol hydroalkenylation was also achieved, which leads to the synthetically valuable conjugated dienyl alcohols (Scheme 2A).[1g]

On the other hand, hydroarylation of an unactivated alkyne allows access to synthetically useful arylalkenes in an atom-efficient manner.[5] With the pioneering work published by Yamaguchi about the phenol or naphthol alkenylation with terminal alkynes,[6] a series of C-alkenylation transformations have been realized.[7−9] These strategies often suffer from shortcomings including severe reaction conditions (strong inorganic acid or Lewis acid used as catalyst and reaction temperature mostly at 120 °C or even higher, Scheme 2B), low effectiveness, and bad selectivity. Therefore, it is still of need to develop new methods for the transformation of this kind under mild catalytic conditions. With our ongoing study in this bifunctional phosphine ligand chemistry, we envisioned that, by using phenol or naphthol as a nucleophile, hydroarylation of alkynes may be realized at ambient temperature with the help of the weak interactions between the aryl hydroxy group and the amide group, as outlined in **A** in Scheme 2B. Besides, such a ligand−substrate interaction would also help prevent the formation of *O*-alkenylated adducts. In this work, we describe such a bifunctional-ligand-enabled efficient gold-catalyzed hydroarylation of alkynes under soft reaction conditions.

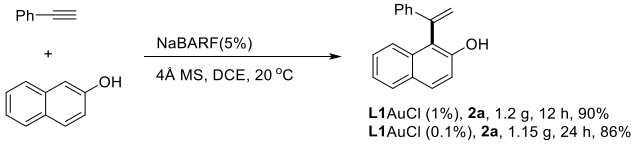
At the outset, phenol was chosen as the nucleophile to implement the design of this chemistry. However, no reaction

Scheme 3. Reaction Scope Study[a]

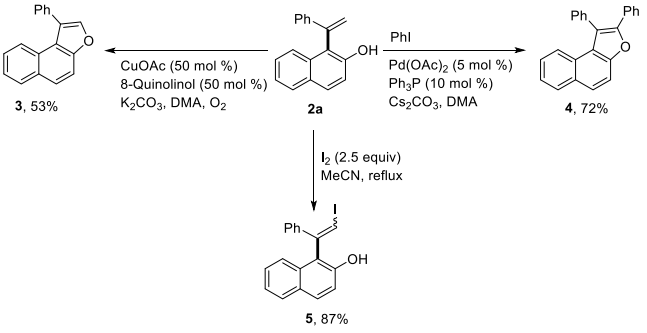


[a]General reaction conditions: reactions run in vials, alkyne (0.2 mmol), naphthol (0.3 mmol), NaBARF (5 mol %), 4 Å MS (50 mg), **L1**AuCl (1 mol %), DCE (2 mL), 20 °C. Isolated yields are reported.

Scheme 4. Gram-Scale Reaction



Scheme 5. Transformations of Product 2a



was observed after extensive exploration of ligands and reaction conditions while phenol was recovered intact. We then

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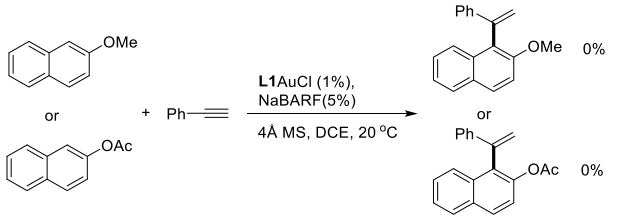
Scheme 6. Mechanism Studies



employed naphthol as the nucleophile. Encouragingly, the expected compoud **2a** was indeed formed in a good yield of 92% when **L1**AuCl was used as the catalyst and NaBARF was used as the chloride abstractor (Table 1, entry 1). Subsequent catalyst screenings revealed that our previously designed amine-functionalized ligands **L2**−**L5** were largely ineffective (entries 2−5). It should be mentioned that the use of common PPh_3AuCl, IPrAuCl, or JohnPhosAuCl in the presence of exogeneous Et_3N or its absence resulted in no reaction at all (entries 6 and 7). Both the gold precatalyst and NaBARF were required for the reaction (entries 8 and 9).[10] Replacing NaBARF by AgOTf (entry 10) or $AgNTf_2$ (entry 11) generated lower yields of the formation of **2a**. Besides, DCE was also found to be very significant for the optimal reaction conditions. With PhF or $PhCF_3$ as the reaction solvent, the yields of **2a** would reduce to only 77 and 82% (entries 12 and 13).

Then, the scope of this chemistry was examined. First, various aliphatic terminal alkynes were explored. As summarized in Scheme 3, when the terminal alkynes were installed by an alkyl group including 1-decanyl (**2b**), phenethyl (**2c**), isobutyl (**2d**), cyclohexyl (**2e**), or cyclopropyl (**2f**), the reactions all proceeded smoothly. Functionalized alkyl groups including OTBS (**2g**, **2h**), benzyloxy (**2i**), chloro (**2j**), and even C−C double bonds (**2k**) are also readily tolerated, highlighting the exceptionally mild nature of this chemistry. Several substituted phenylacetylenes were also examined. Substituents such as CF_3, OMe, Me, Br, or F at the different positions on the benzene ring were tolerated, and the corresponding 1,1-diarylethylenes **2l**−**2p** were generated in excellent yields. Besides, 2-naphthol functionalized by a 7-OTBS group underwent reactions with different terminal alkynes smoothly to afford the desired products **2q**, **2r**, and **2s** in 90, 92, and 88% yields, respectively. With these results in hand, then the challenging internal alkynes were also tested. Early results revealed that replacing the terminal alkynes with internal alkynes including 6-dodecyne and diphenylacetylene resulted in no reaction at this point, even at a higher reaction temperature (90 °C).

A gram-scale formation of **2a** was also carried out under standard conditions, and 1.2 g of the desired product was furnished on a 10 mmol scale (Scheme 4). Moreover, when the reaction was performed with the catalyst loading lowered to 0.1 mol %, 86% yield of the desired product could be generated, albeit a longer reaction time was needed.

The synthetic utilities of this chemistry are also demonstrated by one-step conversions of **2a** to versatile naphtho[2,1-*b*]furan derivatives, as outlined in Scheme 5.[11] In addition, an additional function handle (i.e., iodo) was readily installed into **2a** in an excellent yield upon routine iodination.[12]

It shoud be noted that the hydroarylation transformation did not happen to provide the product at all when the naphthol hydroxyl group was transformed to acetoxy or methoxy (Scheme 6). This result is consistent with the mechanism we proposed.

In conclusion, we have presented an efficient strategy for bifunctional-ligand-enabled gold-catalyzed intermolecular hydroarylation of alkynes under soft reaction conditions. The WangPhos ligand, which was installed with a remote amide group, is shown to be enabling in this transformation. This chemistry exhibits gentle reaction conditions, furnishes excellent yields, and tolerates a broad substrate scope.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02130.

Experimental procedures, characterization data for all new products, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Ting Li − *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China; Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California 93106, United States;* orcid.org/0000-0002-2186-6992; Email: chemlt2015@nynu.edu.cn

Liming Zhang − *Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California 93106, United States;* orcid.org/0000-0002-5306-1515; Email: zhang@chem.ucsb.edu

Authors

Yuhan Yang − *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China*

Baomin Luo − *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China*

Bo Li − *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China*

Luyi Zong − *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China*

Weiguang Kong − *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China*

Hao Yang − *College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China*

Xinpeng Cheng − *Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California 93106, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c02130

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) See, for example: (a) Wang, Z.; Wang, Y.; Zhang, L. Soft Propargylic Deprotonation: Designed Ligand Enables Au-Catalyzed Isomerization of Alkynes to 1,3-Dienes. *J. Am. Chem. Soc.* **2014**, *136*, 8887−8890. (b) Wang, Y.; Wang, Z.; Li, Y.; Wu, G.; Cao, Z.; Zhang, L. A general ligand design for gold catalysis allowing ligand-directed anti-nucleophilic attack of alkynes. *Nat. Commun.* **2014**, *5*, 3470. (c) Xu, Z.; Chen, H.; Wang, Z.; Ying, A.; Zhang, L. One-Pot Synthesis of Benzene-Fused Medium-Ring Ketones: Gold Catalysis-Enabled Enolate Umpolung Reactivity. *J. Am. Chem. Soc.* **2016**, *138*, 5515−5518. (d) Li, X.; Liao, S.; Wang, Z.; Zhang, L. Ligand-Accelerated Gold-Catalyzed Addition of in Situ Generated Hydrazoic Acid to Alkynes under Neat Conditions. *Org. Lett.* **2017**, *19*, 3687−3690. (e) Wang, Z.; Nicolini, C.; Hervieu, C.; Wong, Y.-F.; Zanoni, G.; Zhang, L. Remote Cooperative Group Strategy Enables Ligands for Accelerative Asymmetric Gold Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 16064−16067. (f) Wang, Z.; Ying, A.; Fan, Z.; Hervieu, C.; Zhang, L. Tertiary Amino Group in Cationic Gold Catalyst: Tethered Frustrated Lewis Pairs That Enable Ligand-Controlled Regiodivergent and Stereoselective Isomerizations of Propargylic Esters. *ACS Catal.* **2017**, *7*, 3676−3680. (g) Liao, S.; Porta, A.; Cheng, X.; Ma, X.; Zanoni, G.; Zhang, L. Bifunctional Ligand Enables Efficient Gold-Catalyzed Hydroalkenylation of Propargylic Alcohol. *Angew. Chem., Int. Ed.* **2018**, *57*, 8250−8254. (h) Li, T.; Zhang, L. Bifunctional Biphenyl-2-ylphosphine Ligand Enables Tandem Gold-Catalyzed Propargylation of Aldehyde and Unexpected Cycloisomerization. *J. Am. Chem. Soc.* **2018**, *140*, 17439−17443. (i) Cheng, X.; Wang, Z.; Quintanilla, C. D.; Zhang, L. Chiral Bifunctional Phosphine Ligand Enabling Gold-Catalyzed Asymmetric Isomerization of Alkyne to Allene and Asymmetric Synthesis of 2,5-Dihydrofuran. *J. Am. Chem. Soc.* **2019**, *141*, 3787. (j) Wang, H.; Li, T.; Zheng, Z.; Zhang, L. Efficient Synthesis of α-Allylbutenolides from Allyl Ynoates via Tandem Ligand-Enabled Au(I) Catalysis and the Claisen Rearrangement. *ACS Catal.* **2019**, *9*, 10339−10342. (k) Li, T.; Yang, Y.; Li, B.; Bao, X.; Zhang, L. Gold-Catalyzed Silyl-Migrative Cyclization of Homopropargylic Alcohols Enabled by Bifunctional Biphenyl-2-ylphosphine and DFT Studies. Org. *Org. Lett.* **2019**, *21*, 7791−7794.

(2) Homogeneous gold catalysis. For selected reviews, see: (a) Fürstner, A. Gold Catalysis for Heterocyclic Chemistry: A Representative Case Study on Pyrone Natural Products. *Angew. Chem., Int. Ed.* **2018**, *57*, 4215−4233. (b) Li, Y.; Li, W.; Zhang, J. Gold-Catalyzed Enantioselective Annulations. *Chem. - Eur. J.* **2017**, *23*, 467−512. (c) Zi, W.; Toste, F. D. Recent advances in enantioselective gold catalysis. *Chem. Soc. Rev.* **2016**, *45*, 4567−4589. (d) Asiri, A. M.; Hashmi, A. S. K. Gold-catalysed reactions of diynes. *Chem. Soc. Rev.* **2016**, *45*, 4471−4503. (e) Huple, D. B.; Ghorpade, S.; Liu, R. Recent Advances in Gold-Catalyzed N-and O-Functionalizations of Alkynes with Nitrones, Nitroso, Nitro and Nitroxy Species. *Adv. Synth. Catal.* **2016**, *358*, 1348−1367. (f) Dorel, R.; Echavarren, A. M. Gold(I)-Catalyzed Activation of Alkynes for the Construction of Molecular Complexity. Chem. *Chem. Rev.* **2015**, *115*, 9028−9072. (g) Wang, Y.; Muratore, M. E.; Echavarren, A. M. Gold Carbene or Carbenoid: Is There a Difference? *Chem. - Eur. J.* **2015**, *21*, 7332−7339. (h) Fensterbank, L.; Malacria, M. Molecular Complexity from Polyunsaturated Substrates: The Gold Catalysis Approach. *Acc. Chem. Res.* **2014**, *47*, 953−965. (i) Zhang, L. A Non-Diazo Approach to α-Oxo Gold Carbenes via Gold-Catalyzed Alkyne Oxidation. *Acc. Chem. Res.* **2014**, *47*, 877−888. (j) Hashmi, A. S. K. Dual Gold Catalysis. *Acc. Chem. Res.* **2014**, *47*, 864−876. (k) Fürstner, A.; Davies, P. W. Catalytic Carbophilic Activation: Catalysis by Platinum and Gold π Acids. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410−3449. (l) Pflasterer, D.; Hashmi, A. S. K. Gold catalysis in total synthesis − recent achievements. *Chem. Soc. Rev.* **2016**, *45*, 1331−1367. (m) Hashmi, A. S. K. Gold-Catalyzed Organic Reactions. Chem. *Chem. Rev.* **2007**, *107*, 3180−3211. (n) Hashmi, A. S. K. Homogeneous gold catalysts and alkynes: A successful liaison. *Gold Bulletin* **2003**, *36*, 3−9.

(3) Surry, D. S.; Buchwald, S. L. Biaryl Phosphane Ligands in Palladium-Catalyzed Amination. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338−6361.

(4) (a) Grützmacher, H. Cooperating Ligands in Catalysis. *Angew. Chem., Int. Ed.* **2008**, *47*, 1814−1818. (b) Askevold, B.; Roesky, H. W.; Schneider, S. *ChemCatChem* **2012**, *4*, 307. (c) Khusnutdinova, J. R.; Milstein, D. Metal-Ligand Cooperation. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236−12273. (d) Trincado, M.; Grützmacher, H. Cooperating Ligands in Catalysis. *Cooperative Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA: 2015; p 67.

(5) See: (a) Manikandan, R.; Jeganmohan, M. Recent Advances in the Ruthenium-Catalyzed Hydroarylation of Alkynes With Aromatics: Synthesis of Trisubstituted Alkenes. *Org. Biomol. Chem.* **2015**, *13*, 10420−10436. (b) Boyarskiy, V. P.; Ryabukhin, D. S.; Bokach, N. A.; Vasilyev, A. V. Alkenylation of Arenes and Heteroarenes with Alkynes. *Chem. Rev.* **2016**, *116*, 5894−5986. (c) Petrini, M. Regioselective Direct C-Alkenylation of Indoles. *Chem. - Eur. J.* **2017**, *23*, 16115−16151. (d) Arndt, S.; Borstelmann, J.; Eshagh Saatlo, R.; Antoni, P. W.; Rominger, F.; Rudolph, M.; An, Q.; Vaynzof, Y.; Hashmi, A. S. K. The Gold(I)-Mediated Domino Reaction to Fused Diphenyl Phosphoniumfluorenes: Mechanistic Consequences for Gold-Catalyzed Hydroarylations and Application in Solar Cells. *Chem. - Eur. J.* **2018**, *24*, 7882−7889. (e) Schießl, J.; Rudolph, M.; Hashmi, A. S. K. The Gold-Catalyzed Hydroarylation of Alkynes with Electron-Rich Heteroarenes-A Kinetic Investigation and New Synthetic Possibilities. *Adv. Synth. Catal.* **2017**, *359*, 639−653. (f) Nösel, P.; Müller, V.; Mader, S.; Moghimi, S.; Rudolph, M.; Braun, I.; Rominger, F.; Hashmi, A. S. K. Gold-Catalyzed Hydroarylating Cyclization of 1,2-Bis(2-iodoethynyl)-benzenes. *Adv. Synth. Catal.* **2015**, *357*, 500−506. (g) Hashmi, A. S. K.; Blanco, C. Gold Catalysis: Observation of a Two-Fold Intermolecular Hydroarylation of Unactivated C-C Triple Bonds. *Eur. J. Org. Chem.* **2006**, *2006*, 4340−4342. (h) Hashmi, A. S. K.; Kurpejović, E.; Frey, W.; Bats, J. W. Gold catalysis contra platinum catalysis in hydroarylation contra phenol synthesis. *Tetrahedron* **2007**, *63*, 5879−5885. (i) Hashmi, A. S. K.; Grundl, L. Gold catalysis: five new bonds by a domino hydroarylation/cycloisomerization. *Tetrahedron* **2005**, *61*, 6231−6236.

(6) (a) Yamaguchi, M.; Hayashi, A.; Hirama, M. Ortho-Vinylation and Ortho-Alkenylation of Phenols. *J. Am. Chem. Soc.* **1995**, *117*, 1151−1152. (b) Yamaguchi, M.; Arisawa, M.; Kido, Y.; Hirama, M. 2,6-Divinylation of phenols with ethyne. *Chem. Commun.* **1997**, 1663−1664. (c) Yamaguchi, M. Direct vinylation reactions of phenols. *Pure Appl. Chem.* **1998**, *70*, 1091−1096.

(7) For phenol, see: (a) Kobayashi, K.; Yamaguchi, M. Catalytic Ethenylation Reaction of Phenol Using $SnCl_4$. *Org. Lett.* **2001**, *3*, 241−242. (b) Trost, B. M.; Toste, F. D.; Greenman, K. Atom Economy. Palladium-Catalyzed Formation of Coumarins by Addition of Phenols and Alkynoates via a Net C-H Insertion. *J. Am. Chem. Soc.* **2003**, *125*, 4518−4526. (c) Nevado, C.; Echavarren, A. M. Intramolecular Hydroarylation of Alkynes Catalyzed by Platinum or Gold: Mechanism and endo Selectivity. *Chem. - Eur. J.* **2005**, *11*, 3155−3164. (d) Yadav, J. S.; Subba Reddy, B. V.; Gupta, M. K.; Dash, U.; Pandey, S. K. Gallium(III) Chloride Catalyzed Stereoselective Synthesis of E-Configured α,β-Unsaturated Ketones. *Synlett* **2007**, *2007*, 0809−0811. (e) Yadav, J.; Reddy, B.; Sengupta, S.; Biswas, S. Gallium(III) Chloride Catalyzed Hydroarylation of Arylacetylenes with Naphthols and Phenols: A Facile Synthesis of Vinylarenes. *Synthesis* **2009**, *2009*, 1301−1304. (f) Arcadi, A.; Blesi, F.; Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Marinelli, F. Gold versus silver catalyzed intramolecular hydroarylation reactions of [(3-arylprop-2-ynyl)oxy]-benzene derivatives. *Org. Biomol. Chem.* **2012**, *10*, 9700−9708. (g) Nemoto, T.; Matsuo, N.; Hamada, Y. Gold-Catalyzed Carbocyclization of Phenols with a Terminal Alkyne via an Intramolecular ipso-Friedel-Crafts Alkenylation. *Adv. Synth. Catal.* **2014**, *356*, 2417−2421. (h) Murai, M.; Yamamoto, M.; Takai, K. Rhenium-Catalyzed Regioselective ortho-Alkenylation and [3 + 2 + 1] Cycloaddition of Phenols with Internal Alkynes. *Org. Lett.* **2019**, *21*, 3441−3445. (i) Murai, M.; Yamamoto, M.; Takai, K. Mechanistic Insights into Rhenium-Catalyzed Regioselective C-Alkenylation of Phenols with Internal Alkynes. *Chem. - Eur. J.* **2019**, *25*, 15189−15197.

(8) For naphthol, see: (a) Varghese, S.; Nagarajan, S.; Benzigar, M. R.; Mano, A.; Alothman, Z. A.; Raj, G. A. G.; Vinu, A. 3D Nanoporous FeAl-KIT-5 with a cage type pore structure: a highly efficient and stable

https://dx.doi.org/10.1021/acs.orglett.0c02130
Org. Lett. XXXX, XXX, XXX−XXX

catalyst for hydroarylation of styrene and arylacetylenes. *Tetrahedron Lett.* **2012**, *53*, 1485−1489. (b) Moskalev, M. V.; Yakub, A. M.; Morozov, A. G.; Baranov, E. V.; Kazarina, O. V.; Fedushkin, I. L. Hydroarylation of Alkynes with Phenols in the Presence of Gallium Complexes of a Labile N-Ligand: Synthesis of Chromenes. *Eur. J. Org. Chem.* **2015**, *2015*, 5781. (c) Duarah, G.; Kaishap, P. P.; Sarma, B.; Gogoi, S. Ruthenium(II)-Catalyzed Dearomatized C-H Activation and Annulation Reaction of Vinylnaphthols with Alkynes: Access to Spiro-Pentacyclic Naphthalenones. *Chem. - Eur. J.* **2018**, *24*, 10196−10200. (d) Pramanik, A.; Ghatak, A.; Khan, S.; Bhar, S. Hydroarylation of alkynes and alkenes through alumina-sulfuric acid catalyzed regioselective CC bond formation. *Tetrahedron Lett.* **2019**, *60*, 1091−1095. (e) Wang, Y.-B.; Yu, P.; Zhou, Z.-P.; Zhang, J.; Wang, J.; Luo, S.-H.; Gu, Q.-S.; Houk, K. N.; Tan, B. Rational design, enantioselective synthesis and catalytic applications of axially chiral EBINOLs. Nat. *Catal* **2019**, *2*, 504−513.

(9) (a) Camacho, D. H.; Saito, S.; Yamamoto, Y. 'Anti-Wacker'-type hydroalkoxylation of diynes catalyzed by palladium(0). *Tetrahedron Lett.* **2002**, *43*, 1085−1088. (b) Kuram, M. R.; Bhanuchandra, M.; Sahoo, A. K. Gold-Catalyzed Intermolecular Hydrophenoxylation of Unactivated Internal Alkynes. *J. Org. Chem.* **2010**, *75*, 2247−2258. (c) Oonishi, Y.; Gómez-Suárez, A.; Martin, A. R.; Nolan, S. P. Hydrophenoxylation of Alkynes by Cooperative Gold Catalysis. *Angew. Chem., Int. Ed.* **2013**, *52*, 9767−9671.

(10) (a) Schießl, J.; Schulmeister, J.; Doppiu, A.; Worner, E.; Rudolph, M.; Karch, R.; Hashmi, A. S. K. An Industrial Perspective on Counter Anions in Gold Catalysis: On Alternative Counter Anions. *Adv. Synth. Catal.* **2018**, *360*, 3949−3959. (b) Schießl, J. J.; Schulmeister; Doppiu, A.; Wörner, E.; Rudolph, M.; Karch, R.; Hashmi, A. S. K. An Industrial Perspective on Counter Anions in Gold Catalysis: Underestimated with Respect to "Ligand Effects. *Adv. Synth. Catal.* **2018**, *360*, 2493−2502.

(11) Rao, V. K.; Shelke, G. M.; Tiwari, R.; Parang, K.; Kumar, A. A Simple and Efficient Synthesis of 2,3-Diarylnaphthofurans Using Sequential Hydroarylation/Heck Oxyarylation. *Org. Lett.* **2013**, *15*, 2190−2193.

(12) Rao, V. K.; Kaswan, P.; Shelke, G. M.; Ryan, A.; Jha, M.; Kumar, A. Iodine-Mediated, Microwave-Assisted Synthesis of 1-Arylnaphthofurans via Cyclization of 1-(1'-Arylvinyl)-2-naphthols. *Synthesis* **2015**, *47*, 3990−3996.

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