Organic LETTERS

Letter

pubs.acs.org/OrgLett

# Fluoride-Assisted Activation of Calcium Carbide: A Simple Method for the Ethynylation of Aldehydes and Ketones

Abolfazl Hosseini,[⊥] Daniel Seidel,*[,‡] Andreas Miska,[§] and Peter R. Schreiner*[,⊥]

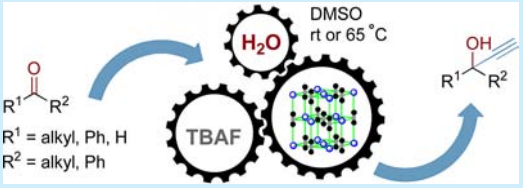
[⊥]Institute of Organic Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany

[‡]Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, United States

[§]Institute of Inorganic and Analytical Chemistry, Justus-Liebig University, Heinrich-Buff-Ring 58, 35392 Giessen, Germany

Supporting Information

**ABSTRACT:** The fluoride-assisted ethynylation of ketones and aldehydes is described using commercially available calcium carbide with typically 5 mol % of TBAF·3$H_2O$ as the catalyst in DMSO. Activation of calcium carbide by fluoride is thought to generate an acetylide "ate"-complex that readily adds to carbonyl groups. Aliphatic aldehydes and ketones generally provide high yields, whereas aromatic carbonyls afford propargylic alcohols with moderate to good yields. The use of calcium carbide as a safe acetylide ion source along with economic amounts of TBAF·3$H_2O$ make this procedure a cheap and operationally simple method for the preparation of propargylic alcohols.




A long neglected safe and cheap source for the formation of sp–sp$^3$ carbon bonds derives from the use of calcium carbide ($CaC_2$) through the addition of acetylides to carbonyl compounds. Although this strategy has been widely explored since the first preparations of propargyl alcohols in 1900[1] using the base-mediated addition of acetylene to carbonyl compounds,[2] further developments would be desirable in view of the ubiquitous availability of $CaC_2$ at industrial scale. Propargyl alcohols are valuable intermediates in organic synthesis. They have been widely used to prepare natural products[3] and biologically active compounds[4] and to obtain valuable intermediates through coupling reactions,[5] additions to triple bonds,[6] and many more. Of the many available methods for their preparation, metal acetylides have been recognized as being particularly useful. Although metal acetylides readily add to carbonyl compounds, this approach often requires the use of 1 equiv of a strong base, low temperatures, dry solvents, and a deprotection step when, for instance, commonly employed trimethylsilyl acetylene is used, which makes such transformations less desirable at large scale.[5,7]

$CaC_2$ on the other hand is an acetylide source that was prepared first by Wöhler in 1862.[8] It was used in carbide lamps, welding, and early automobile headlights.[9] Due to the low solubility of $CaC_2$ in organic solvents and, consequently, its poor reactivity,[10] it is mainly used for the production of acetylene gas and as a drying agent in organic synthesis. The low reactivity of solid $CaC_2$ can be attributed to its insolubility deriving from its highly stable lattice structure. "Monomerized" calcium acetylide, prepared by dissolving calcium metal and acetylene in liquid ammonia, readily reacts with a variety of electrophiles to give the corresponding adducts;[11] however, only a few examples have been described.[12] Similarly, there are only a few reports on the use of $CaC_2$ for synthetic purposes. In 2006, Cheng and co-workers reported the synthesis of symmetric diaryl ethynes from aryl bromides using $CaC_2$.[13] Recently, Kuang et al. reported the triazolation of aryl azides using calcium carbide as the acetylene source, providing 1-monosubstituted aryl 1,2,3-triazoles in moderate to good yields.[14] Zhang et al. developed several new methods for utilizing $CaC_2$ in organic synthesis.[9,10c,e] They suggested that the addition of small amounts of water can speed up reactions by increasing the solubility of $CaC_2$. Using this strategy they synthesized enaminones and propargylic amines through a three-component coupling reaction of $CaC_2$, aryl aldehydes, and amines.[10a] Recently, the same group reported a convenient method for the preparation of propargyl alcohols by reacting $CaC_2$ with aldehydes and ketones in the presence of 50 mol % of cesium carbonate in aqueous DMSO at 60 °C.[10c] Although moderate to good yields were obtained, the high cost of $Cs_2CO_3$ and very large amounts of metal contaminated waste limit the application of such a method. In addition, this method is not applicable to aromatic aldehydes and requires heating. Other methods involve the use of super bases, such as KOH/$H_2O$/DMSO,[15] $Bu_4NBr$/KOH/toluene,[7c] KOH/EtOH/$H_2O$/DMSO,[16] and $Bu_4NOH$/$H_2O$/DMSO,[17] for the addition of acetylides to carbonyls. However, these methods suffer from low yields, the use of a large excess of acetylene gas, equimolar or excess amounts of base as well as molecular sieves, and pretempering of the reaction solutions. We previously reported the use of phase-transfer conditions, TBABr/fluorobenzene/aq. sodium hydroxide as an organocatalytic system for the alkynylation of aldehydes and ketones.[18] We now report a

**Received:** April 26, 2015
**Published:** May 22, 2015

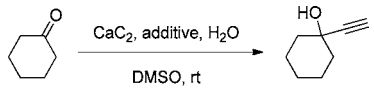
  

DOI: 10.1021/acs.orglett.5b01219
*Org. Lett.* 2015, 17, 2808–2811

novel method for the mild alkynylation of various aldehydes and ketones, utilizing commercial calcium carbide (97% purity) in combination with a fluoride source in DMSO/water.

Initially, cyclohexanone was used as a model substrate to optimize the reaction conditions (Table 1). In the absence of additives, no product (**2a**) was obtained after 22 h, even at 60 °C (Table 1, entries 1 and 2). Upon adding KF (50 mol %), the desired product **2a** was obtained with a conversion of 5% (Table 1, entry 3). The conversion to product **2a** could be improved to over 50% by using 3 equiv of KF, but the reaction was not always reproducible (Table 1, entry 4), owing to the low solubility of potassium fluoride in DMSO.[19] It should be noted that the reaction did not proceed in the absence of added water even after long reaction times (Table 1, entry 5). With 0.5 equiv of CsF as the fluoride source, the reaction proceeded efficiently to furnish the desired product **2a** with excellent conversion (Table 1, entry 6). However, in the case of using a considerably more economic amount of CsF (5 mol %), **2a** was obtained with low conversion (Table 1, entry 7). Several other fluoride salts were subsequently tested (Table 1, entries 8–14). However, only tetrabutylammonium fluoride showed enhanced activity compared to other fluoride sources (Table 1, entries 11–14). The reaction provided nearly quantitative access to **2a** using 70 mol % of TBAF·3H$_2$O after 3 h without additional water. The amount of TBAF·3H$_2$O could readily be reduced to 5 mol % when water was added (95% of **2a**, entry 14). No catalytic activity was observed when other tetrabutylammonium halides were employed, and only low conversion was reached when tetrabutylammonium acetate was used as the catalyst (Table 1, entries 15–18). In comparison to the preparation of **2a** using $Cs_2CO_3$ (0.5 equiv),[10c] TBAF·3H$_2$O appears to be a superior catalyst in this reaction (Table 1, entry 19). Encouraged by these results, we further optimized the reaction conditions (Table S1, Supporting Information (SI)). With the optimized reaction conditions in hand (termed method A), the scope and limitation of the reaction were examined (Table 2).

**Table 1. Evaluation of Reaction Conditions for the Ethynylation of Cyclohexanone**[a]

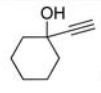
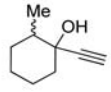
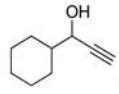
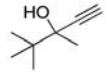
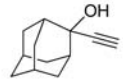
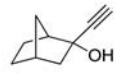
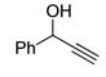



1a 2a

| no. | conv (%)[c] | t [h] | water (equiv)[b] | additive (equiv) |
|---|---|---|---|---|
| 1 | NR[d] | 22 | 3.34 | – |
| 2[e] | NR | 22 | 3.34 | – |
| 3 | 5 | 22 | 3.34 | KF (0.50) |
| 4[f] | 57 | 3 | 3.34 | KF (3.00) |
| 5 | NR | 12 | – | KF (3.00) |
| 6 | 99 | 2 | 3.34 | CsF (0.50) |
| 7 | 29 | 3.5 | 3.34 | CsF (0.05) |
| 8 | NR | 2 | 3.34 | $ZnF_2$ (0.05) |
| 9 | NR | 2 | 3.34 | $CaF_2$ (0.05) |
| 10 | NR | 2 | 3.34 | $CaF_2$ (1.00) |
| 11 | 99 | 3 | 2.10 | TBAF·3H$_2$O (0.70) |
| 12 | 71 | 8 | 0.60 | TBAF·3H$_2$O (0.20) |
| 13 | 99 | 1 | 3.34 | TBAF·3H$_2$O (0.20) |
| 14 | 95 | 2 | 3.34 | TBAF·3H$_2$O (0.05) |
| 15 | NR | 17 | 3.34 | TBACl (0.05) |
| 16 | NR | 45 | 3.34 | TBABr (0.05) |
| 17 | trace | 45 | 3.34 | TBAI (0.05) |
| 18 | 7 | 17 | 3.34 | TBAAc (0.05) |
| 19 | 26 | 3 | 3.34 | $Cs_2CO_3$ (0.50) |

[a]Reaction conditions: **1a** (1 mmol), $CaC_2$ (3 mmol), DMSO (3 mL). [b]Total amount of water (from TBAF·3H$_2$O and added water). [c]GC analysis (conversion of starting material). [d]No reaction. [e]Reaction performed at 60 °C. [f]Average of three runs.

**Table 2. Alkynylation of Aldehydes and Ketones Using TBAF·3H$_2$O and Calcium Carbide As Acetylene Source in DMSO**[a]

| no | product | yield (%)[b] | t [h] | p$K_a$[c] |
|---|---|---|---|---|
| 1 |  (**2a**) | 94 (90) | 2 | 26.4 |
| 2 |  (**2b**)[d] | 93 (87) | 2 | n.a.[e] |
| 3 |  (**2c**) | 93 (90) | 2 | n.a. |
| 4 |  (**2d**) | 68 | 3 | 27.7 |
| 5 |  (**2e**) | 75 | 5 | 27.1 |
| 6 |  (**2f**) | 85[f] | 2 | n.a. |
| 7 |  (**2g**) | 82 | 5 | 29.0 |
| 8 |  (**2h**) | 32 | 4 | - |

[a]Method A: substrate (1 mmol), $CaC_2$ (2.7 mmol), water (2.27 mmol), TBAF·3H$_2$O (0.05 equiv), and DMSO (3 mL) at room temperature. [b]Isolated product yield (values in parentheses refer to gram scale isolated yields). [c]p$K_a$ of corresponding carbonyl substrate in DMSO. [d]*dr*: 2:1 (the diastereomeric ratio was determined by $^1$H NMR). [e]Not available. [f]Isolated product yield after single recrystallization.

The reaction of cyclohexyl aldehydes and ketones (1 equiv), $CaC_2$ (2.7 equiv), and water (2.27 equiv) in 3 mL of DMSO with 0.05 equiv of TBAF·3H$_2$O (0.5 M in DMSO) at room temperature for 2 h afforded the corresponding ethynyl alcohols **2a–c** in high yields (>90%) (Table 2, entries 1–3). No aldol products were observed in these cases according to GC-MS analysis.

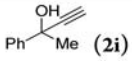
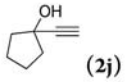
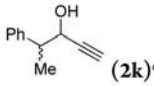
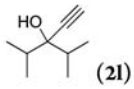
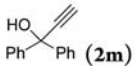
Upon scale-up, the ethylynation of **1a–c** occurred cleanly with a 5 mol % catalyst loading to give the corresponding propargyl alcohols in high yields. Under the same reaction conditions cyclopentanone failed to give the desired product and the reaction afforded the aldol product instead. Although the difference between the p$K_a$ values of cyclohexanone (26.4) and cyclopentanone (25.8) in DMSO is small, we considered the p$K_a$ of 26.4 for the carbonyl component as a lower limit to avoid aldol condensation in the basic medium. It should be pointed out that other factors might be relevant. For instance, it is well-known that cyclohexanone reacts much more readily



DOI: 10.1021/acs.orglett.5b01219
*Org. Lett.* 2015, 17, 2808–2811

with nucleophiles than cyclopentanone, possibly because of strain relief.[20] Under the same conditions, the reaction of aliphatic ketones (pinacolone and 3-pentanone with the p$K_a$ values of 27.7 and 27.1, respectively) gave the ethynyl product exclusively in good yields (Table 2, entries 4 and 5). The reaction of 2-adamantanone under the optimal reaction conditions gave the corresponding propargyl alcohol in 85% isolated product yield (entry 6). Similarly, norcamphor produced the desired 2-*exo*-ethynylbicyclo[2.2.1]heptan-2-ol product in good yield (entry 7). Even highly unreactive (in these types of transformations) benzaldehyde gave 1-phenylpropargyl alcohol (**2h**) in 32% isolated product yield (entry 8). The standard reaction conditions (method A) were ineffective for the alkynylation of acetophenone, very likely due to rapid enolization of acetophenone.[16,21] Therefore, newly optimized conditions (method B) using acetophenone as a model substrate (Table S2, SI) were used for the ethynylation of carbonyl compounds with p$K_a$ values lower than 26. This also allowed the conversion of cyclopentanone to the corresponding product (Table 3, entry 2). In the case of 2-phenylpropionaldehyde, the reaction required heating to 65 °C (Table 3, entry 3). Diisopropyl ketone has proven unreactive with method A, presumably due to significant steric hindrance and deactivation of the carbonyl group through alkyl substitution. However, it afforded 30% of the desired product using method B at 65 °C (Table 3, entry 4).

**Table 3. Alkynylation of Challenging Substrates Using TBAF·3$H_2O$ and Calcium Carbide As Acetylene Source in DMSO[a]**

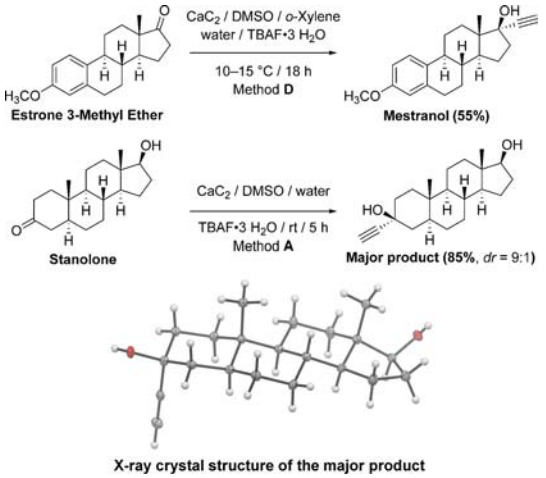
| no | product | yield (%)[b] | $t$ [h] | p$K_a$[c] |
|---|---|---|---|---|
| 1 |  (**2i**) | 53 | 2 | 24.7 |
| 2 |  (**2j**) | 32 | 24 | 25.8 |
| 3[d] |  (**2k**)[e] | 75 | 24 | n.a.[f] |
| 4[d] |  (**2l**) | 30 | 6 | 28.2 |
| 5[g] |  (**2m**) | 53 | 3 | - |

[a]Method B: substrate (1 mmol), $CaC_2$ (12 mmol), water (25 mmol, added over 2 h with a syringe pump), TBAF·3$H_2O$ (0.3 mmol), and DMSO (3 mL) at room temperature. [b]Isolated product yield. [c]p$K_a$ of corresponding carbonyl substrate in DMSO. [d]Reaction performed at 65 °C. [e]*dr*: 2:1 (the diastereomeric ratio was determined by $^1$H NMR). [f]Not available. [g]Method C: substrate (1 equiv), $CaC_2$ (2.7 equiv), water (3.6 equiv), TBAF·3$H_2O$ (0.5 equiv), and DMSO (3 mL) at room temperature.

Benzophenone was the least reactive ketone,[22] and methods A (no reaction) and B (10% conversion) proved unsuitable even after long reaction times (up to 20 h). However, increasing the amounts of TBAF·3$H_2O$ to 50 mol % provided a 53% yield of isolated product **2m** (Table 3, entry 5).

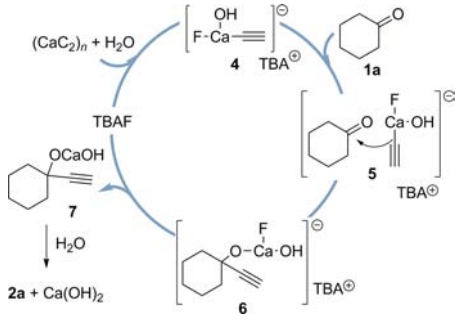
As a further application of our protocol, we used it for the synthesis of pharmacologically active steroids. For instance, the oral contraceptive pro-drug Mestranol can readily be prepared from estrone 3-methyl ether (cf. SI). Similarly, Stanolone can be ethnylated with high yield using method A (Scheme 1) that provides easier and more effective access to the desired product than previously reported procedures.[23] The product structure was also confirmed by X-ray crystallography.

**Scheme 1. Fluoride-Promoted Ethynylation of Steroids Using Calcium Carbide**




The reactivity of metal acetylides toward nucleophilic additions is strongly influenced by their solubility, and it has been demonstrated that addition of chelating agents may increase their reactivity.[24] In terms of mechanism, we note that although calcium acetylide has been considered a monomeric compound, its structure has not been firmly elucidated. However, in the case of phenylacetylide, a structurally related compound, a polymeric structure has been proposed that is partially soluble and slowly depolymerizes in solution, probably giving predominantly a dimer.[25] At the same time, the ability of calcium to form complexes with carbonyl compounds is well-known,[26] so it is likely that Ca···O═C coordination also plays a role in the reactions presented here. Second, calcium ate-complexes bearing, for instance, hexamethyldisilazides have been used for catalytic intramolecular hydroamination reactions.[27] Based on the results presented here and literature reports, a suggested mechanism is illustrated in Scheme 2. The reaction of water with solid calcium carbide gives ethynylcalcium hydroxide, which is activated with fluoride from TBAF·3$H_2O$ to form the corresponding ate-complex **4**. Complex **4** then attacks the carbonyl component (**5**) to give addition product **6**. Subsequently, the product complex **6** regenerates

**Scheme 2. Suggested Mechanism for the Fluorine Catalyzed Ethynylation of Aldehydes and Ketones with $CaC_2$**






DOI: 10.1021/acs.orglett.5b01219
*Org. Lett.* 2015, 17, 2808–2811

the catalyst and liberates calcium salt **7** that is hydrolyzed to produce product **2a** upon workup. Importantly, the reaction did not proceed with acetylene gas instead of calcium carbide with our two protocols. Phenylacetylene, a more acidic alkyne,[28] gave no conversion in the absence of calcium carbide even after 3 h. We thought that it might be possible to perform an acid–base reaction through anion exchange in complex **4** (Scheme 2) using phenylacetylene and concomitant release of acetylene gas. Indeed, addition of cyclohexanone to a solution of phenylacetylene under the conditions of method A afforded 1-(phenylethynyl)cyclohexanol in 70% isolated product yield (see SI for more details).

Although catalytic ethynylation of aldehydes and ketones has previously been achieved, the efficient catalytic system described here has the advantage of being cost-effective, safe, and simple. The mechanistic details of the reaction and the development of asymmetric variants are now under investigation.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, characterization data, and spectra for all compounds, cif file of the X-ray structure of ethynyl-3,17$\beta$-andro-stanediol. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01219.

## ■ AUTHOR INFORMATION

### Corresponding Authors

*E-mail: seidel@rutchem.rutgers.edu.
*E-mail: prs@org.chemie.uni-giessen.de.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract DE-AC02-76SF00515. D.S. is grateful to the Alexander von Humboldt Foundation for a research fellowship for experienced researchers.

## ■ REFERENCES

(1) Favorskii, A. E.; Skosarevskii, M. P. *Zh. Russ. Khim. Ob-va.* **1900**, *32*, 652.
(2) Trofimov, B. A.; Schmidt, E. Y. *Russ. Chem. Rev.* **2014**, *83*, 600.
(3) (a) Axelrod, A.; Eliasen, A. M.; Chin, M. R.; Zlotkowski, K.; Siegel, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3421. (b) Dayaker, G.; Durand, T.; Balas, L. *J. Org. Chem.* **2014**, *79*, 2657.
(4) (a) Piersanti, G.; Bartoccini, F.; Lucarini, S.; Cabri, W.; Stasi, M. A.; Riccioni, T.; Borsini, F.; Tarzia, G.; Minetti, P. *J. Med. Chem.* **2013**, *56*, 5456. (b) Beauglehole, A.; Rieger, J. M.; Thompson, R. D. WO 2005097140 A2, 2005.
(5) (a) Gronnier, C.; Boissonnat, G.; Gagosz, F. *Org. Lett.* **2013**, *15*, 4234. (b) Wang, L.-J.; Zhu, H.-T.; Wang, A.-Q.; Qiu, Y.-F.; Liu, X.-Y.; Liang, Y.-M. *J. Org. Chem.* **2014**, *79*, 204.
(6) (a) Liao, W.-W.; Müller, T. J. J. *Synlett* **2006**, 3469. (b) Schramm, O. G.; Müller, T. J. J. *Adv. Synth. Catal.* **2006**, *348*, 2565.
(7) (a) Xu, C.-F.; Xu, M.; Yang, L.-Q.; Li, C.-Y. *J. Org. Chem.* **2012**, *77*, 3010. (b) Clyburne, J.; Ramnial, T. WO 2006007703 A1, 2006. (c) Deng, X. CN103113188 A, 2013. (d) Saunders, J. H. *Org. Synth.* **1949**, *29*, 47. (e) Chaco, M. C.; Iyer, B. H. *J. Org. Chem.* **1960**, *25*, 186. (f) Wang, J.; Zhu, H.-T.; Li, Y.-X.; Wang, L.-J.; Qiu, Y.-F.; Qiu, Z.-H.; Zhong, M.-J.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2014**, *16*, 2236.
(8) Wöhler, F. *Liebigs Ann.* **1862**, *124*, 220.
(9) Schobert, H. *Chem. Rev.* **2014**, *114*, 1743.
(10) (a) Yu, D.; Sum, Y. N.; Ean, A. C. C.; Chin, M. P.; Zhang, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 5125. (b) Hamberger, M.; Liebig, S.; Friedrich, U.; Korber, N.; Ruschewitz, U. *Angew. Chem., Int. Ed.* **2012**, *51*, 13006. (c) Sum, Y. N.; Yu, D.; Zhang, Y. *Green Chem.* **2013**, *15*, 2718. (d) Kaewchangwat, N.; Sukato, R.; Vchirawongkwin, V.; Vilaivan, T.; Sukwattanasinitt, M.; Wacharasindhu, S. *Green Chem.* **2015**, *17*, 460. (e) Lin, Z.; Yu, D.; Sum, Y. N.; Zhang, Y. *ChemSusChem* **2012**, *5*, 625.
(11) Vaughn, T. H.; Hennion, G. F.; Vogt, R. R.; Nieuwland, J. A. *J. Org. Chem.* **1937**, *2*, 1.
(12) Oroshnik, W.; Mebane, A. D. *J. Am. Chem. Soc.* **1949**, *71*, 2062.
(13) Zhang, W.; Wu, H.; Liu, Z.; Zhong, P.; Zhang, L.; Huang, X.; Cheng, J. *Chem. Commun.* **2006**, *46*, 4826.
(14) Jiang, Y.; Kuang, C.; Yang, Q. *Synlett* **2009**, 3163.
(15) (a) Sobenina, L. N.; Tomilin, D. N.; Petrova, O. V.; Mikhaleva, A. I.; Trofimov, B. A. *Russ. J. Org. Chem.* **2013**, *49*, 356. (b) Tomilin, D. N.; Petrova, O. V.; Sobenina, L. N.; Mikhaleva, A. I.; Trofimov, B. A. *Chem. Heterocycl. Compd.* **2013**, *49*, 341.
(16) Shmidt, E. Y.; Bidusenko, I. A.; Protsuk, N. I.; Mikhaleva, A. I.; Trofimov, B. A. *Russ. J. Org. Chem.* **2013**, *49*, 8.
(17) Schmidt, E. Y.; Cherimichkina, N. A.; Bidusenko, I. A.; Protzuk, N. I.; Trofimov, B. A. *Eur. J. Org. Chem.* **2014**, 4663.
(18) Weil, T.; Schreiner, P. R. *Eur. J. Org. Chem.* **2005**, 2213.
(19) (a) Li, H.; Liu, J.; Chen, X.; Ren, T. *J. Mol. Liq.* **2012**, *166*, 67. (b) Furuya, T.; Kuttruff, C. A.; Ritter, T. *Curr. Opin. Drug Discovery Dev.* **2008**, *11*, 803.
(20) Brown, H. C.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 221.
(21) Beumel, O. F.; Harris, R. F. *J. Org. Chem.* **1964**, *29*, 1872.
(22) Entemann, C. E. J.; Johnson, J. R. *J. Am. Chem. Soc.* **1933**, *55*, 2900.
(23) (a) Kusakabe, T.; Takahashi, T.; Shen, R.; Ikeda, A.; Dhage, Y. D.; Kanno, Y.; Inouye, Y.; Sasai, H.; Mochida, T.; Kato, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 7845. (b) Orr, J. C.; Halpern, O.; Holton, P. G.; Alvarez, F.; Delfin, I.; De La Roz, A.; Ruiz, A. M.; Bowers, A. *J. Med. Chem.* **1963**, *6*, 166.
(24) (a) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 1988. (b) Brandsma, L. *Synthesis of Acetylene, Allenes and Cumulenes: Methods and Techniques*; Elsevier: Oxford, 2004.
(25) (a) Coles, M. A.; Hart, F. A. *J. Organomet. Chem.* **1971**, *32*, 279. (b) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Lomas, S. L.; Mahon, M. F.; Procopiou, P. A.; Suntharalingam, K. *Organometallics* **2008**, *27*, 6300.
(26) Harder, S. *Chem. Rev.* **2010**, *110*, 3852.
(27) (a) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042. (b) Arrowsmith, M.; Crimmin, M. R.; Hill, M. S.; Lomas, S. L.; Heng, M. S.; Hitchcock, P. B.; Kociok-Köhn, G. *Dalton Trans.* **2014**, *43*, 14249. (c) Fischer, R.; Langer, J.; Krieck, S.; Görls, H.; Westerhausen, M. *Organometallics* **2011**, *30*, 1359.
(28) Kobychev, V. B.; Orel, V. B.; Vitkovskaya, N. M.; Trofimov, B. A. *Dokl. Chem.* **2014**, *457*, 126.


DOI: 10.1021/acs.orglett.5b01219
*Org. Lett.* 2015, 17, 2808–2811