



## CuI/TMEDA Catalyzed Solvent Free Homo-Coupling Reaction of Terminal Alkynes towards the Synthesis of Buta-1,3-diynes

AMIT RANJAN PANDEY<sup>1,2</sup>, ADITYA PRAKHAR<sup>1,2</sup>, DURGESH KUMAR TIWARI<sup>1,2</sup>, DEVENDRA PRATAP MISHRA<sup>2</sup> and SUDHIR K. SHARMA<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, Government Degree College, Kant, Shahjahanpur-242223, India

<sup>2</sup>Department of Applied Science and Humanities, Rajkiya Engineering College, Ambedkar Nagar-224122, India

\*Corresponding author: E-mail: [sudhirgdc19@gmail.com](mailto:sudhirgdc19@gmail.com)

Received: 3 December 2021;

Accepted: 28 January 2022;

Published online: 14 February 2022;

AJC-20713

An efficient method for the synthesis of buta-1,3-diynes have been developed *via* copper(I) catalyzed homocoupling reaction of terminal acetylenes in presence of CuI and tetramethylethylenediamine (TMEDA) at 100 °C for 3.0 h under solvent-free conditions. This efficient methodology allowed the homocoupling of five terminal alkynes in moderate to excellent yields.

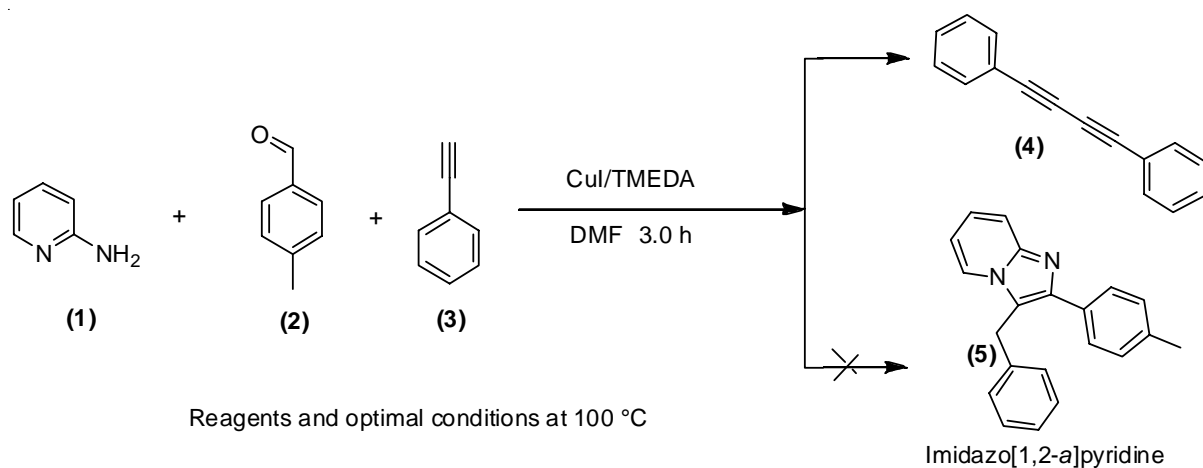
**Keywords:** Sonogashira reaction, Cross-coupling, Bisalkyne, Alkynes, Buta-1,3-diynes.

### INTRODUCTION

Multicomponent reactions are those chemical reactions in which more than three starting materials combine in a single pot to generate a selective product of chemical interest [1-3]. Various multicomponent reactions were performed using alkyne precursors as one component [4-7]. Aiming this in our mind we targeted to synthesize imidazo[1,2-*a*]pyridine derivatives (**5**) using 2-aminopyridine (**1**), 4-methylbenzaldehyde (**2**) and terminal alkyne phenyl acetylene (**3**) in one pot multicomponent method. To develop an optimum reaction condition we used copper(II)chloride as a catalyst with TMEDA in DMF at 100 °C and the reaction was monitored on TLC (**Scheme-I**). After 3.0 h, a dominant spot on TLC was found and after work-up and purification the compound was characterized as *bis* alkyne (**3**) and not imidazo[1,2-*a*]pyridine (**5**) as a required product. Since, the synthesis of buta-1,3-diynes *via* Pd-catalyzed homocoupling reactions of *E*-1,2-diiodoalkenes [8] is already reported, however, the unprecedented reaction product buta-1,3-diyne (**4**) and its derivatives have been found important intermediates in the field of biological sciences as well as in synthetic organic chemistry [9].

These moieties have been widely applied as intermediate building blocks in organic transformations such as in the synthesis of natural products [10,11], pharmaceuticals [12-15] and heterocyclic compounds [16-19]. As already discussed that

buta-1,3-diynes have been utilized for the construction of carbocycles such as benzene [20] and naphthalene [21,22], nitrogen containing 5/6-membered heterocycles such as pyrrole [23], pyrazole [24], triazole [25], naphthtriazoles [26], benzo[*a*]phenanthridine [27], benzoquinolines [24], oxygen based heterocycles such as furan [28], pyrone [29], selenium and sulphur containing heterocycles selenothiophenes [30] and thiophenes [31]. For the synthesis of buta-1,3-diynes several methodologies have been described, employing the dimer formation of starting materials, such as alkynylboronates [32], alkynylsilanes [33], alkynyl halides [34-36], alkynyl Grignard reagents [37] and potassium alkynyl trifluoroborates [38]. The symmetrical buta-1,3-diynes are formed as by product in Sonogashira [39] cross-coupling reactions. The traditional method for the synthesis of these diynes involves the self-coupling of terminal acetylenes initially reported by Glaser [4-7]. Several improvements to this methodology have been developed [40-43], including the Hay procedure, in which *N,N,N',N'*-tetramethylethylenediamine is employed as the ligand [44]. The synthesis of buta-1,3-diynes from terminal acetylenes using environment-friendly reaction conditions has gained a significant attention [45,46]. Despite contributing some good noticeable part of reactions this has drawbacks such as expensive metal catalysts and limited substrate scope. To the best of our knowledge only few reports are available in the literature using solvent free conditions for the conversion of alkyne to buta-1,3-diyne [47,48]. Therefore,



Scheme-I

the development of a mild and economical strategy to synthesize buta-1,3-diyne is highly desirable. Herein, an efficient method for the synthesis of buta-1,3-diyne have been developed *via* copper(I) catalyzed homocoupling reaction of terminal acetylenes in the presence of CuI and tetramethylethylenediamine at 100 °C under solvent-free conditions.

## EXPERIMENTAL

All the reagents and solvents were used without purification and purchased from commercial sources. NMR spectra were recorded with 300/200 MHz spectrometers for  $^1\text{H}$  NMR, 75/50 MHz for  $^{13}\text{C}$  NMR. Chemical shifts  $\delta$  are given in ppm relative to signals of TMS in  $\text{CDCl}_3$  for  $^1\text{H}$  and  $^{13}\text{C}$  NMR. For column chromatography silica gel (100-200 mesh) was used as the stationary phase. All performed reactions were monitored by thin layer chromatography (TLC).

**General procedure for the synthesis of buta-1,3-diyne (4a-e):** A mixture of terminal alkynes **3a-e** (0.2 g, 1.0 equiv.) CuI (10 mol%), TMEDA (0.75 mmol) were placed in round bottom flask containing a stirring bar. The reaction mixture was heated and stirred at 100 °C for 3.0 h. After cooling reaction mixture at ambient temperature and quenching with distilled water and aqueous layer was extracted with ethyl acetate. The extracted organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the organic layer solvent was removed *in vacuo*. The crude material obtained after removal of solvent was purified on a silica gel using ethyl acetate/hexane (1:9 v/v) as an eluent to afford **4a-e**.

**1,4-Bis(phenyl)buta-1,3-diyne (4a):** Yield: 81%; white solid, m.p.: 84-86 °C, IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3458, 2980, 1736, 1642, 1466;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.55-7.51 (m, 4H), 7.36-7.28 (m, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  132.6, 129.3, 128.6, 121.9, 81.7, 73.9 ppm. mass ( $\text{ES}^+$ )  $m/z$  315.2 ( $\text{M}^+ + 1$ ). Anal. calcd. for  $\text{C}_{16}\text{H}_{10}$ : C, 95.02; H, 4.98 Found: C, 95.04; H, 4.96.

**1,4-Bis(4-tert-butylphenyl)buta-1,3-diyne (4b):** Yield (85%), white solid, m.p.: 190-192 °C,  $R_f$  = 0.70 (hexane), IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3458, 2959, 1716, 1653, 1464, 1397, 1262, 1101, 832;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (4H, d,  $J$  = 8.3 Hz, ArH), 7.34 (4H, d,  $J$  = 8.3 Hz, ArH), 1.31 (18H, s,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 152.7, 132.4, 125.6, 119.0, 81.6, 73.7, 35.0, 31.2 ppm. mass ( $\text{ES}^+$ )  $m/z$  315.2 ( $\text{M}^+ + 1$ ). Anal. calcd for  $\text{C}_{24}\text{H}_{26}$ : C, 91.67; H, 8.33 Found: C, 91.65; H, 8.34.

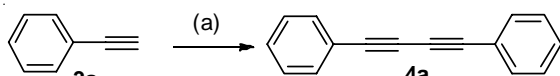
**1,4-Bis(4-methylphenyl)buta-1,3-diyne (4c):** Yield (84%), white solid, m.p.: 180-182 °C,  $R_f$  = 0.68 (hexane), IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3442, 2865, 1648, 1470, 1101, 830;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.14 (4H, d,  $J$  = 8.0 Hz, ArH),  $\delta$  = 7.42 (4H, d,  $J$  = 8.0 Hz, ArH), 2.36 (6H, s,  $\text{CH}_3$ ),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.5, 132.4, 129.2, 118.7, 81.5, 73.4, 21.6 ppm. Mass ( $\text{ES}^+$ )  $m/z$  231.2 ( $\text{M}^+ + 1$ ). Anal. calcd. for  $\text{C}_{18}\text{H}_{14}$ : C, 93.87; H, 6.13 Found: C, 93.88; H, 6.12.

**1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (4d):** Yield (81%), white solid, m.p.: 136-138 °C,  $R_f$  = 0.78 (hexane), IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2844, 2140, 1589, 1510, 1290, 1262, 1168, 1040, 844, 820;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.45 (4H, d,  $J$  = 8.8 Hz, ArH),  $\delta$  = 6.84 (4H, d,  $J$  = 8.8 Hz, ArH), 3.82 (6H, s,  $\text{OCH}_3$ ),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.2, 134.0, 114.1, 113.8, 81.2, 72.9, 55.3 ppm. Mass ( $\text{ES}^+$ )  $m/z$  263.2 ( $\text{M}^+ + 1$ ). Anal. calcd. for  $\text{C}_{18}\text{H}_{14}\text{O}_2$ : C, 82.42; H, 5.38; O, 12.20 Found: C, 82.40; H, 5.40; O, 12.20.

**1,4-Bis(cyclohex-1-en-1-yl)buta-1,3-diyne (4e):** Yield (46%), white solid, m.p.: 66-68 °C,  $R_f$  = 0.58 (hexane), IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 2130, 1430, 1420, 1280, 1256, 1160, 1044, 840, 818;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.23 (2H, s, CH),  $\delta$  = 2.11-2.10 (8H, m,  $\text{CH}_2$ ), 1.63-1.53 (8H, m,  $\text{CH}_2$ ),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 137.6, 120.1, 82.7, 71.7, 28.8, 25.8, 22.4, 21.4, ppm. Mass ( $\text{ES}^+$ )  $m/z$  211.2 ( $\text{M}^+ + 1$ ). Anal. calcd. for  $\text{C}_{16}\text{H}_{18}$ : C, 91.37; H, 8.63, Found: C, 91.38; H, 8.62.

## RESULTS AND DISCUSSION

To establish the reaction method for the synthesis of 1,4-bis(phenyl)buta-1,3-diyne (**4a**) we treated phenylacetylene (**3a**) alone as a standard substrate under the various reaction conditions using  $\text{Na}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$  as bases,  $\text{CuCl}_2$ ,  $\text{CuCl}$ ,  $\text{CuI}$  as catalysts and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as additive and dimethylformamide (DMF) as solvent (**Scheme-II**). The activity of the catalysts was firstly evaluated in detail as shown in Table-1 (entries 1-9). For instance, when copper(II)chloride was used alone and with  $\text{Na}_2\text{CO}_3$  and



(a) Reagents and optimal conditions at 100 °C

Scheme-II

 TABLE-1  
 OPTIMIZATION OF REACTION CONDITIONS  
 (a) FOR THE CONVERSION OF 3a TO 4a

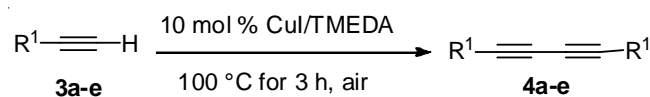
Entry	Catalyst	Base	Additive	Solvent	Time (h)	% Yield of 4a
1	CuCl <sub>2</sub>	–	TMEDA	DMF	3.0	36
2	CuCl <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	TMEDA	DMF	3.5	56
3	CuCl <sub>2</sub>	Cs <sub>2</sub> CO <sub>3</sub>	TMEDA	DMF	3.0	58
4	CuCl	Na <sub>2</sub> CO <sub>3</sub>	TMEDA	DMF	2.0	61
5	CuCl	Cs <sub>2</sub> CO <sub>3</sub>	TMEDA	DMF	2.5	65
6	CuI	Cs <sub>2</sub> CO <sub>3</sub>	TMEDA	DMF	2.0	69
7	CuI	–	–	DMF	4.5	39
8	CuI	–	TMEDA	DMF	3.5	68
9	CuI	TMEDA	–	–	3.0	81

Cs<sub>2</sub>CO<sub>3</sub> bases, corresponding products were prepared in 36%, 56% and 58% yields, respectively to entries 1, 2 and 3. On the other hand, the catalytic activity of copper(I) was significantly appreciating with base and additives (entries 4-9). It is noteworthy that when Cu(I) catalysts were used the desired product was achieved in more than 60% yields in all cases except one reaction condition (entry 7). When homocoupling reaction was performed with CuCl using Na<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>, TMEDA and DMF as solvent, significant increase in the yield was observed (entry 4-6). Thus, further experiments were carried out in absence of TMEDA and Cs<sub>2</sub>CO<sub>3</sub> reaction proceeds slowly and yields dropped to 39% (entries 7). When the reaction was performed without Cs<sub>2</sub>CO<sub>3</sub> using TMEDA as catalyst in DMF and the yield was obtained 68% (entry 8).

A very encouraging result was obtained when phenylacetylene (**3a**) was treated with CuI/TMEDA without solvent as the desired product was synthesized in 81% yield (entry 9) with in 3.0 h. We screened other parameters also such as time, temperature, catalyst loading and the optimum amount of TMEDA. When 10 mol% of CuI was employed with TMEDA, the reaction was completed in 3.5 h and desired buta-1,3-diyne (**4a**) was afforded in 68% yield (entry 8) (Table-1). The optimal condition that led to the synthesis of **4a** in 81% isolated yield (entry 9) involved treatment of **3a** with 10 mol % CuI/TMEDA at 100 °C for 3.0 h without solvent.

The generality of the method for the synthesis of buta-1,3-diynes **4** was established by treating terminal alkynes **3a-e** with copper(I)iodide (10 mol %), *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as base and additive at 100 °C for 3.0 h (Scheme-III).

The crude products after work up were purified on a silica gel column chromatography using ethyl acetate/hexane to afford **4a-e** in 46-85% isolated yields (Table-2).



Scheme-III: Synthesis of buta-1,3-diynes

 TABLE-2  
 SYNTHESIS OF BUTA-1,3-DIYNES

Entry	Substrate (1)	Product (2)	Yield (%)
1	<b>3a</b>	<b>4a</b>	81
2	<b>3b</b>	<b>4b</b>	85
3	<b>3c</b>	<b>4c</b>	84
4	<b>3d</b>	<b>4d</b>	81
5	<b>3e</b>	<b>4e</b>	46

## Conclusion

In conclusion, an efficient solvent free approach for the conversion of terminal alkynes into very useful scaffolds buta-1,3-diynes using CuI/TMEDA as catalyst is developed.

## ACKNOWLEDGEMENTS

The authors acknowledge to Director Uttar Pradesh Higher Education, Prayagraj and The Principal Government Degree College, Kant, Shahjahnpur and The Director, Rajkiya Engineering College Ambedkar Nagar, India for their constant moral supports.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

1. A. Dömling, W. Wang and K. Wang, *Chem. Rev.*, **112**, 3083 (2012); <https://doi.org/10.1021/cr100233r>
2. J. Li, Y. Xu, X. Hu, S. Zhu and L. Liu, *Org. Lett.*, **22**, 9478 (2020); <https://doi.org/10.1021/acs.orglett.0c03451>
3. G. Huang, J. Li, J. Li, J. Li, M. Sun, P. Zhou, L. Chen, Y. Huang, S. Jiang and Y. Li, *J. Org. Chem.*, **85**, 13037 (2020); <https://doi.org/10.1021/acs.joc.0c01733>
4. S.K. Sharma, A.K. Mandadapu, B. Kumar and B. Kundu, *J. Org. Chem.*, **76**, 6798 (2011); <https://doi.org/10.1021/jo201228t>
5. S.K. Sharma, S. Gupta, M. Saifuddin, A.K. Mandadapu, P.K. Agarwal, H.M. Gauniyal and B. Kundu, *Tetrahedron Lett.*, **52**, 65 (2011); <https://doi.org/10.1016/j.tetlet.2010.10.147>
6. S. Gupta, S.K. Sharma, A.K. Mandadapu, H.M. Gauniyal and B. Kundu, *Tetrahedron Lett.*, **52**, 4288 (2011); <https://doi.org/10.1016/j.tetlet.2011.06.021>
7. S.K. Sharma, A.K. Mandadapu, M. Saifuddin, S. Gupta, P.K. Agarwal, A.K. Mandwal, H.M. Gauniyal and B. Kundu, *Tetrahedron Lett.*, **51**, 6022 (2010); <https://doi.org/10.1016/j.tetlet.2010.09.054>
8. S.K. Sharma, *Adv. Org. Chem. Lett.*, **4**, 1 (2017).

9. F. Diederich, P.J. Stang and R.R. Tykwinski, *Acetylene Chemistry: Chemistry, Biology and Material Science*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim (2005).
10. A.L.K. Shi Shun and R.R. Tykwinski, *Angew. Chem. Int. Ed.*, **45**, 1034 (2006); <https://doi.org/10.1002/anie.200502071>
11. F. Bohlmano, T. Burkhardt and C. Zdero, *Naturally Occurring Acetylenes*; Academic Press: London (1973).
12. S.F. Mayer, A.R. Steinreiber, V.A. Orru and K.J. Faber, *Org. Chem.*, **67**, 9115 (2002); <https://doi.org/10.1021/jo020073w>
13. G. Zeni, R.B. Panatieri, E. Lissner, P.H. Menezes, A.L. Braga and H.A. Stefani, *Org. Lett.*, **3**, 819 (2001); <https://doi.org/10.1021/ol006946v>
14. M. Ladika, T.E. Fisk, W.W. Wu and S.D. Jons, *J. Am. Chem. Soc.*, **116**, 12093 (1994); <https://doi.org/10.1021/ja00105a076>
15. A. Stütz, *Angew. Chem. Int. Ed. Engl.*, **26**, 320 (1987); <https://doi.org/10.1002/anie.198703201>
16. S. Gupta, P.K. Agarwal, M. Saifuddin and B. Kundu, *Tetrahedron Lett.*, **52**, 5752 (2011); <https://doi.org/10.1016/j.tetlet.2011.08.079>
17. H. Jiang, W. Zeng, Y. Li, W. Wu, L. Huang and W. Fu, *J. Org. Chem.*, **77**, 5179 (2012); <https://doi.org/10.1021/jo300692d>
18. P. Nun, S. Dupuy, S. Gaillard, A. Poater, L. Cavallo and S.P. Nolan, *Catal. Sci. Technol.*, **1**, 58 (2011); <https://doi.org/10.1039/c0cy00055h>
19. S. Kramer, J.L.H. Madsen, M. Rottländer and T. Skrydstrup, *Org. Lett.*, **12**, 2758 (2010); <https://doi.org/10.1021/ol1008685>
20. V. Gevorgyan, A. Takeda and Y. Yamamoto, *J. Am. Chem. Soc.*, **119**, 11313 (1997); <https://doi.org/10.1021/ja971935r>
21. H. Sun, X. Wu and R. Hua, *Tetrahedron Lett.*, **52**, 4408 (2011); <https://doi.org/10.1016/j.tetlet.2011.06.046>
22. R. Singha, S. Nandi and J.K. Ray, *Tetrahedron Lett.*, **53**, 6531 (2012); <https://doi.org/10.1016/j.tetlet.2012.09.079>
23. Y.-H. Wang, H. Liu, L.-L. Zhu, X.-X. Li and Z. Chen, *Adv. Synth. Catal.*, **353**, 707 (2011); <https://doi.org/10.1002/adsc.201000833>
24. L. Wang, X. Yu, X. Feng and M. Bao, *J. Org. Chem.*, **78**, 1693 (2013); <https://doi.org/10.1021/jo302732v>
25. V. Fiandanese, D. Bottalico, G. Marchese, A. Punzi and F. Capuzzolo, *Tetrahedron*, **65**, 10573 (2009); <https://doi.org/10.1016/j.tet.2009.10.078>
26. A.K. Mandadapu, S.K. Sharma, S. Gupta, D.G.V. Krishna and B. Kundu, *Org. Lett.*, **13**, 3162 (2011); <https://doi.org/10.1021/ol201092k>
27. A.K. Mandadapu, M.D. Dathi, R.K. Arigela and B. Kundu, *Tetrahedron*, **68**, 8207 (2012); <https://doi.org/10.1016/j.tet.2012.07.067>
28. Q. Zheng, R. Hua, J. Jiang and L. Zhang, *Tetrahedron*, **70**, 8252 (2014); <https://doi.org/10.1016/j.tet.2014.09.025>
29. M. Itoh, M. Shimizu, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, **78**, 11427 (2013); <https://doi.org/10.1021/jo401992d>
30. D. Alves, C. Luchese, C.W. Nogueira and G. Zeni, *J. Org. Chem.*, **72**, 6726 (2007); <https://doi.org/10.1021/jo070835t>
31. J. Tang and X. Zhao, *RSC Adv.*, **2**, 5488 (2012); <https://doi.org/10.1039/c2ra20326j>
32. Y. Nishihara, M. Okamoto, Y. Inoue, M. Miyazaki, M. Miyasaka and K. Takagi, *Tetrahedron Lett.*, **46**, 8661 (2005); <https://doi.org/10.1016/j.tetlet.2005.10.056>
33. Y. Nishihara, K. Ikegashira, K. Hirabayashi, J. Ando, A. Mori and T. Hiyama, *J. Org. Chem.*, **65**, 1780 (2000); <https://doi.org/10.1021/jo991686k>
34. Z. Chen, H. Jiang, A. Wang and S. Yang, *J. Org. Chem.*, **75**, 6700 (2010); <https://doi.org/10.1021/jo101216m>
35. S. Xue, L.-G. Meng and Q.-X. Guo, *Synth. Commun.*, **38**, 2243 (2008); <https://doi.org/10.1080/00397910802026568>
36. S.V. Damle, D. Seomoon and P.H. Lee, *J. Org. Chem.*, **68**, 7085 (2003); <https://doi.org/10.1021/jo034727s>
37. M.S. Maji, T. Pfeifer and A. Studer, *Angew. Chem. Int. Ed.*, **47**, 9547 (2008); <https://doi.org/10.1002/anie.200804197>
38. M.W. Paixão, M. Weber, A.L. Braga, J.B. de Azeredo, A.M. Deobald and H.A. Stefani, *Tetrahedron Lett.*, **49**, 2366 (2008); <https://doi.org/10.1016/j.tetlet.2008.02.083>
39. K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, **16**, 4467 (1975); [https://doi.org/10.1016/S0040-4039\(00\)91094-3](https://doi.org/10.1016/S0040-4039(00)91094-3)
40. E. Valenti, M.A. Pericàs and F. Serratosa, *J. Am. Chem. Soc.*, **112**, 7405 (1990); <https://doi.org/10.1021/ja00176a056>
41. P. Cadiot and W. Chodkiewicz, Eds.: H.G. Viehe, In *Chemistry of Acetylenes*, Marcel Dekker: New York, pp 597 (1969).
42. G. Englton and A.R. Galbraith, *Chem. Ind.*, 737 (1956).
43. Q. Sun, Z. Lv, Y. Du, Q. Wu, L. Wang, L. Zhu, X. Meng, W. Chen and F.-S. Xiao, *Chem. Asian J.*, **8**, 2822 (2013); <https://doi.org/10.1002/asia.201300690>
44. A.S. Hay, *J. Org. Chem.*, **27**, 3320 (1962); <https://doi.org/10.1021/jo01056a511>
45. D. Wang, J. Li, N. Li, T. Gao, S. Hou and B. Chen, *Green Chem.*, **12**, 45 (2010); <https://doi.org/10.1039/B917448F>
46. K. Yin, C. Li, J. Li and X. Jia, *Green Chem.*, **13**, 591 (2011); <https://doi.org/10.1039/c0gc00413h>
47. L. Bettanin, G.V. Botteselle, M. Godoi and A.L. Braga, *Green Chem. Lett. Rev.*, **7**, 105 (2014); <https://doi.org/10.1080/17518253.2014.895868>
48. D. Wang, J. Li, N. Li, T. Gao, S. Hou and B. Chen, *Green Chem.*, **12**, 45 (2010); <https://doi.org/10.1039/B917448F>