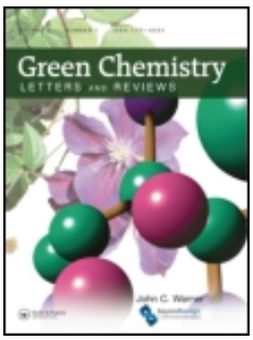

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RESEARCH ARTICLE

Green synthesis of 1,3-diynes from terminal acetylenes under solvent-free conditions

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Herein, we report the microwave-assisted synthesis of 1,3-diynes from terminal acetylenes, catalyzed by CuI and tetramethylethylenediamine, in the presence of air as the oxidant, at 100 °C for only 10 min under solvent-free conditions. This efficient methodology allowed the homocoupling of several terminal alkynes in moderate to excellent yields. Moreover, the same protocol was also applicable for the synthesis of some unsymmetrical 1,3-diynes through the cross-coupling reaction.

Keywords: symmetrical 1,3-diynes; unsymmetrical 1,3-diynes; copper-mediated homocoupling; solvent-free synthesis; microwave (MW)

1. Introduction

1,3-Diynes are compounds which have attracted great importance in the field of biology as well as in synthetic organic chemistry (*1*). In this context, 1,3-diyne derivatives have been widely applied as building blocks in organic transformations (*2*), particularly as intermediates for the synthesis of natural (*3*), pharmaceutical (*4*), and heterocyclic compounds (*5*). Furthermore, these kinds of dyines have been notably used in materials science for the construction of p-conjugated structures (*6*).

Several methodologies to synthesize 1,3-diynes have been described, employing the dimerization of different starting materials, such as alkynylsilanes (*7*), alkynyl halides (*8*), alkynyl Grignard reagents (*9*), alkynylboronates (*10*), and potassium alkynyltrifluoroborates (*11*). In addition, the symmetrical 1,3-diynes are formed as by-products in some cross-coupling reactions, such as the Sonogashira (*12*) and in the preparation of alkynylchalcogenides (*13*).

On the other hand, the most traditional method for the synthesis of these dyines involves the self-coupling of terminal acetylenes, as initially reported by Glaser (*14*). Several improvements to this methodology have been developed (*15*), including the Hay procedure, in which *N,N,N',N'*-tetramethylethylenediamine is employed as the ligand (*16*). The oxidative homocoupling reaction of terminal acetylenes can also be performed with good efficiency with a combination of Pd and Cu salts as a catalytic system (*17*). Nevertheless, most palladium salts are very expensive and require the use of phosphines or amines as ligands in the presence of an inert atmosphere.

More recently, the homocoupling of terminal acetylenes has been developed under palladium-free systems using copper salts as catalysts (*18*). However, generally these protocols require bases and/or additives as well as toxic and carcinogenic solvents (*19*). The development of environmentally friendly methodologies for the synthesis of 1,3-diynes from terminal acetylenes has gained considerable significance and is increasingly reported (*20*). In this context, Niuet al. have described the oxidative homocoupling of terminal acetylenes catalyzed by copper under neat conditions (*21*). However, these methods also have limitations, such as long reaction times.

On the other hand, microwave irradiation has provided higher yields allowing milder conditions and shorter reaction times in several synthetic transformations (*22*). Nonetheless, the use of microwave irradiation for the synthesis of 1,3-diynes from terminal acetylenes is rare and, to our knowledge, only one article addressing this subject has been published (*23*). Despite offering some good features, this protocol has drawbacks such as costly metal catalysts and poor substrate scope. Therefore, the development of a mild and economical strategy to prepare 1,3-diynes is highly desirable.

Thus, in connection with our interest in environmentally friendly reactions (*24*), herein we describe an efficient methodology for the synthesis of 1,3-diynes

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Scheme 1. Homocoupling reaction of terminal acetylenes.

involving the combination of solvent-free conditions and microwave irradiation (Scheme 1).

2. Results and discussion

In order to establish the best reaction conditions, we used phenylacetylene **1a** as a standard substrate, Cs_2CO_3 as a base, TMEDA as an additive, and dimethylformamide (DMF) as a solvent (Table 1).

The activity of the catalysts was firstly evaluated in detail (entries 1–6). For instance, when copper(II) species, such as $CuCl_2$ and $CuBr_2$, were used the corresponding products were prepared in 56% and 53% yields, respectively (entries 1 and 2). However, CuO nano did not prove to be an efficient catalyst for this cross-coupling reaction (entry 3). Similarly, the desired product was not obtained when we employed Cu as a catalyst (entry 4).

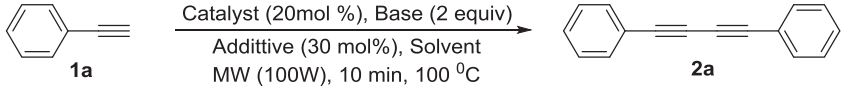
On the other hand, the catalytic activity of copper (I) was significantly higher (entries 5 and 6). It is noteworthy that when CuI was used the desired product was achieved in 90% yield (entry 6). Subsequently, we performed the homocoupling reaction without TMEDA and a significant decrease in the yield was observed (entry 7). Thus, further experiments were carried out using only TMEDA in the absence of Cs_2CO_3 (entries 8 and 9). A very encouraging result was obtained when the reaction was performed without Cs_2CO_3 or the solvent, as the desired product was synthesized in 80% yield (entry 9).

Next, we screened other parameters such as temperature, time, catalyst loading, and the optimum amount of TMEDA (Table 2). When 10 mol% of CuI was employed, no significant change in the yield value was observed, affording the desired 1,3-diyne in 79% yield (entries 1 vs. 2). However, carrying out the reaction with 5 mol% of catalyst furnished the desired product in lower yield (entry 3).

Notably, when the amount of TMEDA was decreased to 1.5 equivalents, the yield of the reaction was enhanced, furnishing the desired product **2a** in 98% yield (entry 4). On the other hand, a significant decrease in the yield was observed employing a lower amount of TMEDA (entry 5). Moreover, a decrease in the temperature and time provided the product **2a** in lower yield (entries 6 and 7).

Focusing on the influence of the microwave irradiation on the reaction, we performed experiments at lower power and under conventional heating (entries 8 and 9). When the reaction was carried out at 50W, a slight decrease in the yield was observed (entry 8). However, when the reaction was carried out under conventional heating, the desired product was obtained in only 38% yield (entry 9).

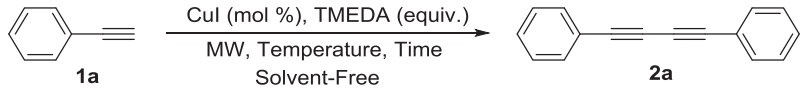
Table 1. Catalyst screening for homocoupling reaction of phenylacetylene.[a]



Entry	Catalyst	Base	Additive	Solvent	Yield (%)[b]
1	$CuCl_2$	Cs_2CO_3	TMEDA	DMF	56
2	$CuBr_2$	Cs_2CO_3	TMEDA	DMF	53
3	CuO nano	Cs_2CO_3	TMEDA	DMF	10
4	Cu	Cs_2CO_3	TMEDA	DMF	–
5	CuCl	Cs_2CO_3	TMEDA	DMF	64
6	CuI	Cs_2CO_3	TMEDA	DMF	90
7	CuI	Cs_2CO_3	–	DMF	20
8	CuI	TMEDA	–	DMF	82
9	CuI	TMEDA	–	–	80

[a]Reaction conditions: phenylacetylene (0.5 mmol), base (1.0 mmol), additive (30 mol%), catalyst (20 mol%), microwave (MW) (100 W), 100 °C, 10 min.
[b]Isolated yields.

Table 2. Screening of temperature, time, and amount of CuI and TMEDA for the homocoupling reaction of phenylacetylene.[a]



Entry	CuI (mol%)	TMEDA (equiv.)	T (°C)	Time (min)	Yield (%)[b]
1	20	2.0	100	10	80
2	10	2.0	100	10	79
3	5	2.0	100	10	73
4	10	1.5	100	10	98
5	10	1.2	100	10	71
6	10	1.5	80	10	65
7	10	1.5	100	5	72
8[c]	10	1.5	100	10	84
9[d]	10	1.5	100	10	38

[a]Reaction conditions: phenylacetylene (0.5 mmol), TMEDA, CuI, and microwave irradiation.
[b]Isolated yields.
[c]The reaction was carried out at 50 W.
[d]The reaction was performed under conventional heating.

Having identified the best reaction conditions, we evaluated the scope of the protocol by using a variety of alkynes (Table 3). Remarkably, electronic effects of substituents in the alkynes provided the desired 1,3-diynes in very high yields. For instance, when either soft or strong electron-releasing groups were employed, the corresponding products were achieved in 83% and 98%, respectively (entries 2 and 3).

However, steric effects have been shown to adversely affect the reaction and the use of alkynes with a methoxy and amino groups at the *ortho* position, for example, afforded the corresponding products in lower yields (entries 4 and 5).

On the other hand, when a substrate containing a withdrawing group at the *meta* position on the aromatic ring was employed, the respective product **2f** was obtained in 87% yield (entry 6).

Applying the same approach, with the exception of alkyne **2j**, we also synthesized a series of symmetrical 1,3-diynes starting from aliphatic alkynes (entries 6–9). Employing propargyl alcohols such as **1g** and **1h**, for example, provided the desired products in moderate to good yield, respectively (entries 7 and 8).

The alkyne **1i** was much less reactive than the other alkynes, furnishing the respective product in 15% yield (entry 9). In order to improve the yield for this case, the reaction was carried out for 30 min at 120 °C, giving the desired product in 45% yield (entry 9).

Additionally, we attempted to extend our protocol to the cross-coupling of two different alkynes (Table 4). Gratifyingly, we were also able to prepare unsymmetrical 1,3-diynes in satisfactory yields, as shown in Table 4. For instance, when phenylacetylene was cross-coupled with alkynes containing donating groups attached to the aromatic ring, the corresponding products **3a–d** were obtained from 52% to 88% yield (entries 1–4). In addition, the unsymmetrical products were achieved in satisfactory yields by using an excess amount of phenylacetylene. In all these reactions, we have also observed the formation of symmetrical diyne, which was easily separated by chromatographic column.

3. Conclusion

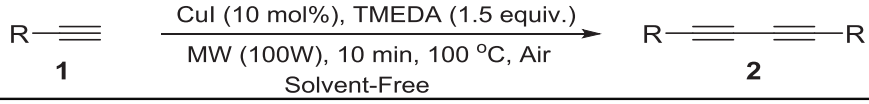
In conclusion, we have developed an economical and eco-friendly procedure for the synthesis of symmetrical and unsymmetrical 1,3-diynes catalyzed by CuI and TMEDA under open to air conditions. Applying this new methodology, the desired products were obtained in moderate to excellent yields. Moreover, the oxidative homocoupling reactions of terminal acetylenes were carried out in the absence of a solvent, in a very short reaction time under microwave irradiation.

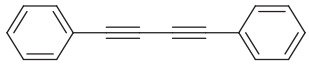
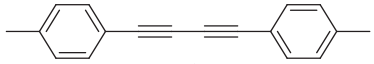
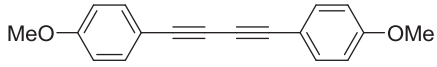
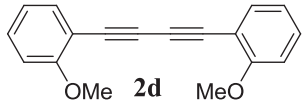
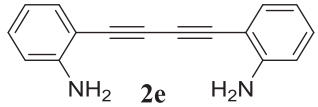
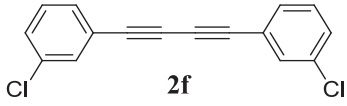
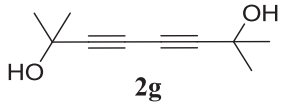
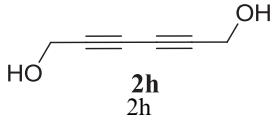
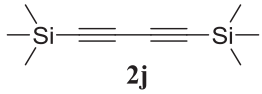
4. Experimental

4.1. General information

Acetylenes and other all reagents were purchased from appropriate commercial sources. Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz. Spectra were recorded in $CDCl_3$ solutions. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz, and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 50 MHz.

Table 3. Microwave synthesis of several symmetrical 1,3-diynes under solvent-free conditions catalyzed by CuI and TMEDA.[a]



Entry	R	Product	Yield (%)[b]
1	C_6H_5 **1a**	 **2a**	98
2	4-$CH_3C_6H_4$ **1b**	 **2b**	83
3	4-$CH_3OC_6H_4$ **1c**	 **2c**	98
4	2-$CH_3OC_6H_4$ **1d**	 **2d**	57
5	2-$NH_2C_6H_4$ **1e**	 **2e**	65
6	3-ClC_6H_4 **1f**	 **2f**	87
7	$HOC(CH_3)_2$ **1g**	 **2g**	35
8	$HOCH_2$ **1h**	 **2h**	65
9	*n*-C_6H_{13} **1i**	 **2i**	15[a] 43[c]
10	$Si(CH_3)_3$ **1j**	 **2j**	Traces

[a]Reaction conditions: acetylene (0.5 mmol), TMEDA (1.5 equiv.), CuI (10 mol%), microwave (MW) (100 W), 100 °C, 10 min.
[b]Isolated yields.
[c]The reaction was carried out at 120 °C for 30 min.

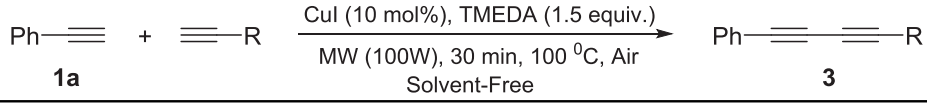
Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to the tetramethylsilane (TMS) (^{1}H NMR) and to the solvent (^{13}C NMR). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25-mm thickness. Most reactions were monitored by TLC for disappearance of starting material. For visualization, TLC plates were either placed under ultraviolet light, stained with iodine vapor, or acidic vanillin.

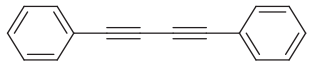
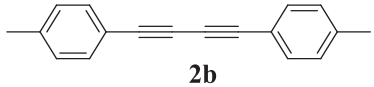
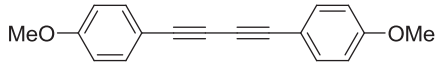
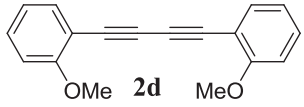
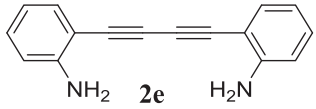
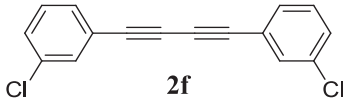
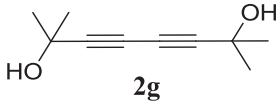
All reactions under microwave irradiation were performed in a 10-mL sealed tube in a commercially available monomode reactor (CEM Discover) with an IR monitoring and non-invasive pressure transducer.

4.2. General procedure for the homocoupling reactions of acetylenes under microwave irradiation

CuI (10 mol%), TMEDA (0.75 mmol), and acetylene (0.5 mmol) were placed in a specific microwave tube equipped with a magnetic stir bar. The sealed reaction tube was placed in the microwave cavity and a maxima irradiation power of 100 W was applied.

Table 4. Solvent-free synthesis of unsymmetrical 1,3-diynes under microwave irradiation.[a]



Entry	R	Product	Yield (%)[b]
1	4-$CH_3C_6H_4$ **1b**	 **2a**	76
2	4-$CH_3OC_6H_4$ **1c**	 **2b**	88
3	2-$CH_3OC_6H_4$ **1d**	 **2c**	71
4	2-$NH_2C_6H_4$ **1e**	 **2d**	52
5	$HOCH_2$ **1h**	 **2e**	21
6	$HOC(CH_3)_2$ **1g**	 **2f**	12
7	3-ClC_6H_4 **1f**	 **2g**	Traces

[a]Reaction conditions: phenylacetylene (3 mmol), RC≡CH (0.5 mmol), CuI (10 mol%), TMEDA (1.5 equiv.), microwave (MW) (100 W), 100 °C, 30 min.
[b]Isolated yield.

When the temperature reached 100 °C, the reaction was stirred for 10 or 30 minutes (see Table 3). After cooling the reaction system at room temperature, it was quenched with water and aqueous layer was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica eluting with appropriate mixture of hexane and ethyl acetate as a solvent.

4.3. General procedure for the cross-coupling reactions between different acetylenes under microwave irradiation

CuI (10 mol%), TMEDA (0.75 mmol), phenylacetylene **1a** (3.0 mmol), and finally other acetylene (0.5 mmol) were placed in a specific microwave tube equipped with a magnetic stir bar. The sealed reaction tube was placed in the microwave cavity and a maxima irradiation power of 100 W was applied. When the temperature reached 100 °C, the reaction was stirred for 30 minutes. After cooling the reaction system at room temperature, it was quenched with water and aqueous layer was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica eluting with appropriate mixture of hexane and ethyl acetate as a solvent.

4.4. Spectral data of synthesized products

*4.4.1. 1,4-diphenyl-1,3-diyne (**2a**) (17f, 19a, 21)*

Yield: 98%; white solid, mp 83–84 °C (lit. 86–88 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.55–7.51 (m, 4H), 7.36–7.28 (m, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) = 132.6, 129.3, 128.6, 121.9, 81.7, 73.9.

*4.4.2. 1,4-dip-tolylbuta-1,3-diyne (**2b**) (17f, 19a, 21)*
Yield: 83%; white solid, mp 184–186 °C (lit. 183–185 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.41 (d, J = 7.82 Hz, 4H), 7.13 (d, J = 7.82 Hz, 4H), 2.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 139.7, 132.5, 129.3, 118.9, 81.7, 73.6, 21.7.

*4.4.3. 1,4-bis(4-methoxyphenyl)buta-1,3diyne(**2c**) (17f, 19a, 21)*
Yield: 98%; white solid, mp 136–138 °C (lit. 138–140 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.45 (d, J = 8.90 Hz, 4H), 6.85 (d, J = 8.90 Hz, 4H), 3.82 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 160.1, 133.4, 114.2, 113.8, 81.2, 72.9, 55.2.

*4.4.4. 1,4-bis(2-methoxyphenyl)buta-1,3-diyne (**2d**) (19b)*
Yield: 57%; yellow solid, mp 136–138 °C (lit. 138–140 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.48 (d, J = 7.58 Hz, 2H), 7.32 (t, J = 7.58 Hz, 2H), 6.90 (m, 4H), 3.90 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 160.7, 133.7, 129.9, 119.8, 110.9, 119.9, 77.9, 77.3, 55.1.

*4.4.5. 2,2'-(buta-1,3-diyne-1,4-diyl)dianiline (**2e**) (18b, 25)*
Yield: 65%;^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.33–7.01 (m, 6H), 6.73–6.65 (m, 2H) 4.70 (s, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm)= 149.4, 132.9, 130.6, 117.9, 114.4, 106.2, 79.6, 71.7. GC–MS: *m/z* (%) 233 (17), 232 (100), 204 (40), 203 (10), 176 (7), 116 (12), 102 (14), 89 (12).

*4.4.6. 1,4-bis(2-chlorophenyl)buta-1,3-diyne (**2f**) (17a)*
Yield: 87%; yellow solid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.51 (s, 2H), 7.43–7.31 (m, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 133.7, 131.6, 129.9, 129.0, 122.6, 79.9, 74.1.

*4.4.7. 2,7-dimethylocta-3,5-diyne-2,7-diol (**2g**) (19a, 21)*
Yield: 35%; white solid, mp 128–130 °C (lit. 132–134 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) 2.05 (s, 2H); 1.53 (s, 12H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) 83.9, 66.3, 65.6, 31.0.

*4.4.8. Hexa-2,4-diyne-1,6-diol (**2h**) (18e)*
Yield: 65%. ^{1}H NMR (DMSO-d_6, 200 MHz) δ (ppm) 4.42 (s, 2H), 4.17 (s, 4H).

*4.4.9. Hexadeca-7,9-diyne (**2i**) (18e, 19a)*
Yield: 43%; yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 2.25 (t, 4H), 1.68–1.25 (m, 16H), 0.89 (t, 6H). GC–MS: *m/z* (%) 203 (0.5), 189 (8.0), 119 (41.0), 91 (100), 67 (59.5), 41 (7.0).

*4.4.10. 1-methyl-4-(phenylbuta-1,3-diynyl)benzene (**3a**) (8a)*
Yield: 76%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.55–7.33 (m, 7H), 7.17–7.13 (m, 2H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 139.6, 132.6, 129.3, 128.6, 122.1, 119.0, 82.9, 82.1, 73.7, 21.8.

*4.4.11. 1-methoxy-4-(phenylbuta-1,3-dyinyl)benzene (**3b**) (8a, 19g)*
Yield: 88%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.55–7.51 (m, 2H), 7.47 (d, J = 8.60 Hz, 2H), 7.36–7.32 (m, 3H), 6.86 (d, J = 8.60 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 160.4, 134.1, 132.4, 129.0, 128.4, 122.1, 114.2, 113.8, 81.8, 81.0, 74.2, 72.8, 55.3.

*4.4.12. 1-methoxy-2-(phenylbuta-1,3-diynyl)benzene (**3c**)* (26)
Yield: 71%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.53–7.43 (m, 2H), 7.36–7.28 (m, 5H), 5.89 (t, J = 8.0 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 161.4, 134.3, 132.3, 130.6, 128.9, 128.3, 121.9, 120.5, 111.0, 110.7.

*4.4.13. 2-(phenylbuta-1,3-diyn-1-yl)aniline (**3d**)* (25)
Yield: 52%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.55–7.50 (m, 2H), 7.37–7.30 (m, 4H), 7.19–7.10 (m, 1H), 6.71–6.63 (m, 2H), 4.31 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 149.7, 133.2, 132.3, 130.8, 129.3, 128.6, 122.0, 118.1, 114.5, 106.3, 82.8, 79.2, 78.8, 74.0.

*4.4.14. 2-phenylpenta-2,4-diyn-1-ol (**3e**) (19a,g)*
Yield: 21%. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 7.47–7.26 (m, 5H), 4.42 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ (ppm) = 132.8, 129.4, 128.6, 127.4, 86.3, 84.6, 75.6, 68.0, 55.1.

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