Synthesis of acetylenic ketones by a Pd-catalyzed carbonylative three-component coupling reaction in [bmim]PF_6[1]

Takahide Fukuyama, Ryo Yamaura, and Ilhyong Ryu

Abstract: A carbonylative three-component coupling reaction of aryl iodides with terminal alkynes catalyzed by $PdCl_2(PPh_3)_2$ was carried out using an ionic liquid, [bmim]PF_6, as the reaction medium, which resulted in good yields of α,β-acetylenic ketones. The low-viscosity ionic liquid, [bmim]NTf_2, was not suitable for this reaction, since the background Sonogashira coupling reaction, a competing reaction, also proceeded.

Key words: carbonylation, palladium, three-component coupling, ionic liquid, α,β-acetylenic ketones.

Résumé : Nous avons procédé à la préparation, avec de bons rendements, de cétones α,β-acétyléniques. Pour cela, nous avons réalisé une réaction de couplage à trois composants, catalysée par le $PdCl_2(PPh_3)_2$ et réalisée dans un milieu liquide ionique formé de [bmim]PF_6, conduisant à la carbonylation des iodures d'aryles. La faible viscosité du liquide ionique [bmim]NTf_2 n'est pas appropriée pour cette réaction puisque la réaction de couplage de Sonogashira qui est en compétition avec se produit.

Mots clés : carbonylation, palladium, couplage à trois composants, liquide ionique, cétone α,β-acétylénique.

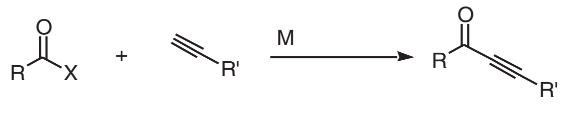
[Traduit par la Rédaction]

Introduction

α,β-Acetylenic ketones are useful intermediates for the synthesis of a variety of important heterocyclic and biologically active compounds (1). While traditional approaches to the synthesis of acetylenic ketones relied on the coupling of a carboxylic acid chloride with a metal acetylide, recent methods have employed Pd- and (or) Cu-catalyzed coupling reactions of acid halides and terminal alkynes (eq. [1]) (2). The carbonylative three-component coupling reaction of aryl halides with terminal alkynes has also been reported (eq. [2]) (3). Kobayashi and Tanaka (3*a*) reported that a three-component coupling reaction of aryl halides with terminal alkynes and CO can be achieved when $PdCl_2$(dppf) is used as a catalyst and Et_3N as a solvent. Alper and coworkers (3*b*) reported that the dimeric palladium hydroxide $[(Ph_3P)Pd(Ph)(\mu\text{-}OH)]_2$ functions as an efficient catalyst for a similar three-component coupling reaction. Mohamed Ahmed and Mori (3*c*) recently reported on a three-component coupling using $PdCl_2(PPh_3)_2$ as the catalyst and aqueous NH_3 (2 equiv.) as a base with THF as the solvent.

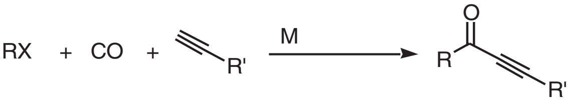
Two component method

[1]



Three component method

[2]



In recent years, ionic liquids have attracted broad attention in organic synthesis as alternatives to volatile organic solvents (4), and we previously reported that the Pd-catalyzed coupling reaction of aryl iodides with terminal alkynes — the Sonogashira coupling reaction — proceeds effectively in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), without the need for a copper co-catalyst (5). We also reported that a low-viscosity ionic liquid, [bmim]NTf_2, is an excellent reaction medium for Pd-catalyzed Mizoroki–Heck, Suzuki–Miyaura, and Stille coupling reactions (6). Herein we report on the carbonylative three-component coupling reaction of an aryl iodide with terminal alkynes, which proceeds smoothly when [bmim]PF_6 is used as the reaction medium (7).

Results and discussion

When iodobenzene (**1a**) was treated with phenylacetylene (**2a**, 1.2 equiv.) and pressurized CO (20 atm (1 atm = 101.325 kPa)) in the presence of 1 mol% $PdCl_2(PPh_3)_2$ and Et_3N (3.6 equiv.) in [bmim]PF_6 at 120 °C for 1 h, the reac-

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This paper is dedicated to Professor Howard Alper.

T. Fukuyama, R. Yamaura, and I. Ryu.[2] Department of Chemistry, Graduate School of Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan.

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[2] Corresponding author (e-mail: ryu@c.s.osakafu-u.ac.jp).

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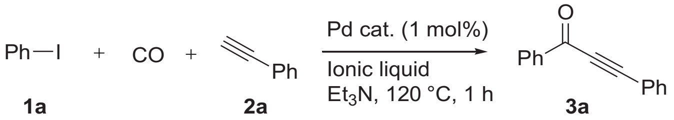
Table 1. Pd-catalyzed carbonylative coupling reaction of **1a** with **2a**.



Entry	Pd	CO (atm)	Et_3N (equiv.)	Ionic liquid	Yield (%)[a,b]
1	$PdCl_2(PPh_3)_2$	20	3.6	$[bmim]PF_6$	82
2	$PdCl_2(PPh_3)_2$	20	3.6	$[bmim]NTf_2$	58 (24)
3	$PdCl_2$	20	3.6	$[bmim]PF_6$	60
4	$PdCl_2(CH_3CN)_2$	20	3.6	$[bmim]PF_6$	62
5	$Pd(OAc)_2$	20	3.6	$[bmim]PF_6$	60
6	$Pd(PPh_3)_4$	20	3.6	$[bmim]PF_6$	63 (13)
7[c]	$PdCl_2(PPh_3)_2$	20	2.0	$[bmim]PF_6$	48
8	$PdCl_2(PPh_3)_2$	10	3.6	$[bmim]PF_6$	52 (21)

Note: Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), Pd-catalyst (1 mol%), ionic liquid (3 mL), 120 °C, 1 h.
[a] Isolated yields by chromatography on SiO_2.
[b] Yield of diphenylacetylene is shown in parentheses.
[c] Reaction was carried out for 2 h.

tion proceeded smoothly to give the acetylenic ketone **3a** in 82% yield (Table 1, entry 1). The reaction was clean, and diphenylacetylene, the noncarbonylated product of the Sonogashira coupling reaction, was not observed. Mohamed Ahmed and Mori (3*c*) previously reported that the reaction proceeded smoothly with aqueous NH_3 as a base. However, when aqueous NH_3 was used as a base in the present system, Michael addition of NH_3 to **3a** became a major reaction course. We also examined a low-viscosity ionic liquid, $[bmim]NTf_2$ (6); however, in this case, the background Sonogashira coupling reaction competed under the conditions employed (entry 2). Reactions using other Pd(II) complexes such as $PdCl_2$, $PdCl_2(CH_3CN)_2$, and $Pd(OAc)_2$ were sluggish, and significant amounts of unreacted **1a** were recovered (entries 3–5). When $Pd(PPh_3)_4$ was used as the catalyst, the Sonogashira coupling reaction competed, giving diphenylacetylene (entry 6). Reducing the amount of amine from 3.6 equiv. to 2 equiv. resulted in lower conversions even when the reaction time was prolonged (2 h) (entry 7). When the reaction was carried out at reduced CO pressure (10 atm), the Sonogashira coupling reaction competed again (entry 8).

Some results for reactions in which various aryl iodides and terminal alkynes were used are shown in Table 2. The reaction of substituted aryl iodides gave the corresponding acetylenic ketones in good yields (entries 1–6). Iodobenzenes containing a halogen atom (Br, Cl, or F) at the 4-position gave the coupling products, with the halogen atoms intact (entries 4–6). The reaction of 1-iodonaphthalene (**1h**) and 2-iodothiophene (**1i**) with **2a** also gave carbonylated products **3h** and **3i**, respectively (entries 7 and 8). Both *p*-acetylphenylacetylene and *p*-methoxyphenylacetylene could be used in this reaction (entries 9 and 10). The reaction of *tert*-butylacetylene (**2d**) gave the coupling product **3l** in relatively low yield, but when *N*-methylpiperidine was employed as a base, the yield was increased to 76% (entry 11).

When the reaction of **1a** with 2-methyl-3-butyne-2-ol (**2e**) was carried out using *N*-methylpiperidine as the base, 3-furanone **4** was obtained as the major product (eq. [3]) (8). An experiment using milder reaction conditions (100 °C, 10 atm) gave a mixture of acetylenic ketone **3m** and **4**. When the isolated **3m** was exposed to the same reaction system, furanone **4** was formed, suggesting that the initially formed **3m** served as the precursor for **4** (9).

It is well known that imidazolium-based ionic liquids react with Pd complexes to give Pd *N*-heterocyclic carbene complexes, which are thought to be the key catalyst species in many reactions in which a Pd–ionic liquid system is used (10). This may also be true for the present system, since the Pd carbene complex (which contains one imidazolylidene, one triphenylphosphine, and two chlorine ligands (6)) readily catalyzed the reaction of **1a** with **2a** to give **3a** in 73% yield (eq. [4]). We also investigated the reusability of the catalyst and the reaction medium for this reaction system. Both the catalyst and the reaction medium can be reused but with a slight decrease in efficiency (Scheme 1).

[3]

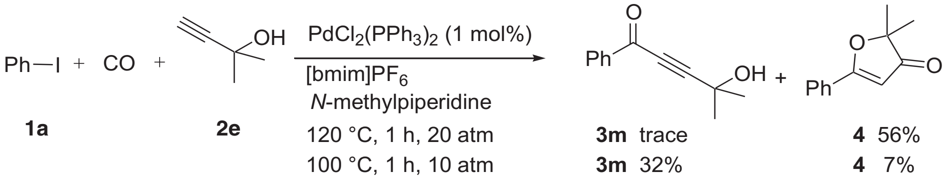
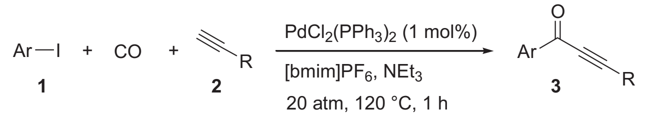
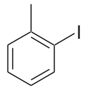
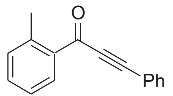
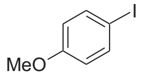
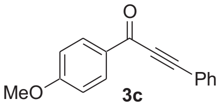
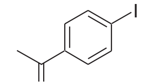
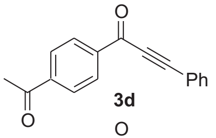
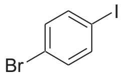
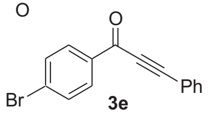
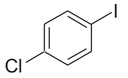
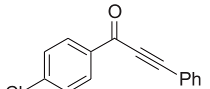
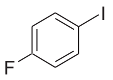
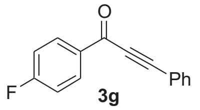
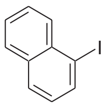
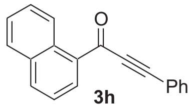
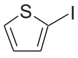
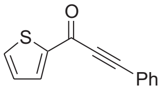
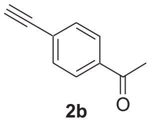
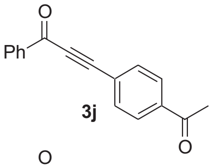
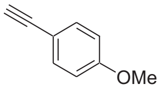
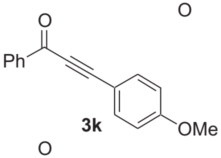
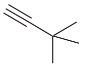
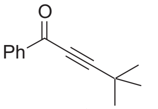


Table 2. $PdCl_2(PPh_3)_2$-catalyzed carbonylative coupling reaction of aryl iodides with terminal alkynes in $[bmim]PF_6$.



Entry	Ar—I **1**	Alkyne **2**	Product **3**	Yield (%)[a]
1	 **1b**	 **2a**	 **3b**	82
2	 **1c**	**2a**	 **3c**	82
3	 **1d**	**2a**	 **3d**	78
4	 **1e**	**2a**	 **3e**	76
5	 **1f**	**2a**	 **3f**	79
6	 **1g**	**2a**	 **3g**	81
7[b]	 **1h**	**2a**	 **3h**	78
8	 **1i**	**2a**	 **3i**	78
9[b]	Ph—I **1a**	 **2b**	 **3j**	80
10	**1a**	 **2c**	 **3k**	80
11[c]	**1a**	 **2d**	 **3l**	76

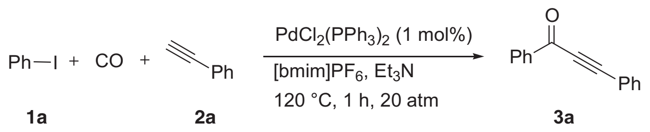
Note: Reaction conditions: **1** (1 mmol), **2** (1.2 mmol), $PdCl_2(PPh_3)_2$ (1 mol%), $[bmim]PF_6$ (3 mL), Et_3N (3.6 mmol) 120 °C, 1 h.

[a] Isolated yields after chromatography on SiO_2.

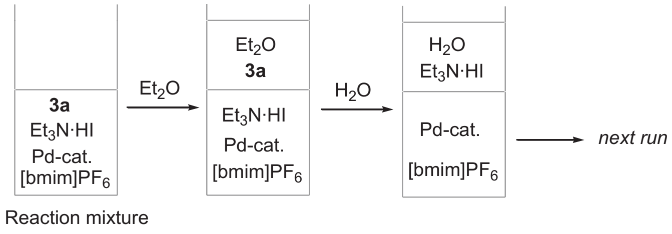
[b] Reaction carried out under 30 atm of CO.

[c] *N*-Methylpiperidine was used as the base.

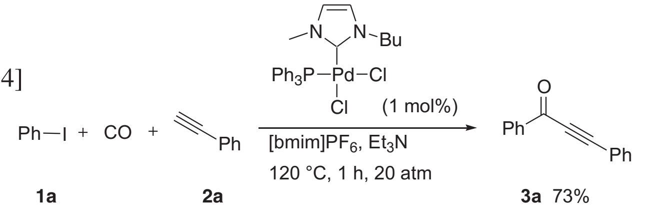
Scheme 1. Recycling of the Pd catalyst and $[bmim]PF_6$ and workup process (1 atm = 101.325 kPa).



Run	1	2	3
Yield (%)	82	68	61



[4]



Conclusions

The findings herein show that when using $[bmim]PF_6$ as a reaction medium, the Pd-catalyzed carbonylative three-component coupling reaction of aryl iodides with terminal alkynes proceeds efficiently to give α,β-acetylenic ketones in good yields. The low-viscosity ionic liquid, $[bmim]NTf_2$, which is an excellent reaction medium for typical Pd-catalyzed coupling reactions, is not suitable for the present reaction because of the competing Sonogashira coupling reaction.

Experimental section

General information

^1H NMR spectra were recorded on a JEOL JMN-AL400 (400 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. ^{13}C NMR spectra were recorded with a JEOL JMN-AL400 (100 MHz). Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions are reported in reciprocal centimeters. Mass spectra were obtained on a Shimadzu GCMS-QP 5050A instrument. High resolution mass spectra were recorded with a JEOL MS700 spectrometer. Coupling products were purified by flash chromatography on silica gel (nacalai tesque, Silica Gel 60, 230–400 mesh) and, if necessary, were further purified by recycling preparative HPLC (JAI LC-908) equipped with a GPC column and using $CHCl_3$ as eluant. All products, except for **3j**, were known compounds and were identified by comparison with literature data.

Typical procedure for the $PdCl_2(PPh_3)_2$-catalyzed three-component coupling reaction

A magnetic stirring bar, [bmim]PF_6 (3 mL), $PdCl_2(PPh_3)_2$ (0.01 mmol, 7 mg), iodobenzene (**1a**) (1 mmol, 204 mg), Et_3N (3.6 mmol, 0.5 mL), and phenylacetylene **2a** (1.2 mmol, 122 g) were placed in a 50 mL stainless autoclave lined with a glass liner. The autoclave was closed, purged three times with 10 atm of carbon monoxide, pressurized to 20 atm with CO, and then heated at 120 °C for 1 h. Excess CO was discharged at room temperature. The product was extracted from the reaction mixture by the addition of Et_2O (5 mL), followed by decantation of the ether solution of the product. This was repeated an additional four times. The residue was purified by flash chromatography on silica gel (eluant hexane : EtOAc = 10:1) to give 166 mg (82%) of **3a**.

Recycling of Pd catalyst and [bmim]PF_6

After the reaction, the product was extracted from the reaction mixture with Et_2O (5 × 5 mL), and ammonium salts were removed by extraction with water (5 × 5 mL). Both the Et_2O and water were degassed by N_2 bubbling prior to use. Excess Et_2O and water were removed under reduced pressure, and the remaining ionic liquid layer, containing the Pd catalyst, was used in the next run.

1,3-Diphenyl-2-propynone (3a) (3b)

A white solid. mp 46–48 °C (lit. (3*b*) value mp 46 to 47 °C). IR (KBr) (cm^{-1}): 2199, 1641. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.44 (m, 2H), 7.46–7.54 (m, 3H), 7.61–7.65 (m, 1H), 7.67–7.71 (m, 2H), 8.20–8.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 86.80, 93.01, 119.98, 128.52, 129.44, 130.70, 132.94, 134.01, 136.77, 177.86. EI-MS *m*/*z* (rel intensity): 206 ([M]$^+$, 45), 178 (100), 129 (46), 51 (23).

1-(2-Tolyl)-3-phenyl-2-propynone (3b) (11)

A colorless oil. IR (neat) (cm^{-1}): 2197, 1638. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.67 (s, 3H), 7.25–7.30 (m, 1H), 7.36–7.48 (m, 5H), 7.64–7.68 (m, 2H), 8.28–8.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.81, 88.28, 91.65, 120.18, 125.77, 128.50, 130.45, 132.03, 132.75, 133.03, 135.55, 140.28, 179.54. EI-MS *m*/*z* (rel intensity): 220 ([M]$^+$, 26), 219 (100), 191 (72), 189 (21), 131 (23), 91 (21). HR-MS (EI) *m*/*z* calcd. for $C_{16}H_{12}O$: 220.0888 ([M]$^+$); found: 220.0894.

1-(4-Metoxyphenyl)-3-phenyl-2-propynone (3c) (3b)

A white solid. mp 96–98 °C (lit. (3*b*) value mp 97 to 98 °C). IR (KBr) (cm^{-1}): 2199, 1630. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.89 (s, 3H), 6.96–7.00 (m, 2H), 7.39–7.43 (m, 2H), 7.45–7.50 (m, 1H), 7.65–7.69 (m, 2H), 8.16–8.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.38, 86.74, 92.09, 113.71, 120.08, 128.47, 130.04, 130.43, 131.73, 132.73, 164.30, 176.37. EI-MS *m*/*z* (rel intensity): 236 ([M]$^+$, 79), 209 (20), 208 (100), 193 (95), 165 (53), 129 (42), 75 (20).

1-[4-(1-Oxoethyl)phenyl]-3-phenyl-2-propynone (3d) (3c)

A white solid. mp 101 to 102 °C (lit. (3*c*) value mp 103 to 104 °C). IR (KBr) (cm^{-1}): 2197, 1684, 1634. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.66 (s, 3H), 7.42–7.46 (m, 2H), 7.49–7.53 (m, 1H), 7.69–7.72 (m, 2H), 8.06–8.10 (m, 2H), 8.28–8.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.79, 86.64, 94.11, 119.55, 128.28, 128.62, 129.50, 130.98, 133.01, 139.61, 140.62, 176.87, 197.20. EI-MS *m*/*z* (rel intensity): 248 ([M]$^+$, 67), 233 (100), 205 (34), 177 (20), 176 (33), 129 (71), 103 (27), 75 (28).

1-(4-Bromophenyl)-3-phenyl-2-propynone (3e) (3b)

A white solid. mp 106 to 107 °C (lit. (3*b*) value mp 106 to 107 °C). IR (KBr) (cm^{-1}): 2199, 1651. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.46 (m, 2H), 7.48–7.52 (m, 1H), 7.65–7.69 (m, 4H), 8.06–8.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 86.68, 93.78, 119.94, 128.83, 129.65, 131.01, 131.08, 132.07, 133.20, 135.77, 176.85. EI-MS *m*/*z* (rel intensity): 285 ([M]$^+$, 41), 284 (40), 258 (54), 256 (57), 176 (41), 129 (100), 88 (32), 75 (37), 51 (20).

1-(4-Chlorophenyl)-3-phenyl-2-propynone (3f) (3b)

A white solid. mp 104 to 105 °C (lit. (3*b*) value mp 104 °C). IR (KBr) (cm^{-1}): 2199, 1654. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.45 (m, 2H), 7.46–7.52 (m, 3H), 7.66–7.69 (m, 2H), 8.13–8.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 86.68, 93.69, 119.98, 129.04, 129.07, 130.93, 131.05, 133.16, 135.41, 140.76, 176.66. EI-MS *m*/*z* (rel intensity): 240 ([M]$^+$, 55), 214 (31), 212 (100), 176 (33), 129 (83), 75 (43), 51 (21).

1-(4-Fluorophenyl)-3-phenyl-2-propynone (3g) (12)

A white solid. mp 100–102 °C. IR (KBr) (cm^{-1}): 2206, 1634. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15–7.21 (m, 2H), 7.40–7.45 (m, 2H), 7.47–7.51 (m, 1H), 7.66–7.69 (m, 2H), 8.22–8.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 86.68, 93.45, 115.97 (J = 22.1 Hz), 120.03, 128.81, 131.01, 132.32 (J = 9.6 Hz), 133.15, 133.49, 166.53 (J = 257.2 Hz), 176.45. EI-MS *m*/*z* (rel intensity): 224 ([M]$^+$, 41), 196 (100), 129 (52), 75 (23).

1-(1-Naphthyl)-3-phenyl-2-propynone (3h) (2c)

A white solid. mp 94 to 95 °C (lit. (2*c*) value mp 95 °C). IR (KBr) (cm^{-1}): 2195, 1634. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.44 (m, 2H), 7.46–7.50 (m, 1H), 7.56–7.62 (m, 2H), 7.66–7.72 (m, 3H), 7.90–7.93 (m, 1H), 8.08–8.12 (m, 1H), 8.63–8.66 (m, 1H), 9.21–9.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 88.63, 91.82, 120.44, 124.60, 126.10, 126.88, 128.78, 129.07, 130.74, 130.84, 133.02, 133.05, 133.97, 134.69, 135.25, 179.83. EI-MS *m*/*z* (rel intensity): 256 ([M]$^+$, 100), 228 (50), 226 (47), 202 (21), 129 (35), 114 (35), 113 (33), 101 (15), 75 (21), 51 (21).

3-Phenyl-1-(2-thiophenyl)-2-propynone (3i) (13)

A colorless oil. IR (neat) (cm^{-1}): 2199, 1616. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17–7.20 (m, 2H), 7.40–7.44 (m, 2H), 7.46–7.51 (m, 1H), 7.64–7.68 (m, 2H), 7.72–7.74 (m, 1H), 8.00–8.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 86.34, 91.61, 119.71, 128.25, 128.56, 130.74, 132.87, 135.00, 135.18, 144.74, 169.60. EI-MS *m*/*z* (rel intensity): 212 ([M]$^+$, 46), 184 (100), 129 (26).

3-[4-(1-Oxoethyl)phenyl]-1-phenyl-2-propynone (3j)

A white solid. mp 115 to 116 °C. IR (KBr) (cm^{-1}): 2202, 1684, 1642. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.64 (s, 3H), 7.51–7.56 (m, 2H), 7.63–7.68 (m, 1H), 7.76–7.79 (m, 2H), 7.98–8.02 (m, 2H), 8.20–8.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.75, 88.80, 91.23, 124.71, 128.45, 128.81, 129.65, 133.14, 134.49, 136.66, 138.15, 177.71, 197.08. EI-MS *m*/*z* (rel intensity): 248 ([M]$^+$, 72), 233 (100), 205 (53), 177 (22), 176 (48), 88 (20). HR-MS (EI) *m*/*z* calcd. for $C_{16}H_{12}O$: 248.0837 ([M]$^+$); found: 248.0839.

3-(4-Metoxyphenyl)-1-phenyl-2-propynone (3k) (2c)

A white solid. mp 77–79 °C (lit. (2*c*) value mp 81 to 82 °C). IR (KBr) (cm^{-1}): 2189, 1600. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.86 (s, 3H), 6.92–6.94 (m, 2H), 7.48–7.53 (m, 2H), 7.60–7.66 (m, 3H), 8.20–8.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.50, 86.99, 94.45, 111.92, 114.54, 128.66, 129.54, 134.00, 135.21, 137.13, 161.85, 178.08. EI-MS *m*/*z* (rel intensity): 236 ([M]$^+$, 100), 208 (53), 193 (58), 165 (31), 159 (94), 77 (20), 51 (20).

4,4-Dimethyl-1-phenyl-2-pentyn-1-one (3l) (3b)

A colorless oil. IR (neat) (cm^{-1}): 2211, 1649. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.38 (s, 9H), 7.44–7.52 (m, 2H), 7.56–7.62 (m, 1H), 8.10–8.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.13, 30.26, 78.19, 104.04, 128.55, 129.58, 133.90, 137.09, 178.44. EI-MS *m*/*z* (rel intensity): 186 ([M]$^+$, 25), 143 (50), 128 (30), 105 (100), 77 (35), 51 (22).

4-Hydroxy-4-methyl-1-phenyl-2-pentyn-1-one (3m) (3b)

A colorless oil. IR (neat) (cm^{-1}): 2212, 1645. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.67 (s, 6H), 7.46–7.51 (m, 2H), 7.59–7.64 (m, 1H), 8.10–8.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.69, 65.22, 79.81, 98.27, 128.55, 129.58, 134.22, 136.41, 178.02. EI-MS *m*/*z* (rel intensity): 188 ([M]$^+$, 8), 173 (100), 145 (22), 105 (27), 95 (22), 77 (44), 53 (70), 51 (33).

2,2-Dimethyl-5-phenyl-3(2H)-furanone (4) (14)

A yellow oil. IR (neat) (cm^{-1}): 3103, 1694. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48 (s, 6H), 5.96 (s, 1H), 7.45–7.50 (m, 2H), 7.52–7.56 (m, 1H), 7.80–7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.22, 88.99, 98.61, 127.22, 128.89, 129.20, 132.67, 183.49, 206.99. EI-MS *m*/*z* (rel intensity): 188 ([M]$^+$, 20), 102 (100).

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