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Palladium-catalyzed carbonylative coupling of (chloromethyl)arenes with terminal arylalkynes to produce 1,4-diaryl-3-butyn-2-ones†

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A convenient and efficient method for the synthesis of 1,4-diaryl-3-butyn-2-ones is described. The carbonylative coupling reactions of (chloromethyl)arenes with terminal arylalkynes proceeded smoothly in the presence of a $PdCl_2(PPh_3)_2$ catalyst under mild reaction conditions to produce the corresponding 1,4-diaryl-3-butyn-2-ones in satisfactory to excellent yields.

1. Introduction

The development of convenient and efficient methods for the synthesis of alkynones has attracted considerable attention. Alkynones represent an interesting structural motif and are frequently found in various bioactive molecules.[1] Alkynones have also been utilized as key intermediates in the synthesis of natural products,[2] heterocycles,[3] and 2-naphthols.[4] Palladium-catalyzed carbonylative coupling reactions have become a straightforward and efficient method for the synthesis of carbonyl group-containing compounds.[5] Over the past three decades, the palladium-catalyzed carbonylative Sonogashira coupling reaction of aryl iodides/bromides with terminal alkynes to produce alkynones has been widely explored.[6] However, to the best of our knowledge, only two examples have been reported of the palladium-catalyzed carbonylative coupling reaction of benzyl chlorides with terminal alkynes.[7] Moreover, the use of (chloromethyl)naphthalenes as starting materials in this type of carbonylative coupling reaction has not been reported so far.

In the course of our research into η^3-benzylpalladium chemistry,[8,9] we found that the carbonylative coupling reaction of 1-(chloromethyl)naphthalenes with terminal arylalkynes can also be carried out in the presence of a palladium catalyst under very mild conditions to produce alkynones, namely, 1,4-diaryl-3-butyn-2-ones, in satisfactory to excellent yields. The carbonylative coupling reaction of benzyl chlorides with terminal arylalkynes was also successful using the same catalytic system with a mere enhancement of the reaction temperature. The results are reported in this paper.

2. Results and discussion

In the initial studies conducted, the reaction of 1-(chloromethyl)naphthalene (**1a**) with phenylacetylene (**2a**) in the presence of carbon monoxide (CO) was chosen as a model for optimization of the reaction conditions.[10] The optimization included the selection of the most suitable palladium catalyst, base, and solvent. The results are summarized in Table 1. Several palladium catalysts, which include $PdCl_2/PPh_3$, $Pd(OAc)_2/PPh_3$, $Pd_2(dba)_3/PPh_3$, $Pd(PPh_3)_4$, and $PdCl_2(PPh_3)_2$, were initially tested in dioxane at 40 °C using triethyl amine (NEt_3) as a base (entries 1–5). Among the palladium catalysts tested, $PdCl_2(PPh_3)_2$ exhibited a higher catalytic activity than all the others. The bases were then screened using $PdCl_2(PPh_3)_2$ and dioxane as the catalyst and solvent, respectively (entries 5–7). NEt_3 proved to be the best base. The solvents were finally screened using $PdCl_2(PPh_3)_2$ and NEt_3 as the catalyst and base, respectively. Polar (dioxane, tetrahydrofuran (THF), ethanol, and isopropyl alcohol (IPA)) and nonpolar (CH_2Cl_2, toluene) solvents were examined (entries 5 and 8–12). The use of dioxane as the solvent led to the formation of the carbonylative coupling product, 1-(naphthalen-1-yl)-4-phenylbut-3-yn-2-one (**3a**), with the highest yield. The yield of **3a** decreased when the reaction temperature was reduced to 30 °C (entry 13) or when the CO pressure was reduced to 0.25 MPa (entry 14). Therefore, the subsequent palladium-catalyzed carbonylative coupling reactions of various (chloromethyl)naphthalenes with terminal arylalkynes were conducted in the presence of $PdCl_2(PPh_3)_2$ as the catalyst,

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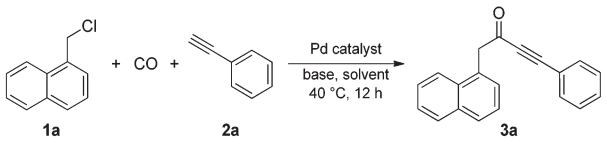
[b]*Department of Dermatology & Venereology, The First Hospital of Jilin University, Changchun 130021, China. E-mail: liuhesong126@126.com; Fax: +86-431-85654528; Tel: +86-431-88782663*

† Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data for isolated compounds. See DOI: 10.1039/c3ra42972e

Table 1 Reaction condition screening[a]



Entry	Pd catalyst	Base	Solvent	Yield[b] (%)
1[c]	$PdCl_2/PPh_3$	NEt_3	Dioxane	28
2[c]	$Pd(OAc)_2/PPh_3$	NEt_3	Dioxane	64
3[cd]	$Pd_2(dba)_3/PPh_3$	NEt_3	Dioxane	79
4	$Pd(PPh_3)_4$	NEt_3	Dioxane	25
5	$PdCl_2(PPh_3)_2$	NEt_3	Dioxane	95
6	$PdCl_2(PPh_3)_2$	NaOAc	Dioxane	79
7	$PdCl_2(PPh_3)_2$	K_3PO_4	Dioxane	31
8	$PdCl_2(PPh_3)_2$	NEt_3	THF	57
9	$PdCl_2(PPh_3)_2$	NEt_3	Ethanol	46
10	$PdCl_2(PPh_3)_2$	NEt_3	IPA	72
11	$PdCl_2(PPh_3)_2$	NEt_3	CH_2Cl_2	89
12	$PdCl_2(PPh_3)_2$	NEt_3	Toluene	55
13[e]	$PdCl_2(PPh_3)_2$	NEt_3	Dioxane	52
14[f]	$PdCl_2(PPh_3)_2$	NEt_3	Dioxane	82

[a] Reaction conditions: 1-chloromethylnaphthalene (**1a**, 0.5 mmol, 88.3 mg), phenylacetylene (0.6 mmol, 61.3 mg), Pd catalyst (5 mol%), base (0.75 mmol), and CO (0.5 MPa) in solvent (2.0 mL) at 40 °C for 12 h. [b] GC yield; benzylideneacetone was used as an internal standard. [c] 10 mol% PPh_3 was used. [d] 2.5 mol% $Pd_2(dba)_3$ was used. [e] The reaction was carried out at 30 °C. [f] The reaction was carried out at a CO pressure of 0.25 MPa.

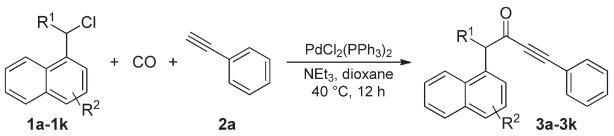
and by using NEt_3 as the base in dioxane under a CO pressure of 0.5 MPa at 40 °C for 12 h.

Phenylacetylene (**2a**) was used as the terminal arylalkyne to determine the scope of chloride substrates at the optimized conditions. The results are summarized in Table 2. The reaction of 1-(chloromethyl)naphthalene (**1a**), the simplest chloride substrate, was completed within 12 h and produced 1-(naphthalen-1-yl)-4-phenyl-3-butyn-2-one (**3a**) in 91% yield (entry 1). The reactions of the 1-(chloromethyl)naphthalenes **1b** and **1c** with a methyl group in the *ortho* or *para* position also proceeded smoothly to produce the corresponding products **3b** and **3c** in excellent yields (entries 2 and 3; 94% and 96% yields, respectively). However, a subsequent investigation showed that the reactivity of the chloride substrate decreased when an *ortho* methoxy group was present.[11] The carbonylative coupling product **3d** was obtained in only 32% yield when 1-(chloromethyl)-2-methoxynaphthalene (**1d**) was used as a substrate (entry 4). 1-(Chloromethyl)-4-bromonaphthalene (**1e**) regioselectively underwent the carbonylative coupling reaction to produce **3e** in 98% yield (entry 5). The Br atom linked to the aromatic ring was maintained in the product **3e** under the optimized conditions, which provides an opportunity for the further functionalization of this compound. The reactions of the substrates **1f–1i** with an aliphatic group α to the chlorine atom were then investigated. Even substrate **1f**, which has a Csp^3–H β hydrogen, underwent the carbonylative coupling reaction smoothly, and produced **3f** as the sole product in 85% yield (entry 6). No β-hydride elimination product was observed.[12] The introduction of a relatively big aliphatic group onto the benzylic position of the chloride substrates led to the formation of alkynones in low yields or no reaction at all (entries 7–9). The reaction of substrate **1j** with a phenyl group linked to the benzylic position was finally investigated. No reaction was observed (entry 10). These results indicate that the reactivity of the chloride substrates was strongly influenced by the steric effect of the substituents that are linked to the benzylic position.

1a was then used as the chloride substrate to determine the scope of terminal arylalkyne substrates at the optimized conditions. The results are shown in Table 3. The reactions of 2-methylphenyl acetylene (**2b**), 3-methylphenyl acetylene (**2c**), and 4-methylphenyl acetylene (**2d**) proceeded smoothly to produce **4b–4d** in good yields (entries 1–3, 79%–87%). These results suggest that the reactivity of arylalkynes was not influenced by substituent steric effects. A good yield of the product **4e** was also observed when 4-methoxyphenyl acetylene (**2e**) was used in the carbonylative coupling reaction (entry 4, 93%). Carbonylative coupling products **4f** and **4g** were obtained in excellent yields (92% and 88%, respectively) from the reactions of arylalkyne substrates **2f** and **2g** with an electron-withdrawing group F or Br in the *para* position (entries 5 and 6). Notably, the employed reaction conditions can tolerate an aldehyde group being linked to the benzene ring of the arylalkyne. The desired product **4h** was obtained in 62% yield from the reaction of 4-ethynylbenzaldehyde (**2h**) (entry 7). The arylalkyne substrate bearing the strong electron-withdrawing group NO_2 underwent the carbonylative coupling reaction smoothly to produce the target product in a good yield (entry 8, 82% yield).

The successful formation of alkynones from the carbonylative Sonogashira coupling reaction of 1-(chloromethyl)-naphthalenes with terminal arylalkynes encouraged us to examine the carbonylative Sonogashira coupling of benzyl chlorides with phenylacetylene. The results are summarized in Table 4. No reaction was observed when the carbonylative Sonogashira coupling reaction of benzyl chloride (**5a**) with **2a** was conducted under the same conditions as those employed in the reactions of 1-(chloromethyl)naphthalenes (entry 1). Product **6a** was obtained in 46% yield when the reaction temperature was increased from 40 °C to 60 °C (entry 2). The yield of product **6a** was further improved to 85% when the reaction temperature was increased to 80 °C (entry 3). Therefore, the subsequent palladium-catalyzed carbonylative coupling reactions of various benzyl chlorides with **2a** were conducted at 80 °C. The reactions of benzyl chlorides **5b–5d** with Me, MeO, and F in the *para* position, respectively, proceeded smoothly to produce **6b–6d** in good yields (entries 4–6, 76%–87%). Moderate yields were observed when 2-methoxybenzyl chloride (**5e**) and 2-bromobenzyl chloride (**5f**) were used as starting materials (entries 7 and 8, 60% and 65%). These results indicate that the reactivity of a benzyl chloride substrate is influenced by an *ortho* substituent.

Table 2 Palladium-catalyzed carbonylative Sonogashira coupling of 1-(chloromethyl)naphthalenes with phenylacetylene[a]



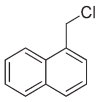
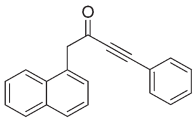
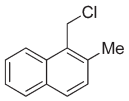
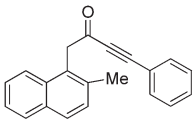
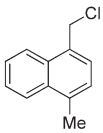
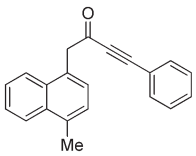
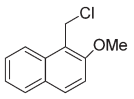
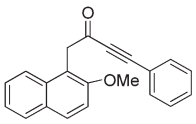
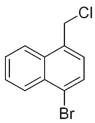
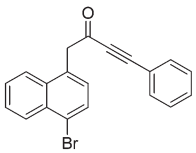
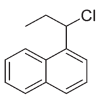
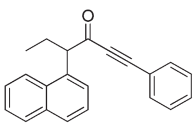
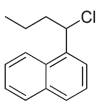
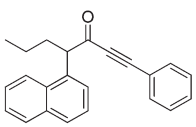
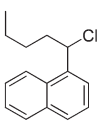
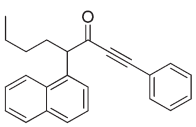
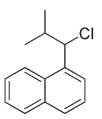
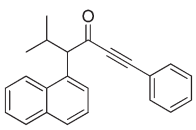
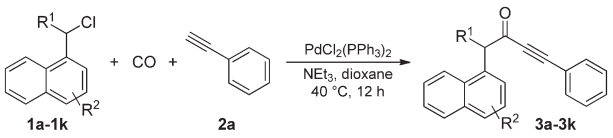
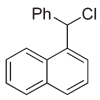
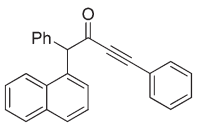
Entry	Chloromethyl naphthalene **1**		Product **3**		Yield[b] (%)
1		**1a**		**3a**	91
2		**1b**		**3b**	94
3		**1c**		**3c**	96
4		**1d**		**3d**	32
5		**1e**		**3e**	98
6		**1f**		**3f**	85
7		**1g**		**3g**	51
8		**1h**		**3h**	57
9		**1i**		**3i**	NR[c]

Table 2 (*Continued*)



Entry	Chloromethyl naphthalene **1**		Product **3**		Yield[b] (%)
10		**1j**		**3j**	NR[c]

[a] Reaction conditions: 1-(chloromethyl)naphthalene substrate (**1a–1j**, 0.5 mmol), phenylacetylene (0.6 mmol, 61.3 mg), $PdCl_2(PPh_3)_2$ (5 mol%, 17.5 mg), NEt_3 (1.5 equiv., 151.8 mg), and CO (0.5 MPa) in dioxane (2.0 mL) at 40 °C for 12 h. [b] Isolated yield. [c] No reaction; the starting materials were recovered.

3. Conclusions

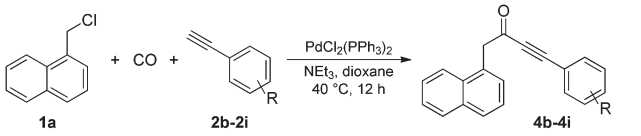
In conclusion, a simple and efficient method for the synthesis of alkynones was established. The carbonylative coupling reaction of 1-(chloromethyl)naphthalenes with terminal arylalkynes proceeded smoothly in the presence of a $PdCl_2(PPh_3)_2$ catalyst under mild reaction conditions (40 °C, 0.5 MPa CO) without the addition of any external phosphine ligands. Although benzyl chlorides exhibited relatively low reactivities, they could also undergo this type of carbonylation reaction smoothly in the presence of the same catalysis system by merely changing the reaction temperature to 80 °C.

4. Experimental section

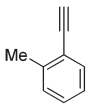
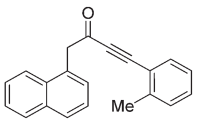
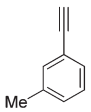
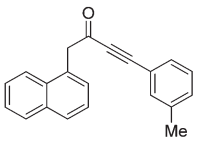
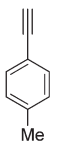
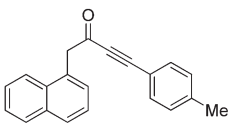
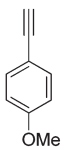
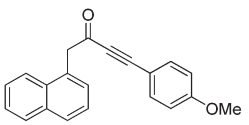
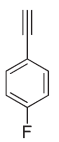
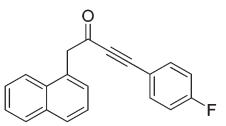
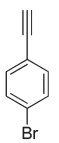
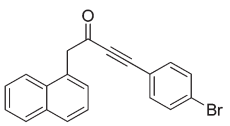
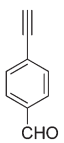
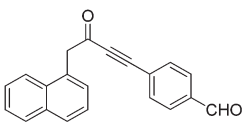
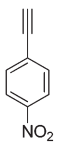
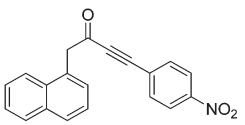
General information

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^1H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as the solvent and internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometer or a GC-TOF mass spectrometer. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous $KMnO_4$. Flash chromatography was carried out on SiO_2 (silica gel 60, 200–300 mesh). Melting points were determined using a micro-melting point apparatus and are uncorrected.

Table 3 Palladium-catalyzed carbonylative Sonogashira coupling of 1-(chloromethyl)naphthalene with various terminal arylalkynes[a]

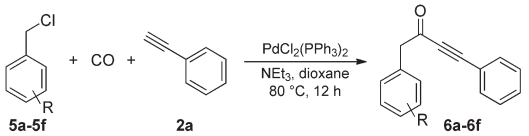


1a 2b-2i 4b-4i

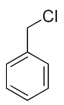
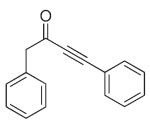
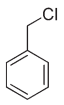
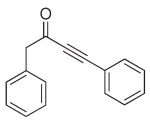
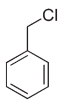
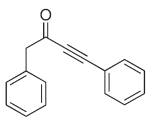
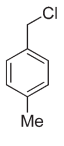
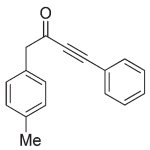
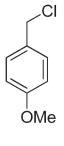
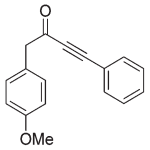
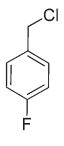
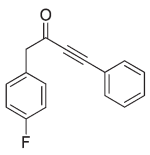
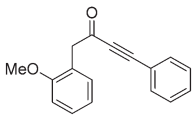
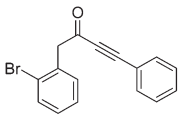
Entry	Arylalkyne **2**	Product **4**	Yield[b] (%)
1	 **2b**	 **4b**	79
2	 **2c**	 **4c**	84
3	 **2d**	 **4d**	87
4	 **2e**	 **4e**	93
5	 **2f**	 **4f**	92
6	 **2g**	 **4g**	88
7	 **2h**	 **4h**	62
8	 **2i**	 **4i**	82

[a] Reaction conditions: 1-(chloromethyl)naphthalene (**1a**, 0.5 mmol, 88.3 mg), arylalkyne (**2b–2i**, 0.6 mmol), $PdCl_2(PPh_3)_2$ (5 mol%, 17.5 mg), NEt_3 (1.5 equiv., 151.8 mg), and CO (0.5 MPa) in dioxane (2.0 mL) at 40 °C for 12 h. [b] Isolated yield.

Table 4 Palladium-catalyzed carbonylative Sonogashira coupling of benzyl chlorides with phenylacetylene[a]



5a-5f 2a 6a-6f

Entry	Benzyl chloride **5**	Product **6**	Yield[b] (%)
1	 **5a**	 **6a**	NR[c]
2	 **5a**	 **6a**	46[d]
3	 **5a**	 **6a**	85
4	 **5b**	 **6b**	82
5	 **5c**	 **6c**	76
6	 **5d**	 **6d**	87
7	 **5e**	 **6e**	60
8	 **5f**	 **6f**	65

[a] Reaction conditions: benzyl chlorides (**3a–3f**, 0.5 mmol), phenylacetylene (0.6 mmol, 61.3 mg), $PdCl_2(PPh_3)_2$ (5 mol%, 17.5 mg), NEt_3 (1.5 equiv., 151.8 mg), and CO (0.5 MPa) in dioxane (2.0 mL) at 40 °C for 12 h. [b] Isolated yield. [c] No reaction was observed at 40 °C; the starting materials were recovered. [d] The reaction was conducted at 60 °C.

The chlorides (**1a**, **1c**, **1e**, **5a**, **5b** and **5d**) and terminal arylalkynes (**2b–2i**) are commercially available. The starting materials **1b**, **1d**, **1f** and **1j**, **5c**, **5e**, and **5f** appear in the literature.[8a,b] Unless otherwise noted, carbon monoxide (99.5%) was used without further purification.

General procedure for obtaining products 3, 4 and 6

$PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol), chloride substrate (**1** or **5**, 0.5 mmol), terminal arylalkyne (**2**, 0.6 mmol), freshly distilled NEt_3 (75.9 mg, 0.75 mmol), and freshly distilled dioxane (2 mL) were placed in a 25 mL autoclave with a magnetic stir bar under a N_2 atmosphere. The autoclave was purged with CO three times, filled with CO to 0.5 MPa pressure, and heated to 40 °C for 12 h. The autoclave was allowed to cool to room temperature and the remaining CO was vented. The resultant mixture was evaporated *in vacuo* to give the crude product, which was then purified *via* silica gel chromatography (eluent: ethyl acetate–petroleum ether = 1 : 30 to 1 : 10) to afford the 1,4-diaryl-3-butyn-2-one product **3**, **4** or **6**.

1-(Naphthalen-1-yl)-4-phenylbut-3-yn-2-one (3a)[13]. Yellow solid (122.3 mg, 91% yield), mp: 62–64 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (dd, J = 8.1, 0.8 Hz, 1H), 7.88–7.80 (m, 2H), 7.55–7.45 (m, 4H), 7.37–7.31 (m, 1H), 7.25–7.21 (m, 4H), 4.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.4, 134.0, 133.2, 132.5, 131.0, 130.0, 128.9, 128.8, 128.6, 128.5, 126.6, 126.0, 125.6, 124.1, 119.8, 93.2, 87.8, 49.9; IR (KBr) ν (cm^{-1}) 3061, 2925, 2203, 1778, 1664, 1597, 1511, 1489, 1443, 1398, 1283, 1159, 1084, 1070, 999, 922, 802, 781, 759, 688; HRMS (EI) Calcd for $C_{20}H_{14}O$ 270.1045 $[M]^+$, found 270.1052.

1-(2-Methylnaphthalen-1-yl)-4-phenylbut-3-yn-2-one (3b). Yellow solid (133.6 mg, 94% yield), mp: 84–86 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.52 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.45 (dd, J = 11.0, 3.9 Hz, 1H), 7.40–7.34 (m, 2H), 7.28–7.19 (m, 4H), 4.41 (s, 2H), 2.59 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.1, 135.4, 133.1, 132.9, 132.6, 130.8, 129.1, 128.6, 128.5, 128.0, 127.1, 126.6, 124.9, 123.7, 119.7, 92.3, 87.9, 45.4, 20.8; IR (KBr) ν (cm^{-1}) 3443, 3038, 2971, 2205, 1662, 1597, 1571, 1489, 1383, 1276, 1115, 1027, 923, 853, 811, 787, 763, 741, 691, 599; HRMS (EI) Calcd for $C_{21}H_{16}O$ 284.1201 $[M]^+$, found 284.1206.

1-(4-Methylnaphthalen-1-yl)-4-phenylbut-3-yn-2-one (3c). Yellow oil (136.4 mg, 96% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (dd, J = 9.4, 4.9 Hz, 2H), 7.55–7.47 (m, 2H), 7.37–7.20 (m, 7H), 4.29 (s, 2H), 2.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.5, 134.7, 133.2, 132.5, 130.8, 128.62, 128.56, 128.1, 126.4, 126.2, 125.8, 125.0, 124.6, 119.9, 92.9, 87.9, 50.0, 19.6; IR (neat) ν (cm^{-1}) 3069, 2925, 2203, 1664, 1596, 1489, 1443, 1282, 1100, 1076, 999, 832, 801, 756, 688; HRMS (EI) Calcd for $C_{21}H_{16}O$ 284.1201 $[M]^+$, found 284.1202.

1-(2-Methoxynaphthalen-1-yl)-4-phenylbut-3-yn-2-one (3d). Yellow solid (48.1 mg, 32% yield), mp: 78–80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90–7.77 (m, 3H), 7.48 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.38–7.28 (m, 3H), 7.28–7.18 (m, 4H), 4.41 (s, 2H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.9, 155.4, 133.5, 133.1, 130.6, 129.6, 129.2, 128.6, 128.5, 127.0, 123.5, 123.1, 120.0, 115.2, 113.1, 91.6, 87.9, 56.6, 42.0; IR (KBr) ν (cm^{-1}) 3059, 3001, 2936, 2839, 2203, 1667, 1626, 1595, 1514, 1489, 1464, 1406, 1384, 1350, 1325, 1253, 1182, 1147, 1112, 1086, 1047, 1025, 999, 953, 855, 809, 758, 689; HRMS (EI) Calcd for $C_{21}H_{16}O_2$ 300.1150 $[M]^+$, found 300.1154.

1-(4-Bromonaphthalen-1-yl)-4-phenylbut-3-yn-2-one (3e). Yellow oil (171.1 mg, 98% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.31–8.26 (m, 1H), 7.98–7.93 (m, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.61–7.53 (m, 2H), 7.39–7.34 (m, 1H), 7.32–7.24 (m, 5H), 4.30 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.7, 133.7, 133.3, 132.4, 132.0, 131.1, 130.2, 129.8, 129.3, 128.8, 128.2, 127.5, 124.7, 123.3, 119.7, 93.6, 87.8, 49.9; IR (neat) ν (cm^{-1}) 3068, 2924, 2202, 1759, 1666, 1594, 1566, 1508, 1489, 1443, 1379, 1284, 1256, 1226, 1198, 1161, 1102, 1076, 1042, 99, 925, 828, 790, 758, 688, 664, 613, 566, 535, 512; HRMS (EI) Calcd for $C_{20}H_{13}BrO$ 348.0150 and 350.0129 $[M]^+$, found 348.0151 and 350.0136.

4-(Naphthalen-1-yl)-1-phenylhex-1-yn-3-one (3f). Yellow solid (126.6 mg, 85% yield), mp: 68–70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.80 (dd, J = 5.2, 0.6 Hz, 1H), 7.59–7.47 (m, 4H), 7.34–7.22 (m, 5H), 4.54 (t, J = 7.2 Hz, 1H), 2.38–2.51 (m, 1H), 2.10–1.99 (m, 1H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.8, 134.3, 134.2, 133.0, 132.4, 130.6, 129.1, 128.5, 128.2, 126.5, 125.9, 125.7, 125.6, 123.5, 119.9, 92.4, 87.6, 57.9, 24.7, 12.4; IR (KBr) ν (cm^{-1}) 3058, 2966, 2933, 2875, 2200, 1666, 1596, 1575, 1510, 1489, 1456, 1444, 1396, 1280, 1133, 1059, 1028, 999, 951, 928, 782, 758, 735, 689, 606; HRMS (EI) Calcd for $C_{22}H_{18}O$ 298.1358 $[M]^+$, found 298.1363.

4-(Naphthalen-1-yl)-1-phenylhept-1-yn-3-one (3g). Yellow solid (79.6 mg, 51% yield), mp: 88–89 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.83 (dd, J = 6.9, 1.6 Hz, 1H), 7.62–7.57 (m, 1H), 7.56–7.50 (m, 3H), 7.38–7.32 (m, 1H), 7.29–7.21 (m, 4H), 4.67 (t, J = 7.2 Hz, 1H), 2.49–2.37 (m, 1H), 2.08–1.98 (m, 1H), 1.52–1.36 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.9, 134.5, 134.2, 133.0, 132.3, 130.6, 129.1, 128.5, 128.2, 126.5, 126.0, 125.8, 125.6, 123.5, 119.9, 92.5, 87.6, 56.0, 33.6, 21.0, 14.2; IR (KBr) ν (cm^{-1}) 3060, 2958, 2930, 2871, 2201, 1667, 1596, 1489, 1443, 1396, 1277, 1070, 920, 784, 758, 688, 607; HRMS (EI) Calcd for $C_{23}H_{20}O$ 312.1514 $[M]^+$, found 312.1521.

4-(Naphthalen-1-yl)-1-phenyloct-1-yn-3-one (3h). Yellow solid (92.9 mg, 57% yield), mp: 53–55 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, J = 8.5 Hz, 1H), 7.38–7.32 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.63–7.52 (m, 4H), 7.37–7.33 (m, 1H), 7.25 (d, J = 4.3 Hz, 4H), 4.68 (t, J = 7.1 Hz, 1H), 2.51–2.44 (m, 1H), 2.12–2.02 (m, 1H), 1.53–1.35 (m, 4H), 0.93 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.9, 134.5, 134.2, 133.1, 132.4, 130.6, 129.1, 128.5, 128.2, 126.5, 126.0, 125.8, 125.7, 123.5, 119.9, 92.5, 87.7, 56.3, 31.2, 30.0, 22.8, 14.0; IR (KBr) ν (cm^{-1}) 3059, 2956, 2930, 2859, 2199, 2047, 1942, 1666, 1596, 1511, 1489, 1465, 1443, 1396, 1282, 1133, 1071, 998, 934, 782, 758, 689; HRMS (EI) Calcd for $C_{24}H_{22}O$ 326.1671 $[M]^+$, found 326.1664.

1-(Naphthalen-1-yl)-4-(o-tolyl)but-3-yn-2-one (4b). Yellow oil (112.1 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, J = 8.2 Hz, 1H), 7.89–7.78 (m, 2H), 7.56–7.44 (m, 4H), 7.27–7.23 (m, 2H), 7.09 (dd, J = 15.7, 7.9 Hz, 2H), 4.34 (s, 2H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.6, 142.3, 134.0, 133.8, 132.5, 130.8, 130.0, 129.7, 128.9, 128.8, 128.4, 126.6, 126.0, 125.7, 125.6, 124.0, 119.6, 92.0, 91.5, 50.0, 20.31; IR (neat) ν

(cm^{-1}) 3060, 2922, 2198, 1663, 1598, 1484, 1295, 1274, 1119, 1038, 950, 785, 760, 714, 617, 603; HRMS (ES) Calcd for $C_{21}H_{16}ONa$ 307.1099 $[M + Na]^+$, found 307.1105.

1-(Naphthalen-1-yl)-4-(m-tolyl)but-3-yn-2-one (4c). Yellow oil (119.4 mg, 84% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 4.0 Hz, 1H), 7.81 (dd, J = 8.5, 3.9 Hz, 1H), 7.55–7.41 (m, 4H), 7.17–6.97 (m, 4H), 4.32 (s, 2H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.4, 138.4, 134.0, 133.7, 132.5, 131.8, 130.3, 130.1, 128.9, 128.5, 126.6, 126.0, 125.6, 124.1, 119.5, 93.7, 87.6, 49.9, 21.1; IR (neat) ν (cm^{-1}) 3047, 2921, 2188, 1718, 1664, 1597, 1511, 1483, 1456, 1398, 1297, 1208, 1098, 1017, 884, 786, 775, 732, 688; HRMS (ES) Calcd for $C_{21}H_{16}ONa$ 307.1099 $[M + Na]^+$, found 307.1095.

1-(Naphthalen-1-yl)-4-(p-tolyl)but-3-yn-2-one (4d). Yellow oil (123.6 mg, 87% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 8.2 Hz, 1H), 7.87–7.71 (m, 2H), 7.53–7.37 (m, 4H), 7.12 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 4.29 (s, 2H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.4, 141.7, 134.0, 133.2, 132.5, 130.2, 129.4, 128.9, 128.5, 126.6, 126.0, 125.7, 124.1, 116.7, 94.0, 88.1, 50.0, 21.8; IR (neat) ν (cm^{-1}) 3046, 2920, 2198, 2147, 1759, 1662, 1605, 1509, 1445, 1398, 1289, 1217, 1083, 951, 875, 817, 784, 732, 707; HRMS (ES) Calcd for $C_{21}H_{16}ONa$ 307.1099 $[M + Na]^+$, found 307.1490.

4-(4-Methoxyphenyl)-1-(naphthalen-1-yl)but-3-yn-2-one (4e). Yellow solid (139.6 mg, 93% yield), mp: 84–86 °C. ^1H NMR ($CDCl_3$, 400 MHz) 8.08 (d, J = 8.1 Hz, 1H), 7.96–7.85 (m, 2H), 7.61–7.50 (m, 4H), 7.25 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 4.39 (s, 2H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.4, 161.8, 135.2, 134.0, 132.5, 130.3, 128.8, 128.4, 126.6, 126.0, 125.6, 124.2, 114.3, 111.4, 94.6, 87.9, 55.4, 49.8; IR (KBr) ν (cm^{-1}) 3312, 3043, 2900, 2553, 2184, 1665, 1601, 1509, 1326, 1296, 1253, 1184, 1109, 1066, 1027, 916, 835, 808, 784, 775, 731; HRMS (ES) Calcd for $C_{21}H_{16}O_2Na$ 323.1048 $[M + Na]^+$, found 323.1054.

4-(4-Fluorophenyl)-1-(naphthalen-1-yl)but-3-yn-2-one (4f). Yellow solid (132.6 mg, 92% yield), mp: 91–93 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.3 Hz, 1H), 7.85–7.75 (m, 2H), 7.51–7.35 (m, 4H), 7.17–7.11 (m, 2H), 6.93–6.80 (m, 2H), 4.28 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.3, 164.0 (d, $^1J_{C-F}$ = 252.4 Hz), 135.5, 135.4, 134.0, 132.5, 130.0, 128.9, 128.6, 126.7, 126.0, 125.7, 124.1, 116.1 (d, $^2J_{C-F}$ = 22.2 Hz), 115.8 (d, $^3J_{C-F}$ = 3.5 Hz), 92.2, 87.7, 49.9; IR (KBr) ν (cm^{-1}) 3064, 2204, 1760, 1666, 1598, 1505, 1398, 1352, 1328, 1291, 1233, 1186, 1098, 1039, 1015, 951, 910, 838, 792, 778, 732, 711, 690; HRMS (EI) Calcd for $C_{20}H_{13}FO$ 288.0950 $[M]^+$, found 288.0958.

4-(4-Bromophenyl)-1-(naphthalen-1-yl)but-3-yn-2-one (4g). Yellow solid (153.5 mg, 88% yield), mp: 148–150 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.5 Hz, 1H), 7.88–7.79 (m, 2H), 7.54–7.44 (m, 4H), 7.36 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 4.32 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.2, 134.4, 133.9, 132.4, 131.9, 129.8, 128.9, 128.6, 126.6, 126.0, 125.7, 125.6, 124.0, 118.6, 91.8, 88.5, 49.8; IR (KBr) ν (cm^{-1}) 3315, 3061, 2904, 2204, 1762, 1665, 1597, 1584, 1485, 1395, 1279, 1236, 1217, 1186, 1110, 1085, 1011, 951, 825, 781, 650, 608, 557, 530, 510; HRMS (ES) Calcd for $C_{20}H_{13}BrONa$ 371.0047 and 373.0027 $[M + Na]^+$, found 371.0038 and 373.0017.

4-(4-(Naphthalen-1-yl)-3-oxobut-1-yn-1-yl)benzaldehyde (4h). Yellow oil (92.4 mg, 62% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 9.96 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.90–7.83 (m, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.57–7.47 (m, 4H), 7.36 (d, J = 8.1 Hz, 2H), 4.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.2, 185.0, 137.0, 133.9, 133.4, 132.4, 129.5, 129.4, 128.93, 128.91, 128.7, 126.7, 126.1, 125.7, 125.5, 123.9, 90.8, 89.7, 49.9; IR (neat) ν (cm^{-1}) 3060, 2924, 2840, 2735, 2205, 1702, 1668, 1602, 1564, 1511, 1389, 1327, 1303, 1280, 1204, 1167, 1102, 1083, 953, 911, 830, 792, 780, 699; HRMS (EI) Calcd for $C_{21}H_{14}O_2$ 298.0994 $[M]^+$, found 298.1003.

1-(Naphthalen-1-yl)-4-(4-nitrophenyl)but-3-yn-2-one (4i). Yellow solid (104.6 mg, 82% yield), mp: 149–151 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.12 (ddd, J = 8.0, 4.0, 4.0 Hz, 2H), 7.97 (d, J = 8.2 Hz, 1H), 7.92–7.83 (m, 2H), 7.58–7.46 (m, 4H), 7.34 (ddd, J = 8.0, 4.0, 4.0 Hz, 2H), 4.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.7, 148.4, 134.0, 133.6, 132.4, 129.4, 128.9, 128.7, 126.7, 126.3, 126.1, 125.6, 123.84, 123.76, 123.6, 90.4, 89.2, 49.8; IR (KBr) ν (cm^{-1}) 3104, 3062, 2949, 2914, 2210, 1668, 1596, 1521, 1345, 1287, 1187, 1107, 1013, 916, 859, 839, 781, 749, 712, 686; HRMS (ES) Calcd for $C_{20}H_{13}NO_3Na$ 338.0793 $[M + Na]^+$, found 338.0786.

1,4-Diphenylbut-3-yn-2-one (6a)[7b]. Yellow solid (93.6 mg, 85% yield), ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47–7.20 (m, 10H), 3.93 (s, 2H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 185.2, 133.3, 133.1, 130.8, 129.9, 128.7, 128.6, 127.4, 119.9, 92.9, 87.7, 52.2.

4-Phenyl-1-(*p*-tolyl)but-3-yn-2-one (6b)[7b]. Yellow oil (96.1 mg, 82% yield), ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47–7.37 (m, 3H), 7.35–7.28 (m, 2H), 7.21–7.13 (m, 4H), 3.87 (s, 2H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.4, 137.1, 133.1, 130.8, 130.2, 129.8, 129.5, 128.7, 119.9, 92.7, 87.9, 51.9, 21.2.

1-(4-Methoxyphenyl)-4-phenylbut-3-yn-2-one (6c)[14]. Brown oil (95.1 mg, 76% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47–7.31 (m, 5H), 7.22 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 3.85 (s, 2H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.6, 159.0, 133.1, 130.9, 130.8, 128.6, 125.2, 119.9, 114.2, 92.7, 87.8, 55.3, 51.3.

1-(4-Fluorophenyl)-4-phenylbut-3-yn-2-one (6d)[7b]. Yellow solid (103.6 mg, 87% yield), ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47–7.40 (m, 3H), 7.36–7.24 (m, 4H), 7.05 (dd, J = 8.8, 8.8 Hz, 2H), 3.89 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.9, 162.3 (d, $^1J_{C-F}$ = 244.4 Hz), 133.1, 131.5, 131.4, 131.0, 128.7, 119.7, 115.6 (d, $^2J_{C-F}$ = 21.3 Hz), 93.1, 87.6, 76.8, 51.2.

1-(2-Methoxyphenyl)-4-phenylbut-3-yn-2-one (6e). Yellow oil (75.1 mg, 60% yield). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.49–7.40 (m, 3H), 7.37–7.25 (m, 3H), 6.91 (d, J = 7.7 Hz, 1H), 6.87–6.83 (m, 2H), 3.90 (s, 2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.0, 159.9, 134.6, 133.1, 130.8, 129.7, 128.6, 122.3, 119.9, 115.5, 113.0, 92.9, 87.7, 55.2, 52.2; IR (neat) ν (cm^{-1}) 3356, 2934, 2837, 2203, 1666, 1598, 1585, 1489, 1454, 1256, 1107, 1047, 930, 759, 689, 616; HRMS (EI) Calcd for $C_{17}H_{14}O_2$ 250.0994 $[M]^+$, found 250.0991.

1-(2-Bromophenyl)-4-phenylbut-3-yn-2-one (6f). Yellow solid (97.2 mg, 65% yield), mp: 48–50 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.62 (d, J = 7.9 Hz, 1H), 7.45–7.41 (m, 3H), 7.38–7.30 (m, 4H), 7.22–7.15 (m, 1H), 4.10 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.0, 133.9, 133.4, 133.1, 132.2, 131.0, 129.4, 128.7, 127.8, 125.6, 119.9, 93.0, 87.8, 52.2; IR (KBr) ν (cm^{-1}) 3059, 2203, 1668, 1595, 1570, 1489, 1442, 1279, 1129, 1077, 1026, 999, 757,

688, 596, 554; HRMS (EI) Calcd for $C_{16}H_{11}OBr$ 297.9993 and 299.9973 $[M]^+$, found 297.9999 and 299.9965.

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