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Efficient synthesis of enynes by tetraphosphine–palladium-catalysed reaction of vinyl bromides with terminal alkynes

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Abstract—Through the use of $[PdCl(C_3H_5)]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane as catalyst, a range of vinyl bromides undergoes Sonogashira cross-coupling reaction with a variety of alkynes, leading to the corresponding 1,3-enynes in good yields. The reaction tolerates several alkynes such as phenylacetylene, dec-1-yne, 2-methylbut-1-en-3-yne a range of alk-1-ynols, 3,3-diethoxyprop-1-yne and a propargyl amine. Higher reactions rates were observed in the presence of phenylacetylene, dec-1-yne, but-3-yn-1-ol, pent-4-yn-1-ol, 3,3-diethoxyprop-1-yne or 1,1-dipropyl-2-propynylamine than with propargyl alcohol, 3-methoxy-prop-1-yne or 2-methylbut-1-en-3-yne. This catalyst can be used at low loading even for reactions of sterically hindered vinyl bromides such as bromotriphenylethylene or 2-bromo-3-methyl-but-2-ene.

1. Introduction

Enynes are fundamental building blocks in organic synthesis. The palladium-catalysed so-called Sonogashira reaction is one of the most powerful methods for the synthesis of such compounds.[1–4] Cross-coupling palladium-catalysed reactions between aryl halides and alkynes have been largely described.[5–12] On the other hand, if the reactions between terminal acetylene and vinyl halides have been recognized since the mid-seventies,[13–14] their applications usually need harsh reaction conditions and high catalyst loadings. The most widely used catalysts for this reaction are $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$, associated with copper(I) iodide.[15–28] But these catalysts are not very efficient in terms of the ratio substrate/catalyst and 5–10% catalyst had to be used.[15–22] With these catalysts, several reactions conditions have been tested in order to improve the yields. For example, 1-trialkylsilyl-1-alkynes can be coupled directly with vinyl triflates using 1% $Pd(PPh_3)_4$ as catalyst in the presence of Bu_4NF and AgI.[23] Mori et al. have reported the coupling of terminal alkynes with vinyl bromides catalyzed by 1% $Pd(PPh_3)_4$ using Bu_4NF as additive.[24] Polymethylhydrosiloxane in association with $PdCl_2(PPh_3)_2$ can be used to promote the reaction between *E*-β-bromostyrene and 2-methyl-3-butyn-2-ol using 5% catalyst in the presence of CsF at room temperature.[25] Some results were reported in ionic liquids using 5% catalyst.[26] This reaction has also been performed in aqueous media using water soluble sulfonated triphenylphosphine ligand for the coupling of vinyl iodides.[27] A few other ligands have also been tested for this coupling. An *N*-heterocyclic carbene palladium catalyst has shown efficiency comparable to $Pd(PPh_3)_4$.[28] With an imidazolium carbene ligand good results were obtained for the coupling of 1-bromocyclohex-1-ene using 3% of palladium catalyst.[29] Alami et al. obtained high yields of adducts using 5% of $PdCl_2(PhCN)_2$ catalyst without added ligand at room temperature for the coupling reaction between vinyl chloride and alkynes.[30] The reaction between vinyl iodides and terminal alkynes can also be performed in aqueous media using potassium fluoride, palladium submicron powder, cuprous iodide and PPh_3.[31] Despite these recent advances, there still remained a need for a general protocol using low-catalyst loading for Sonogashira reactions in the presence of vinyl halides. Moreover, the efficiency of tetraphosphine ligands for the cross-coupling of vinyl halides with alkynes has not been reported.

2. Results and discussion

In order to find stable and efficient palladium catalysts, we have prepared the tetrapodal phosphine ligand, *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl) cyclopentane or Tedicyp (Fig. 1).[32] We have already reported the results

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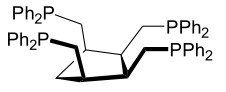


Tedicyp

Figure 1.

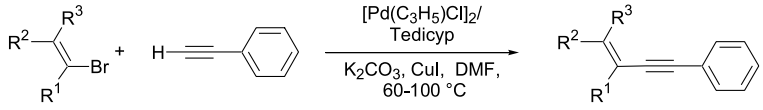
obtained in allylic substitution,[32] in Heck reaction,[33] in Suzuki cross-coupling[34] and in Sonogashira reaction[35–40] using Tedicyp as ligand. For example, we obtained a turnover number (TON) of 2,800,000 for the coupling of 3,5-bis(trifluoromethyl)bromobenzene with phenylacetylene.[35] We have also recently reported the Sonogashira coupling of sterically congested aryl bromides,[36] of heteroaryl halides,[37] of a range of aryl chlorides with as little as 0.01% catalyst without addition of co-catalysts,[38] and also the reactivity of several alkynols[39] or propargyl amines.[40] Here, we wish to report on the efficiency of Tedicyp ligand for the reaction of vinyl bromides with terminal alkynes such as phenylacetylene, dec-1-yne, 2-methylbut-1-en-3-yne, a range of alk-1-ynols, 3,3-diethoxyprop-1-yne and a propargyl amine.

For this study, based on our previous results,[35–40] DMF was chosen as the solvent and potassium carbonate as the base. The reactions were performed at 60–100 °C under argon in the presence of a ratio 1:2 of $[Pd(C_3H_5)Cl]_2$/Tedicyp as catalyst and 5% copper(I) iodide as co-catalyst. At higher temperatures (120–140 °C), lower yields were obtained due to partial polymerization of the substrates and products. The dimerisation of the alkynes was also detected in some cases. In order to obtain high conversions of the aryl bromides we have used 2 equiv of alkyne for all the reactions, however, most of the reactions should proceed with 1.2–1.5 equiv of alkyne. Some decomposition of the products was observed for long time reactions, so the reactions were stopped at 20 h.

First, we tried to couple phenylacetylene with a range of vinyl bromides (Scheme 1, Table 1). As expected, the reaction of β-bromostyrene with phenylacetylene proceeds nicely. The reaction can be performed with as little as 0.0001% catalyst (TON: 520,000) (Table 1, entry 3). The same reaction performed with dppe as ligand (Table 1, entry 2), led to the coupling adduct **1** in 12% yield in the presence of 0.001% catalyst (TON: 12,000). With a mixture of *Z* and *E* 1-bromoprop-1-ene (ratio *Z*/*E*: 45/55) a good yield was also obtained for a ratio S/C of 10,000 (Table 1, entries 4 and 5). A selectivity of 95% in favour of *E* isomer was obtained using 0.01% catalyst (Table 1, entry 5). This high selectivity in *E* isomer probably comes partially from the higher reactivity of (*E*)-1-bromoprop-1-ene[41] and also from partial isomerisation of (*Z*)-1-bromoprop-1-ene into (*E*)-1-bromoprop-1-ene under basic conditions.[42]

Then, we studied the reactivity of three α-substituted vinyl bromides. 2-Bromoprop-1-ene, 2-bromobut-1-ene and 3-bromobut-3-en-1-ol led to the coupling 1,3-enynes **3–5** in good yields using 0.01% catalyst (Table 1, entries 6–9). The highest TON was obtained with 2-bromobut-1-ene, with a yield of 48% for a ratio substrate/catalyst of 50,000 (Table 1, entry 8). The synthesis of tetrasubstituted alkenes was also possible by Sonogashira cross-coupling reactions with this catalyst. Sterically hindered substrates bromotriphenylethylene or 2-bromo-3-methylbut-2-ene reacts cleanly with phenylacetylene. For the reactions with these substrates TONs of 3300 and 6000 were obtained, respectively, (Table 1, entries 10–12).

Having demonstrated that a variety of vinyl bromides can be efficiently cross-coupled with phenylacetylene, we have investigated the scope of this reaction using dec-1-yne and 2-methylbut-1-en-3-yne (Scheme 2, Table 2), and also with



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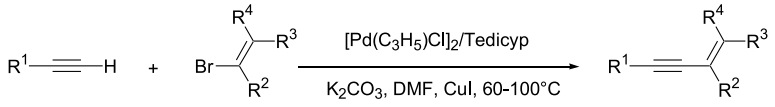
Scheme 1.

Table 1. Cross-coupling reactions of vinyl bromides with phenylacetylene (Scheme 1)

Entry	Vinyl bromide	Ratio substrate/catalyst	Temperature (°C)	Product number	Ratio *Z* (**a**)/*E* (**b**)	Yield (%)[a]
1	β-Bromostyrene[b]	100,000	100	**1a**,**b**	10/90	100[c]
2	β-Bromostyrene[b]	100,000	100	**1a**,**b**	10/90	12[c,d]
3	β-Bromostyrene[b]	1000,000	100	**1a**,**b**	10/90	52
4	1-Bromoprop-1-ene[e]	1000	60	**2a**,**b**	05/95	100[c]
5	1-Bromoprop-1-ene[e]	10,000	60	**2a**,**b**	05/95	85
6	2-Bromoprop-1-ene	10,000	60	**3**	—	75
7	2-Bromobut-1-ene	10,000	80	**4**	—	100[c]
8	2-Bromobut-1-ene	50,000	80	**4**	—	48
9	3-Bromobut-3-en-1-ol	10,000	80	**5**	—	85
10	2-Bromo-3-methyl-but-2-ene	10,000	80	**6**	—	60
11	Bromotriphenylethylene	1000	100	**7**	—	86
12	Bromotriphenylethylene	10,000	100	**7**	—	33[c]

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/Tedicyp = 1:2, vinyl bromide (1 equiv), phenylacetylene (2 equiv), K_2CO_3 (2 equiv), CuI (0.05 equiv), DMF, 20 h, isolated yields.
[b] β-Bromostyrene was a mixture of *Z* and *E* isomers, ratio *Z*/*E*: 10/90.
[c] GC and NMR yield.
[d] Reaction performed with dppe (ratio Pd/dppe: 1:2).
[e] 1-Bromoprop-1-ene was a mixture of *Z* and *E* isomers, ratio *Z*/*E*: 45/55.



Scheme 2.

Table 2. Cross-coupling reactions of vinyl bromides with dec-1-yne and 2-methylbut-1-en-3-yne (Scheme 2)

Entry	Vinyl bromide	Alkyne	Ratio substrate/catalyst	Temperature (°C)	Product number	Ratio *Z* (**a**)/*E* (**b**)	Yield (%)[a]
1	β-Bromostyrene[b]	Dec-1-yne	10,000	100	**8a**,**b**	10/90	90
2	Bromotriphenylethylene	Dec-1-yne	100	100	**9**	—	97
3	2-Bromobut-1-ene	Dec-1-yne	1000	80	**10**	—	99
4	2-Bromo-3-methylbut-2-ene	Dec-1-yne	100	80	**11**	—	89
5	2-Bromo-3-methylbut-2-ene	Dec-1-yne	1000	80	**11**	—	31[c]
6	1-Bromoprop-1-ene[d]	Dec-1-yne	100	60	**12a**,**b**	13/87	100[c]
7	1-Bromoprop-1-ene[d]	Dec-1-yne	1000	60	**12a**,**b**	05/95	65
8	2-Bromoprop-1-ene	Dec-1-yne	100	60	**13**	—	100[c]
9	2-Bromoprop-1-ene	Dec-1-yne	1000	60	**13**	—	51
10	β-Bromostyrene	2-Methylbut-1-en-3-yne	100	80	**14a**,**b**	10/90	59[e]
11	Bromotriphenylethylene	2-Methylbut-1-en-3-yne	50	80	**15**	—	60[e]

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/Tedicyp = 1:2, vinyl bromide (1 equiv), alkyne (2 equiv), K_2CO_3 (2 equiv), CuI (0.05 equiv), DMF, 20 h.
[b] β-Bromostyrene was a mixture of *Z* and *E* isomers, ratio *Z*/*E*: 10/90.
[c] GC and NMR yield.
[d] 1-Bromoprop-1-ene was a mixture of *Z* and *E* isomers, ratio *Z*/*E*: 45/55.
[e] Reaction performed in autoclave.

several functionalized alkynes: propargyl alcohol, 3-methoxyprop-1-yne, but-1-yn-3-ol, but-3-yn-1-ol, pent-4-yn-1-ol, 3,3-diethoxyprop-1-yne and 1,1-dipropyl-2-propynylamine (Scheme 2, Table 3).

2-Bromobut-1-ene, 1-bromoprop-1-ene and 2-bromoprop-1-ene were efficiently cross-coupled with dec-1-yne using 0.1% catalyst (Table 2, entries 3, 7, 9). The best result with dec-1-yne was obtained using β-bromostyrene (TON of 9000) (Table 2, entry 1). Sterically congested substrates, bromotriphenylethylene (entry 2), and 2-bromo-3-methylbut-2-ene (Table 2, entry 4) led to the corresponding enynes **9** and **11** in good yields but 1% catalyst were used. The reactions performed with the enyne: 2-methylbut-1-en-3-yne were much slower. This might be due to the coordination of the olefinic bond to palladium. With β-bromostyrene and bromotriphenylethylene the reactions had to be performed using 1–2% catalyst in order to obtain satisfactory yields of adducts **14** and **15** (Table 2, entries 10 and 11).

Next, we studied the reactivity of functionalized alkynes (Table 3). Several reactions were performed using a range of alkyn-1-ol derivatives. With alkynols, relatively low TONs were observed in comparison to those obtained with phenylacetylene or dec-1-yne. In the presence of the most reactive vinyl bromide: β-bromostyrene, the coupling reaction with propargyl alcohol was successful using 0.1% catalyst (Table 3, entry 2). With bromotriphenylethylene 1% catalyst had to be used to obtain product **17** in 74% yield (Table 3, entry 3). A similar reactivity was obtained using the protected propargyl alcohol: 3-methoxyprop-1-yne (Table 3, entries 6–8). Using but-1-yn-3-ol and but-3-yn-1-ol, the reaction with β-bromostyrene or 2-bromobut-1-ene, gave the desired products **22**–**24** and **26** using 0.1–0.01% catalyst (Table 3, entries 9–13 and 16). Slower reactions were observed with bromotriphenylethylene, 3-bromobut-3-en-1-ol and 2-bromo-3-methyl-but-2-ene (Table 3, entries 14, 15, 17 and 18).

We also performed a few reactions with pent-4-yn-1-ol (Table 3, entries 19–26). Better yields were obtained using the same amount of catalyst than with but-3-yn-1-ol. β-Bromostyrene, 1-bromoprop-1-ene and 2-bromoprop-1-ene reacts in satisfactory yields with a ratio substrate/catalyst of 10,000 (Table 3, entries 20, 24 and 26). We had already observed with aryl bromides a similar trend for the reactivity of alkynols: pent-4-yn-1-ol > but-3-yn-1-ol > propargyl alcohol.[39] (*E*)-3-Methylpent-2-en-4-yn-1-ol reacts cleanly with β-bromostyrene or 2-bromobut-1-ene to give the corresponding dienyne derivatives **33** and **34** (Table 3, entries 27 and 28). The Tedicyp–palladium system also provides an efficient catalyst for the coupling of vinyl bromides with propiolaldehyde diethyl acetal (Table 3, entries 29–35). With this alkyne, a very high TON of 72,000 was obtained for the coupling with β-bromostyrene. Finally, we were pleased to observe that 1,1-dipropyl-2-propynylamine with one of the less reactive vinyl bromide: 2-bromo-3-methylbut-2-ene gave **39** with a high TON of 6300 (Table 3, entries 36–37).

In conclusion, in the presence of the Tedicyp–palladium catalyst, Sonogashira reactions of several vinyl bromides, including sterically demanding ones, with a wide variety of

Table 3. Cross-coupling reactions of vinyl bromides with alkynols, 3,3-diethoxyprop-1-yne and a propargylamine (Scheme 2)

Entry	Vinyl bromide	Alkyne	Ratio substrate/catalyst	Temperature (°C)	Ratio *Z* (**a**)/*E* (**b**)	Product number	Yield (%)[a]
1	β-Bromostyrene[b]	Propargyl alcohol	100	100	10/90	**16a**,**b**	80
2	β-Bromostyrene[b]	Propargyl alcohol	1000	100	10/90	**16a**,**b**	40[c]
3	Bromotriphenylethylene	Propargyl alcohol	100	100	—	**17**	74
4	2-Bromobut-1-ene	Propargyl alcohol	100	80	—	**18**	96
5	2-Bromo-3-methylbut-2-ene	Propargyl alcohol	50	80	—	**19**	98
6	β-Bromostyrene[b]	3-Methoxyprop-1-yne	100	100	10/90	**20a**,**b**	100[c]
7	β-Bromostyrene[b]	3-Methoxyprop-1-yne	1000	100	10/90	**20a**,**b**	75
8	Bromotriphenylethylene	3-Methoxyprop-1-yne	100	100	—	**21**	74
9	β-Bromostyrene[b]	But-1-yn-3-ol	1000	100	10/90	**22a**,**b**	98
10	2-Bromobut-1-ene	But-1-yn-3-ol	100	80	—	**23**	100[c]
11	2-Bromobut-1-ene	But-1-yn-3-ol	1000	80	—	**23**	56
12	β-Bromostyrene[b]	But-3-yn-1-ol	1000	100	10/90	**24a**,**b**	97
13	β-Bromostyrene[b]	But-3-yn-1-ol	10,000	100	10/90	**24a**,**b**	29[c]
14	Bromotriphenylethylene	But-3-yn-1-ol	100	100	—	**25**	78
15	Bromotriphenylethylene	But-3-yn-1-ol	1000	100	—	**25**	20[c]
16	2-Bromobut-1-ene	But-3-yn-1-ol	1000	80	—	**26**	83
17	3-Bromobut-3-en-1-ol	But-3-yn-1-ol	100	80	—	**27**	96
18	2-Bromo-3-methylbut-2-ene	But-3-yn-1-ol	100	80	—	**28**	85
19	β-Bromostyrene[b]	Pent-4-yn-1-ol	1000	100	10/90	**29a**,**b**	95
20	β-Bromostyrene[b]	Pent-4-yn-1-ol	10,000	100	10/90	**29a**,**b**	62[c]
21	Bromotriphenylethylene	Pent-4-yn-1-ol	100	100	—	**30**	98
22	Bromotriphenylethylene	Pent-4-yn-1-ol	1000	100	—	**30**	25[c]
23	1-Bromoprop-1-ene[d]	Pent-4-yn-1-ol	1000	60	40/60	**31a**,**b**	98
24	1-Bromoprop-1-ene[d]	Pent-4-yn-1-ol	10,000	60	04/96	**31a**,**b**	37[c]
25	2-Bromoprop-1-ene	Pent-4-yn-1-ol	1000	60	—	**32**	90
26	2-Bromoprop-1-ene	Pent-4-yn-1-ol	10,000	60	—	**32**	28[c]
27	β-Bromostyrene[b]	(*E*)-3-Methylpent-2-en-4-yn-1-ol	500	100	10/90	**33a**,**b**	88
28	2-Bromobut-1-ene	(*E*)-3-Methylpent-2-en-4-yn-1-ol	100	80	—	**34**	80
29	β-Bromostyrene[b]	3,3-Diethoxyprop-1-yne	100,000	100	10/90	**35a**,**b**	72
30	Bromotriphenylethylene	3,3-Diethoxyprop-1-yne	100	100	—	**36**	95
31	Bromotriphenylethylene	3,3-Diethoxyprop-1-yne	1000	100	—	**36**	22[c]
32	2-Bromobut-1-ene	3,3-Diethoxyprop-1-yne	100	80	—	**37**	100[c]
33	2-Bromobut-1-ene	3,3-Diethoxyprop-1-yne	1000	80	—	**37**	70
34	2-Bromoprop-1-ene	3,3-Diethoxyprop-1-yne	100	60	—	**38**	100[c]
35	2-Bromoprop-1-ene	3,3-Diethoxyprop-1-yne	1000	60	—	**38**	68
36	2-Bromo-3-methylbut-2-ene	1,1-Dipropyl-2-propynylamine	1000	80	—	**39**	100[c]
37	2-Bromo-3-methylbut-2-ene	1,1-Dipropyl-2-propynylamine	10,000	80	—	**39**	63

[a] Conditions: catalyst: $[ClPd(C_3H_5)]_2$/Tedicyp=1:2, vinyl bromide (1 equiv), alkyne (2 equiv), K_2CO_3 (2 equiv), CuI (0.05 equiv), DMF, 20 h.
[b] β-Bromostyrene was a mixture of *Z* and *E* isomers, ratio *Z*/*E*: 10/90.
[c] GC and NMR yield.
[d] 1-Bromoprop-1-ene was a mixture of *Z* and *E* isomers, ratio *Z*/*E*: 45/55.

terminal alkynes can be performed with as little as 0.1–0.0001% with the most reactive vinyl bromides and several alkynes. The highest TONs were obtained with phenylacetylene, dec-1-yne, but-3-yn-1-ol, pent-4-yn-1-ol, 3,3-diethoxyprop-1-yne or 1,1-dipropyl-2-propynylamine. The reactions performed with propargyl alcohol, 3-methoxyprop-1-yne or 2-methylbut-1-en-3-yne required larger amounts of catalyst. The most reactive vinyl bromide was β-bromostyrene, but α-substituted vinyl bromides such as 1-bromoprop-1-ene or 2-bromobut-1-ene also gave the coupling adducts in high TONs. Furthermore, this catalyst can be used at low loading even for the reactions of sterically hindered vinyl bromides such as bromotriphenylethylene or 2-bromo-3-methylbut-2-ene. We believe that this system compares favourably with other catalysts that have been reported for this process.

3. Experimental

General remarks. All reactions were run under argon in Schlenk tubes using vacuum lines. DMF analytical grade was not distilled before use. Commercial potassium carbonate (99+), CuI (98%), vinyl bromides and terminal alkynes were used without purification. The reactions were followed by GC and NMR for high boiling point substrates and by GC for low boiling point substrates. ^1H and ^{13}C spectrum were recorded with a Bruker 300 MHz spectrometer in $CDCl_3$ solutions. GC/MS were recorded with a Varian Saturn 2100T spectrometer. Chemical shift are reported in ppm relative to $CDCl_3$ (7.25 for ^1H NMR and 77.0 for ^{13}C NMR). Flash chromatographies were performed on silica gel (230–400 mesh). GC and NMR yields in the tables are conversions of the vinyl halides into the product calculated with GC and ^1H NMR spectrum of the crude mixtures.

3.1. Preparation of the Pd–Tedicyp catalyst

An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (30 mg, 81 mmol) and Tedicyp (140 mg, 162 mmol). Ten millilitre of anhydrous DMF were added, then the solution was stirred at room temperature for 10 min. The appropriate catalyst concentration was obtained by successive dilutions. ^{31}P NMR (162 MHz, $CDCl_3$) δ 25 (w=80 Hz), 19.4 (w=110 Hz).

3.2. General procedure

In a typical experiment, the vinyl halide (1 mmol), terminal alkynes (2 mmol), CuI (0.05 mmol, 0.01 g) and K_2CO_3 (0.276 g, 2 mmol) were dissolved in DMF (3 mL) under an argon atmosphere. The prepared Pd–Tedicyp catalyst complex (see tables) was then transferred to the reaction flask via cannula. The reaction mixture was stirred at the appropriate temperature for 20 h. Then, the solution was diluted with H_2O (2 mL), and the product was extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The product was purified by silica gel column chromatography.

3.2.1. (*Z*)-1,4-Diphenylbut-1-en-3-yne (1a) and (*E*)-1,4-diphenylbut-1-en-3-yne (1b). From β-bromostyrene (0.128 mL, 1 mmol) and phenylacetylene (0.220 mL, 2 mmol), products **1a/1b** (10/90) were obtained in 52% (0.106 g) yield. *Compound* **1a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.43 (m, 2H), 7.35–7.32 (m, 2H), 7.28–7.20 (m, 6H), 6.62 (d, J=12.0 Hz, 1H), 5.87 (d, J=12.0 Hz, 1H). *Compound* **1b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.43 (m, 2H), 7.35–7.32 (m, 2H), 7.28–7.20 (m, 6H), 7.03 (d, J=16.2 Hz, 1H), 6.36 (d, J=16.2 Hz, 1H).

3.2.2. (*Z*)-1-Phenylpent-3-en-1-yne (2a) and (*E*)-1-phenylpent-3-en-1-yne (2b). From 1-bromoprop-1-ene (0.085 mL, 1 mmol) and phenylacetylene (0.220 mL, 2 mmol), products **2a/2b** (05/95) were obtained in 85% (0.121 g) yield. *Compound* **2a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.36–7.30 (m, 3H), 6.05 (dq, J=10.6, 6.8 Hz, 1H), 5.71 (dq, J=10.6, 1.7 Hz, 1H), 1.98 (dd, J=6.8, 1.7 Hz, 3H). *Compound* **2b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.33–7.28 (m, 3H), 6.25 (dq, J=15.8, 6.8 Hz, 1H), 5.71 (dq, J=15.8, 1.7 Hz, 1H), 1.84 (dd, J=6.8, 1.7 Hz, 3H).

3.2.3. 3-Methyl-1-phenylbut-3-en-1-yne (3). From 2-bromoprop-1-ene (0.088 mL, 1 mmol) and phenylacetylene (0.220 mL, 2 mmol), product **3** was obtained in 75% (0.107 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.33–7.28 (m, 3H), 5.43 (s, 1H), 5.33 (s, 1H), 2.02 (s, 3H).

3.2.4. 2-Ethyl-4-phenylbut-1-en-3-yne (4). From 2-bromobut-1-ene (0.102 mL, 1 mmol) and phenylacetylene (0.220 mL, 2 mmol), product **4** was obtained in 48% (0.075 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.34–7.28 (m, 3H), 5.38 (s, 1H), 5.28 (s, 1H), 2.27 (q, J=7.1 Hz, 2H), 1.15 (t, J=7.1 Hz, 3H).

3.2.5. 3-Methylene-5-phenylpent-4-yn-1-ol (5). From 3-bromobut-3-en-1-ol (0.099 mL, 1 mmol) and phenylacetylene (0.220 mL, 2 mmol), product **5** was obtained in 85% (0.146 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.40 (m, 2H), 7.32–7.28 (m, 3H), 5.44 (s, 1H), 5.33 (s, 1H), 3.85 (t, J=6.2 Hz, 2H), 2.44 (t, J=6.2 Hz, 2H).

3.2.6. 2,3-Dimethyl-5-phenylpent-2-en-4-yne (6). From 2-bromo-3-methylbut-2-ene (0.151 mL, 1 mmol) and phenylacetylene (0.220 mL, 2 mmol), product **6** was obtained in 60% (0.102 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.40 (m, 2H), 7.34–7.28 (m, 3H), 2.00 (s, 3H), 1.87 (s, 3H), 1.77 (s, 3H).

3.2.7. 1,1,2,4-Tetraphenylbut-1-en-3-yne (7). From bromotriphenylethylene (0.335 g, 1 mmol) and phenylacetylene (0.220 mL, 2 mmol), product **7** was obtained in 86% (0.307 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67–7.65 (m, 2H), 7.45–7.40 (m, 6H), 7.31–7.16 (m, 10H), 7.13–7.11 (m, 2H).

3.2.8. (*Z*)-1-Phenyldodec-1-en-3-yne (8a) and (*E*)-1-phenyldodec-1-en-3-yne (8b). From β-bromostyrene (0.128 mL, 1 mmol) and dec-1-yne (0.361 mL, 2 mmol), products **8a/8b** (10/90) were obtained in 90% (0.216 g) yield. *Compound* **8a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.30 (m, 5H), 6.61 (d, J=12.1 Hz, 1H), 5.88 (d, J=12.1 Hz, 1H), 2.40 (t, J=6.9 Hz, 2H), 1.64–1.55 (m, 2H), 1.46–1.32 (m, 10H), 0.90–0.87 (m, 3H). *Compound* **8b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.30 (m, 5H), 6.90 (d, J=16.2 Hz, 1H), 6.18 (d, J=16.2 Hz, 1H), 2.40 (t, J=6.9 Hz, 2H), 1.64–1.55 (m, 2H), 1.46–1.32 (m, 10H), 0.90–0.87 (m, 3H).

3.2.9. 1,1,2-Triphenyldodec-1-en-3-yne (9). From bromotriphenylethylene (0.335 g, 1 mmol) and dec-1-yne (0.361 mL, 2 mmol), product **9** was obtained in 97% (0.381 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.26–7.20 (m, 5H), 7.10–7.00 (m, 6H), 6.91 (m, 2H), 2.19 (t, J=6.8 Hz, 2H), 1.38–1.19 (m, 12H), 0.87–0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 142.8, 141.4, 139.6, 130.6, 130.0, 128.4, 127.9, 127.8, 127.7, 127.3, 127.1, 126.8, 121.5, 91.1, 78.9, 32.5, 30.1, 29.4, 29.2, 29.2, 23.1, 18.2, 14.0; MS (70 eV); *m/z* (%) 392 ($M^{+\cdot}$, 100); $C_{30}H_{32}$: calcd C 91.78, H 8.22. Found C 91.89, H 8.31.

3.2.10. 2-Ethyldodec-1-en-3-yne (10). From 2-bromobut-1-ene (0.102 mL, 1 mmol) and dec-1-yne (0.361 mL, 2 mmol), product **10** was obtained in 99% (0.190 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19 (s, 1H), 5.13 (s, 1H), 2.30 (t, J=6.8 Hz, 2H), 2.16 (q, J=7.1 Hz, 2H), 1.55–1.50 (m, 2H), 1.42–1.39 (m, 2H), 1.30 (br s, 8H), 1.08 (t, J=7.1 Hz, 3H), 0.88 (t, J=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.8, 118.3, 90.2, 80.9, 31.8, 30.7, 29.2, 29.1, 28.8, 28.8, 22.6, 19.7, 14.1, 12.8; MS (70 eV); *m/z* (%) 192 ($M^{+\cdot}$, 1), 79 (100); $C_{14}H_{24}$: calcd C 87.42, H 12.58. Found C 87.28, H 12.34.

3.2.11. 2,3-Dimethyltridec-2-en-4-yne (11). From 2-bromo-3-methyl-but-2-ene (0.151 mL, 1 mmol) and dec-1-yne (0.361 mL, 2 mmol), product **11** was obtained in 89% (0.183 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (t, J=6.8 Hz, 2H), 1.90 (s, 3H), 1.77 (s, 3H), 1.70 (s, 3H), 1.55–1.50 (m, 2H), 1.42–1.39 (m, 2H), 1.26 (br s, 8H), 0.87 (t, J=6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 111.9, 91.3, 82.3, 31.8, 29.2, 29.1, 29.1, 28.9, 23.3, 22.6, 19.7, 19.5, 18.9, 14.1; MS (70 eV); *m/z* (%) 206 ($M^{+\cdot}$, 100), 107 (100); $C_{15}H_{26}$: calcd C 87.30, H 12.70. Found C 87.20, H 12.67.

3.2.12. (*Z*)-Tridecen-4-yne (12a) and (*E*)-tridecen-4-yne (12b). From 1-bromoprop-1-ene (0.085 mL, 1 mmol) and dec-1-yne (0.361 mL, 2 mmol), products **12a/12b** (05/95)

were obtained in 65% (0.116 g) yield. *Compound* **12a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (dq, J=10.4, 6.6 Hz, 1H), 5.35 (dq, J=10.4, 1.7 Hz, 1H), 2.25 (t, J=6.7 Hz, 2H), 1.87 (dd, J=6.6, 1.7 Hz, 3H), 1.55–1.50 (m, 2H), 1.42–1.39 (m, 2H), 1.30 (br s, 8H), 0.88 (t, J=6.8 Hz, 3H). *Compound* **12b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (dq, J=15.7, 6.8 Hz, 1H), 5.45 (dq, J=15.7, 1.7 Hz, 1H), 2.25 (t, J=6.7 Hz, 2H), 1.73 (dd, J=6.8, 1.7 Hz, 3H), 1.55–1.50 (m, 2H), 1.42–1.39 (m, 2H), 1.30 (br s, 8H), 0.88 (t, J=6.8 Hz, 3H).

3.2.13. 2-Methyldodec-1-en-3-yne (13). From 2-bromoprop-1-ene (0.088 mL, 1 mmol) and dec-1-yne (0.361 mL, 2 mmol), product **13** was obtained in 51% (0.091 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18 (s, 1H), 5.11 (s, 1H), 2.28 (t, J=6.8 Hz, 2H), 1.86 (s, 3H), 1.54–1.47 (m, 2H), 1.40–1.27 (m, 10H), 0.88 (t, J=6.6 Hz, 3H).

3.2.14. (*Z*)-5-Methyl-1-phenyl-1,5-hexadien-3-yne (14a) and (*E*)-5-methyl-1-phenyl-1,5-hexadien-3-yne (14b). From β-bromostyrene (0.128 mL, 1 mmol) and 2-methylbut-1-en-3-yne (0.190 mL, 2 mmol), products **14a/14b** (10/90) were obtained in 59% (0.099 g) yield. *Compound* **14a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.28 (m, 5H), 6.68 (d, J=12.1 Hz, 1H), 5.86 (d, J=12.1 Hz, 1H), 5.40 (s, 1H), 5.34 (s, 1H), 2.03 (s, 3H). **14b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.28 (m, 5H), 6.99 (d, J=16.2 Hz, 1H), 6.33 (d, J=16.2 Hz, 1H), 5.40 (s, 1H), 5.31 (s, 1H), 2.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 136.3, 128.7, 128.5, 128.1, 126.2, 121.8, 108.1, 92.9, 87.9, 23.4; $C_{13}H_{12}$: calcd C 92.81, H 7.19. Found C 92.68, H 7.30.

3.2.15. 5-Methyl-1,1,2-triphenylhexa-1,5-dien-3-yne (15). From bromotriphenylethylene (0.335 g, 1 mmol) and 2-methylbut-1-en-3-yne (0.190 mL, 2 mmol), product **15** was obtained in 60% (0.192 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.26–7.20 (m, 5H), 7.10–7.00 (m, 6H), 6.91 (m, 2H), 5.19 (s, 1H), 5.17 (s, 1H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 142.8, 141.4, 139.6, 130.6, 131.7, 130.0, 128.4, 128.0, 127.8, 127.7, 127.3, 127.1, 126.8, 121.8, 121.5, 91.2, 90.9, 22.1; MS (70 eV); *m*/*z* (%): 320 ($M^{+\cdot}$, 100); $C_{25}H_{20}$: calcd C 93.71, H 6.29. Found C 93.54, H 6.38.

3.2.16. (*Z*)-5-Phenylpent-4-en-2-yn-1-ol (16a) and (*E*)-5-phenylpent-4-en-2-yn-1-ol (16b). From β-bromostyrene (0.128 mL, 1 mmol) and propargyl alcohol (0.116 mL, 2 mmol), products **16a/16b** (10/90) were obtained in 80% (0.126 g) yield. *Compound* **16a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H), 6.60 (d, J=12.1 Hz, 1H), 5.86 (d, J=12.1 Hz, 1H), 4.44 (s, 2H), 2.25 (s, 1H). *Compound* **16b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H), 6.96 (d, J=16.5 Hz, 1H), 6.17 (d, J=16.5 Hz, 1H), 4.44 (s, 2H), 2.25 (s, 1H).

3.2.17. 1,1,2-Triphenylpent-1-en-3-yn-5-ol (17). From bromotriphenylethylene (0.335 g, 1 mmol) and propargyl alcohol (0.116 mL, 2 mmol), product **17** was obtained in 74% (0.230 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.34–7.30 (m, 5H), 7.16–7.10 (m, 6H), 7.01–6.99 (m, 2H), 4.45 (s, 2H), 2.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 142.9, 141.3, 139.6, 130.5, 130.1, 128.4, 128.0, 127.8, 127.7, 127.3, 127.1, 126.8, 121.5, 91.1, 84.7, 51.0; MS (70 eV); *m*/*z* (%) 310 ($M^{+\cdot}$, 100); $C_{23}H_{18}O$: calcd C 89.00, H 5.85. Found C 88.90, H 5.62.

3.2.18. 4-Ethylpent-4-en-2-yn-1-ol (18). From 2-bromobut-1-ene (0.102 mL, 1 mmol) and propargyl alcohol (0.116 mL, 2 mmol), product **18** was obtained in 96% (0.106 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28 (s, 1H), 5.21 (s, 1H), 4.36 (s, 2H), 2.14 (q, J=7.5 Hz, 2H), 1.06 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.6, 120.3, 87.0, 85.6, 51.3, 30.1, 12.7; $C_7H_{10}O$: calcd C 76.33, H 9.15. Found C 76.52, H 9.27.

3.2.19. 4,5-Dimethylhex-4-en-2-yn-1-ol (19). From 2-bromo-3-methylbut-2-ene (0.151 mL, 1 mmol) and propargyl alcohol (0.116 mL, 2 mmol), product **19** was obtained in 98% (0.122 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) 4.42 (s, 2H), 1.92 (s, 3H), 1.79 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 111.0, 88.3, 87.6, 51.8, 23.5, 19.9, 18.5.

3.2.20. (*Z*)-1-Methoxy-5-phenylpent-4-en-2-yne (20a) and (*E*)-1-methoxy-5-phenylpent-4-en-2-yne (20b). From β-bromostyrene (0.128 mL, 1 mmol) and 3-methoxyprop-1-yne (0.169 mL, 2 mmol), products **20a/20b** (10/90) were obtained in 75% (0.129 g) yield. *Compound* **20a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H), 6.60 (d, J=12.1 Hz, 1H), 5.86 (d, J=12.1 Hz, 1H), 4.00 (s, 2H), 3.10 (s, 3H). *Compound* **20b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H), 6.96 (d, J=16.5 Hz, 1H), 6.17 (d, J=16.5 Hz, 1H), 4.00 (s, 2H), 3.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 136.1, 128.8, 128.3, 126.2, 111.3, 91.1, 84.7, 61.0, 52.8; MS (70 eV); *m*/*z* (%): 172 ($M^{+\cdot}$, 65), 128 (100); $C_{12}H_{12}O$: calcd C 83.69, H 7.02. Found C 83.91, H 7.14.

3.2.21. 5-Methoxy-1,1,2-triphenylpent-1-en-3-yne (21). From bromotriphenylethylene (0.335 g, 1 mmol) and 3-methoxyprop-1-yne (0.169 mL, 2 mmol), product **21** was obtained in 74% (0.240 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.34–7.30 (m, 5H), 7.16–7.10 (m, 6H), 7.01–6.99 (m, 2H), 4.15 (s, 2H), 3.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 142.8, 141.4, 139.6, 130.6, 130.0, 128.4, 128.0, 127.8, 127.7, 127.3, 127.1, 126.8, 121.5, 91.1, 85.6, 60.3, 52.8; MS (70 eV); *m*/*z* (%): 324 ($M^{+\cdot}$, 100); $C_{24}H_{20}O$: calcd C 88.85, H 6.21. Found C 88.72, H 6.10.

3.2.22. (*Z*)-1-Phenylhex-1-en-3-yn-5-ol (22a) and (*E*)-1-phenylhex-1-en-3-yn-5-ol (22b). From β-bromostyrene (0.128 mL, 1 mmol) and but-1-yn-3-ol (0.157 mL, 2 mmol), products **22a/22b** (10/90) were obtained in 98% (0.168 g) yield. *Compound* **22a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.29 (m, 5H), 6.69 (d, J=12.1 Hz, 1H), 5.72 (d, J=12.1 Hz, 1H), 4.70 (q, J=6.4 Hz, 1H), 2.06 (s, 1H), 1.50 (d, J=6.4 Hz, 3H). *Compound* **22b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.29 (m, 5H), 6.94 (d, J=16.1 Hz, 1H), 6.15 (d, J=16.1 Hz, 1H), 4.70 (q, J=6.4 Hz, 1H), 2.06 (s, 1H), 1.50 (d, J=6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 136.1, 128.7, 128.6, 126.2, 107.4, 93.1, 83.2, 58.9, 24.3; $C_{12}H_{12}O$: calcd C 83.69, H 7.02. Found C 83.87, H 7.18.

3.2.23. 2-Ethylhex-1-en-3-yn-5-ol (23). From 2-bromobut-1-ene (0.102 mL, 1 mmol) and but-1-yn-3-ol (0.157 mL, 2 mmol), product **23** was obtained in 56% (0.069 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28 (s, 1H), 5.22 (s, 1H), 4.65 (q, J=6.4 Hz, 1H), 2.14 (q, J=7.5 Hz, 2H), 1.88 (s, 1H), 1.47 (d, J=6.4 Hz, 3H), 1.07 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.6, 120.2, 90.7, 84.4, 58.8, 30.2, 24.4, 12.7; $C_8H_{12}O$: calcd C 77.38, H 9.74. Found C 77.54, H 9.57.

3.2.24. (*Z*)-1-Phenylhex-1-en-3-yn-5-ol (24a) and (*E*)-1-phenylhex-1-en-3-yn-5-ol (24b). From β-bromostyrene (0.128 mL, 1 mmol) and but-3-yn-1-ol (0.151 mL, 2 mmol), products **24a/24b** (10/90) were obtained in 97% (0.167 g) yield. *Compound* **24a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.24 (m, 5H), 6.62 (d, J=12.0 Hz, 1H), 5.87 (d, J=12.0 Hz, 1H), 3.76 (t, J=6.3 Hz, 2H), 2.64 (t, J=6.3 Hz, 2H), 2.44 (s, 1H). **24b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.24 (m, 5H), 6.90 (d, J=16.4 Hz, 1H), 6.14 (d, J=16.4 Hz, 1H), 3.76 (t, J=6.3 Hz, 2H), 2.64 (t, J=6.3 Hz, 2H), 2.44 (s, 1H).

3.2.25. 1,1,2-Triphenylhex-1-en-3-yn-5-ol (25). From bromotriphenylethylene (0.335 g, 1 mmol) and but-3-yn-1-ol (0.151 mL, 2 mmol), product **25** was obtained in 78% (0.253 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.37 (m, 2H), 7.35–7.28 (m, 5H), 7.17–7.10 (m, 6H), 6.98 (m, 2H), 3.55 (t, J=5.8 Hz, 2H), 2.50 (t, J=5.8 Hz, 2H), 1.50 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 142.8, 141.4, 139.6, 130.6, 130.0, 129.4, 128.0, 127.8, 127.7, 127.3, 127.1, 126.8, 121.5, 93.5, 83.4, 61.8, 21.2; MS (70 eV); *m/z* (%): 324 ($M^{+\cdot}$, 100), 293 (10), 215 (14); $C_{24}H_{20}O$: calcd C 88.85, H 6.21. Found C 88.74, H 6.35.

3.2.26. 2-Ethylhex-1-en-3-yn-5-ol (26). From 2-bromobut-1-ene (0.102 mL, 1 mmol) and but-3-yn-1-ol (0.151 mL, 2 mmol), product **26** was obtained in 83% (0.103 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.22 (s, 1H), 5.16 (s, 1H), 3.71 (t, J=6.2 Hz, 2H), 2.58 (t, J=6.2 Hz, 2H), 2.12 (q, J=7.1 Hz, 2H), 1.06 (t, J=7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.1, 119.4, 85.9, 82.9, 61.1, 30.5, 23.7, 12.8; MS (70 eV); *m/z* (%): 124 ($M^{+\cdot}$, 69), 79 (100); $C_8H_{12}O$: calcd C 77.38, H 9.74. Found C 77.50, H 9.70.

3.2.27. 5-Methylenhept-3-yn-1,7-diol (27). From 3-bromobut-3-en-1-ol (0.099 mL, 1 mmol) and but-3-yn-1-ol (0.151 mL, 2 mmol), product **27** was obtained in 96% (0.134 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (s, 1H), 5.23 (s, 1H), 3.75 (t, J=6.3 Hz, 2H), 3.70 (t, J=6.2 Hz, 2H), 2.53 (t, J=6.3 Hz, 2H), 2.35 (t, J=6.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.6, 123.4, 87.7, 82.5, 61.4, 61.4, 40.9, 24.0; MS (70 eV); *m/z* (%): 140 ($M^{+\cdot}$, 3), 91 (100); $C_8H_{12}O_2$: calcd C 68.54, H 8.63. Found C 68.61, H 8.80.

3.2.28. 2,3-Dimethylhept-2-en-4-yn-7-ol (28). From 2-bromo-3-methylbut-2-ene (0.151 mL, 1 mmol) and but-3-yn-1-ol (0.151 mL, 2 mmol), product **28** was obtained in 85% (0.117 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (t, J=6.2 Hz, 2H), 2.69 (t, J=6.2 Hz, 2H), 1.89 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 111.4, 86.9, 84.4, 61.4, 23.9, 23.4, 19.7, 18.8; MS (70 eV); *m/z* (%): 138 ($M^{+\cdot}$, 100); $C_9H_{14}O$: calcd C 78.21, H 10.21. Found C 78.04, H 10.34.

3.2.29. (*Z*)-1-Phenylhept-1-en-3-yn-7-ol (29a) and (*E*)-1-phenylhept-1-en-3-yn-7-ol (29b). From β-bromostyrene (0.128 mL, 1 mmol) and pent-4-yn-1-ol (1.86 mL, 20 mmol), products **29a/29b** (10/90) were obtained in 95% (0.177 g) yield. *Compound* **29a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 6.65 (d, J=11.9 Hz, 1H), 5.87 (d, J=11.9 Hz, 1H), 3.76 (t, J=6.4 Hz, 2H), 2.26 (t, J=6.3 Hz, 2H), 1.86 (tt, J=6.4, 6.3 Hz, 2H). *Compound* **29b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 6.90 (d, J=16.2 Hz, 1H), 6.14 (d, J=16.2 Hz, 1H), 3.76 (t, J=6.4 Hz, 2H), 2.26 (t, J=6.3 Hz, 2H), 1.86 (tt, J=6.4, 6.3 Hz, 2H).

3.2.30. 1,1,2-Triphenylhept-1-en-3-yn-7-ol (30). From bromotriphenylethylene (0.335 g, 1 mmol) and pent-4-yn-1-ol (1.86 mL, 20 mmol), product **30** was obtained in 98% (0.331 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H), 7.34–7.26 (m, 5H), 7.13–7.09 (m, 6H), 6.98 (m, 2H), 3.75 (t, J=6.4 Hz, 2H), 2.26 (t, J=6.3 Hz, 2H), 1.86 (tt, J=6.4, 6.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 143.0, 141.4, 139.7, 130.9, 130.2, 129.8, 127.8, 127.7, 127.6, 127.4, 127.0, 126.8, 121.8, 93.3, 83.5, 61.4, 30.8, 16.1; MS (70 eV); *m/z* (%): 338 ($M^{+\cdot}$, 100); $C_{25}H_{22}O$: calcd C 88.72, H 6.55. Found C 88.87, H 6.41.

3.2.31. (*Z*)-Oct-6-en-4-yn-1-ol (31a) and (*E*)-oct-6-en-4-yn-1-ol (31b). From 1-bromoprop-1-ene (0.085 mL, 1 mmol) and pent-4-yn-1-ol (1.86 mL, 20 mmol), products **31a/31b** (40/60) were obtained in 98% (0.122 g) yield. *Compound* **31a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dq, J=10.8, 6.8 Hz, 1H), 5.42 (dtq, J=10.8, 1.9, 1.7 Hz, 1H), 3.75 (t, J=6.2 Hz, 2H), 2.46 (td, J=6.9, 1.9 Hz, 2H), 1.75 (m, 5H). *Compound* **31b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (dq, J=15.9, 6.8 Hz, 1H), 5.44 (dtq, J=15.9, 2.1, 1.7 Hz, 1H), 3.75 (t, J=6.2 Hz, 2H), 2.46 (td, J=6.8, 2.1 Hz, 2H), 1.82 (m, 5H).

3.2.32. 2-Methylhept-1-en-3-yn-7-ol (32). From 2-bromoprop-1-ene (0.088 mL, 1 mmol) and pent-4-yn-1-ol (1.86 mL, 20 mmol), product **32** was obtained in 90% (0.112 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.20 (s, 1H), 5.14 (s, 1H), 3.76 (t, J=6.3 Hz, 2H), 2.43 (t, J=7.0 Hz, 2H), 1.86 (s, 3H), 1.76 (tt, J=7.0, 6.3 Hz, 2H).

3.2.33. (*E,Z*)-3-Methyl-7-phenylhepta-2,6-dien-4-yn-1-ol (33a) and (*E,E*)-3-methyl-7-phenylhepta-2,6-dien-4-yn-1-ol (33b). From β-bromostyrene (0.128 mL, 1 mmol) and (*E*)-3-methylpent-2-en-4-yn-1-ol (0.192 g, 2 mmol), product **33a/33b** (10/90) were obtained in 88% (0.175 g) yield. *Compound* **33a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.24 (m, 5H), 6.63 (d, J=11.8 Hz, 1H), 6.04 (tq, J=6.8, 1.3 Hz, 1H), 5.80 (d, J=11.8 Hz, 1H), 4.24 (d, J=6.8 Hz, 2H), 1.88 (d, J=1.3 Hz, 3H). *Compound* **33b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.24 (m, 5H), 6.93 (d, J=16.0 Hz, 1H), 6.27 (d, J=16.0 Hz, 1H), 6.04 (tq, J=6.8, 1.3 Hz, 1H), 4.24 (d, J=6.8 Hz, 2H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 136.2, 135.5, 128.7, 128.5, 126.2, 120.8, 108.0, 93.9, 87.2, 59.0, 17.5; $C_{14}H_{14}O$: calcd C 84.81, H 7.12. Found C 84.70, H 7.07.

3.2.34. (*E*)-6-Ethyl-3-methylhepta-2,6-dien-4-yn-1-ol (34). From 2-bromobut-1-ene (0.102 mL, 1 mmol) and (*E*)-3-methylpent-2-en-4-yn-1-ol (0.192 g, 2 mmol), product **34** was obtained in 80% (0.120 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.97 (tq, J=6.8, 1.3 Hz, 1H), 5.26 (s, 1H), 5.20 (s, 1H), 4.20 (d, J=6.8 Hz, 2H), 2.18 (q, J=7.6 Hz, 2H), 1.84 (d, J=1.3 Hz, 3H), 1.08 (t, J=7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 133.1, 120.8, 119.8, 91.3, 88.1, 59.1, 30.3, 17.5, 12.8; $C_{10}H_{14}O$: calcd C 79.96, H 9.39. Found C 79.87, H 9.50.

3.2.35. (*Z*)-5,5-Diethoxy-1-phenylpent-1-en-3-yne (35a) and (*E*)-5,5-diethoxy-1-phenylpent-1-en-3-yne (35b). From β-bromostyrene (0.128 mL, 1 mmol) and 3,3-diethoxyprop-1-yne (0.287 mL, 2 mmol), products **35a/35b** (10/90) were obtained in 72% (0.166 g) yield. *Compound* **35a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.24 (m, 5H), 6.69 (d, J=12.1 Hz, 1H), 5.80 (d, J=12.1 Hz, 1H), 5.29 (s, 1H), 3.80 (m, 2H), 3.65 (m, 2H), 1.25 (dd, J=7.2, 7.0 Hz, 6H). *Compound* **35b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.29 (m, 5H), 7.01 (d, J=16.2 Hz, 1H), 6.17 (d, J=16.2 Hz, 1H), 5.48 (s, 1H), 3.76 (dq, J=9.5, 7.0 Hz, 2H), 3.61 (dq, J=9.5, 7.2 Hz, 2H), 1.25 (dd, J=7.2, 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 135.8, 128.8, 128.6, 126.3, 106.7, 91.7, 86.3, 84.4, 60.8, 15.0; $C_{15}H_{18}O_2$: calcd C 78.23, H 7.88. Found C 78.46, H 7.91.

3.2.36. 5,5-Diethoxy-1,1,2-triphenylpent-1-en-3-yne (36). From bromotriphenylethylene (0.335 g, 1 mmol) and 3,3-diethoxyprop-1-yne (0.287 mL, 2 mmol), product **36** was obtained in 95% (0.363 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.44 (m, 2H), 7.33–7.30 (m, 2H), 7.29–7.26 (m, 3H), 7.16–7.08 (m, 6H), 7.03–6.99 (m, 2H), 5.30 (s, 1H), 3.48 (m, 4H), 1.15 (dd, J=7.2, 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 143.0, 141.5, 139.5, 131.3, 130.6, 130.4, 128.3, 128.2, 128.2, 128.1, 127.8, 127.5, 120.9, 92.2, 88.3, 87.7, 61.1, 15.5; $C_{27}H_{26}O_2$: calcd C 84.78, H 6.85. Found C 84.61, H 7.01.

3.2.37. 5,5-Diethoxy-2-ethylpent-1-en-3-yne (37). From 2-bromo-but-1-ene (0.102 mL, 1 mmol) and 3,3-diethoxyprop-1-yne (0.287 mL, 2 mmol), product **37** was obtained in 70% (0.127 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36 (s, 1H), 5.34 (s, 1H), 5.25 (s, 1H), 3.73 (dq, J=9.4, 7.2 Hz, 2H), 3.58 (dq, J=9.4, 7.0 Hz, 2H), 2.16 (q, J=7.5 Hz, 2H), 1.22 (dd, J=7.2, 7.0 Hz, 6H), 1.06 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.0, 121.4, 91.6, 85.6, 84.0, 60.7, 29.9, 15.0, 12.6; $C_{11}H_{18}O_2$: calcd C 72.49, H 9.95. Found C 72.40, H 9.82.

3.2.38. 5,5-Diethoxy-2-methylpent-1-en-3-yne (38). From 2-bromoprop-1-ene (0.088 mL, 1 mmol) and 3,3-diethoxyprop-1-yne (0.287 mL, 2 mmol), product **38** was obtained in 68% (0.114 g) yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.37 (s, 1H), 5.36 (s, 1H), 5.27 (s, 1H), 3.75 (dq, J=9.6, 7.2 Hz, 2H), 3.58 (dq, J=9.6, 7.0 Hz, 2H), 1.89 (s, 3H), 1.24 (dd, J=7.2, 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.7, 123.3, 91.8, 86.4, 83.3, 60.8, 23.1, 15.1.

3.2.39. (2,3-Dimethylhex-2-en-4-yn-6-yl)dipropylamine (39). From 2-bromo-3-methylbut-2-ene (0.151 mL, 1 mmol) and 1,1-dipropyl-2-propynylamine (0.349 mL, 1 mmol) product **39** was obtained in 63% (0.131 g) yield. Thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (s, 2H), 2.43 (t, J=7.6 Hz, 4H), 1.92 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H), 1.48 (tq, J=7.6, 7.3 Hz, 4H), 0.89 (t, J=7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 111.6, 86.7, 85.4, 55.8, 42.6, 23.5, 20.7, 19.7, 18.9, 11.9; MS (70 eV); *m/z* (%): 208 ($M^{+\cdot}$, 18), 178 (100); $C_{14}H_{25}N$: calcd C 81.09, H 12.15. Found C 80.90, H 12.28.

Registry No.: **1a**, 13343-78-7; **1b**, 13343-79-8; **2**, 21979-82-8; **3**, 10469-89-3; **4**, 732284-08-1; **5**, 124475-73-6; **6a**, 31552-04-2; **6b**, 31552-03-1; **7**, 1463-04-3; **8a**, 845749-45-3; **8b**, 220185-68-2; **12a**, 171781-58-1; **12b**, 243870-53-3; **13**, 71313-54-7; **16a**, 374897-65-1; **16b**, 103606-73-1; **19**, 6822-09-9; **20a**, 845749-46-4; **22a**, 180787-32-0; **24**, 53081-56-4; **29a**, 114092-63-6; **29b**, 114092-61-4; **31**, 258819-00-0; **32**, 69719-47-7; **38**, 32365-41-6.

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