# Copper(II) Acetate/1,4-Diphenyl-1,4-diazabuta-1,3-diene Catalyzed Sonogashira Cross-Coupling of Aryl Halides with Terminal Alkynes under Aerobic and Solvent-Free Conditions

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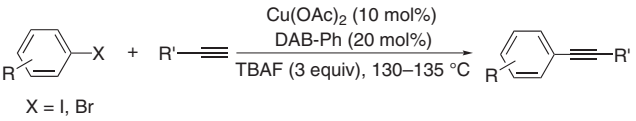
**Abstract:** The Sonogashira cross-coupling of aryl halides with terminal alkynes catalyzed by an inexpensive copper(II) acetate/1,4-diphenyl-1,4-diazabuta-1,3-diene [$Cu(OAc)_2$/DAB-Ph] catalytic system is reported. A series of ligands, including diazabutadiene systems, *N*,*N*-dimethylglycine, L-proline, ethylenediamine, and phosphines, were evaluated, and 1,4-diphenyl-1,4-diazabuta-1,3-diene provided the best results. In the presence of copper(II) acetate (10 mol%), 1,4-diphenyl-1,4-diazabuta-1,3-diene (20 mol%), and tetrabutylammonium fluoride (3 equiv), a number of aryl iodides or bromides were treated smoothly with alkynes to afford the corresponding products in moderate to excellent yields. It is noteworthy that the reaction is conducted under aerobic and solvent-free conditions.

**Key words:** copper(II) acetate, diazabutadiene, Sonogashira cross-coupling reaction, aryl halide, terminal alkyne

The cross-coupling of aryl halides with terminal alkynes (the Sonogashira cross-coupling reaction) represents one of the most valuable synthetic methods in organic chemistry.[1–9] Generally, a palladium(0) complex is chosen, invariably as the catalyst in the presence of a ligand (often a phosphine).[2–6] However, the palladium catalysts are expensive; to satisfy economic concerns, the use of inexpensive metals as catalysts[7–9] could be a solution to this problem, as well as the recovery and recycling of the expensive palladium catalysts.[2,6] Among the inexpensive metals catalysts, copper catalysts, such as copper(I) iodide, Cu(phen)($PPh_3$)Br, and copper nanoclusters, have been employed in the Sonogashira cross-coupling reaction.[8,9] However, there are only a few reports of the extension of the Sonogashira reaction to aryl bromides.[8b–d] Miura and co-workers first reported the copper-catalyzed Sonogashira reaction, but the scope was limited to aryl iodides.[8a] In 2004, Rothenberg and co-workers[8b] reported that the Sonogashira reaction of aryl iodides and activated aryl bromides catalyzed by copper nanoclusters gave satisfactory results under ligand-free conditions. Ma and Liu[8c] found that copper(I) iodide combined with *N*,*N*-dimethylglycine as the catalytic system could couple deactivated aryl bromides. Guo and co-worker have also employed copper(I) iodide/ethylenediamine as the catalytic system for the coupling of aryl iodides or bromides.[8d] Although 1,10-phenanthroline (phen) was used as a ligand in the Cu(phen)($PPh_3$)Br or [Cu(phen)($PPh_3$)$_2$]$NO_3$ catalyzed Sonogashira coupling, the substrates were aryl iodides and vinyl iodides.[9] Furthermore, almost all of these protocols must be performed under an inert gas to reduce the occurrence of the Glaser reaction (the oxidative homocoupling of terminal alkynes)[10] and using harmful solvents (DMF, DMSO, dioxane, or toluene etc.) as the media. In view of economic and environmental requirements, the challenge is to develop more active copper catalytic systems to allow direct coupling of a large range of aryl halides with alkynes under aerobic and solvent-free conditions. Here, we wish to report a highly active and inexpensive catalytic system that employs tetrabutylammonium fluoride as a base and 1,4-diphenyl-1,4-diazabuta-1,3-diene (DAB-Ph) as a ligand for copper(II) acetate catalyzed couplings of aryl halides with terminal alkynes without the aid of degasification and without solvent (Equation 1).[11] Moreover, the presence of either *N*,*N*-dimethylformamide or inert gas has a deleterious effect on the reaction.




**Equation 1**

Our preliminary study was carried out on the cross-coupling of 1-iodo-4-methoxybenzene (**1a**) with phenylacetylene (**2a**), a model reaction, under aerobic and solvent-free conditions (Table 1). To the best of our knowledge, only two divalent copper salts [$CuCl_2$ and $Cu(OAc)_2$] were evaluated for the Sonogashira reaction of iodobenzene with phenylacetylene using *N*,*N*-dimethylformamide as the medium and potassium carbonate as the base under nitrogen.[8a] The results showed that the reaction catalyzed by copper(II) chloride/triphenylphosphine was unsuccessful, but copper(II) acetate/triphenylphosphine was found to be an effective catalytic system for the coupling (diphenylacetylene; 88% yield, and 1,4-diphenylbutadiyne, 5% yield). Thus, we decided to perform the reaction of the iodide **1a** with alkyne **2a**, copper(II) acetate, triphenylphosphine (**L1**), and potassium carbonate under

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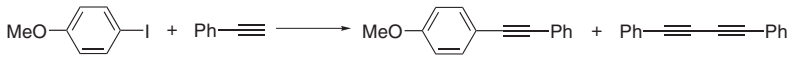
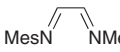
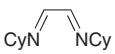
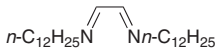
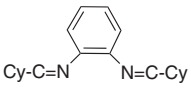
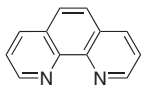
solvent-free conditions. Unfortunately, the target product **3** was obtained in only 10% yield together with 1,4-diphenylbutadiyne (**4**) in 56% yield after 24 hours under air (Table 1, entry 1). Very recently, we reported a fast and general dichlorobis(triphenylphosphine)palladium catalyzed Sonogashira cross-coupling reaction under solvent-free conditions;[5a] tetrabutylammonium fluoride was observed to be an effective base for the reaction. Thus, tetrabutylammonium fluoride was examined as a suitable base; however, the yield of **3** increased only slightly (15% yield; Table 1, entry 2). Another phosphine ligand, tricyclohexylphosphine (**L2**), gave almost identical results (Table 1, entry 3). It is pleasing to observe that treatment of **1a** with alkyne **2a**, copper(II) acetate, and tetrabutylammonium fluoride afforded a 43% yield of **3** without the aid of any ligands and solvents (Table 1, entry 4). The results encouraged us to further explore and optimize the conditions. Initially, a series of alternative ligands, including

**Table 1** Copper-Catalyzed Sonogashira Cross-Coupling Reaction of 1-Iodo-4-methoxybenzene (**1a**) with Phenylacetylene (**2a**)[a]




**1a** **2a** **3** **4**

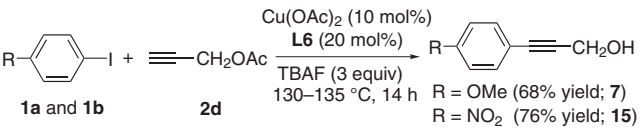
| Entry | [Cu] | Ligand | | Time (h) | Yield[b] (%) | |
|---|---|---|---|---|---|---|
| | | | | | **3** | **4** |
| 1[c] | $Cu(OAc)_2$ | $Ph_3P$ | **L1** | 24 | 10 | 56 |
| 2 | $Cu(OAc)_2$ | $Ph_3P$ | **L1** | 20 | 15 | 35 |
| 3 | $Cu(OAc)_2$ | $Cy_3P$ | **L2** | 20 | 13 | 30 |
| 4 | $Cu(OAc)_2$ | – | – | 21 | 43 | 53 |
| 5 | $Cu(OAc)_2$ | $Me_2NCH_2CO_2H{\cdot}HCl$ | **L3** | 20 | 70 | trace |
| 6 | $Cu(OAc)_2$ | L-proline | **L4** | 20 | 59 | 26 |
| 7 | $Cu(OAc)_2$ | $H_2NCH_2CH_2NH_2$ | **L5** | 20 | 21 | 44 |
| 8 | $Cu(OAc)_2$ |  | **L6** | 14 | 86 | 0 |
| 9 | $Cu(OAc)_2$ |  | **L7** | 14 | 81 | 0 |
| 10 | $Cu(OAc)_2$ |  | **L8** | 14 | 84 | 0 |
| 11 | $Cu(OAc)_2$ |  | **L9** | 19 | 85 | 0 |
| 12 | $Cu(OAc)_2$ |  | **L10** | 14 | 56 | trace |
| 13 | $Cu(OAc)_2$ |  | **L11** | 14 | 78 | 0 |
| 14 | $Cu(OAc)_2$ |  | **L12** | 20 | 66 | trace |
| 15 | CuI | | **L6** | 20 | 45 | 26 |
| 16 | CuO | | **L6** | 18 | trace | 18 |
| 17[d] | $Cu(OAc)_2$ | | **L6** | 15 | 28 | 29 |
| 18[e] | $Cu(OAc)_2$ | | **L6** | 14 | 60 | trace |
| 19[f] | $Cu(OAc)_2$ | | **L6** | 14 | 85 | 0 |

[a] Unless otherwise indicated, the reaction conditions were as follows: **1a** (0.5 mmol), **2a** (0.65 mmol), [Cu] (10 mol%), ligand (20 mol%), TBAF (3 equiv), air, 130–135 °C.
[b] Isolated yield. Yield of **4** on base of the amount of **2a**.
[c] $K_2CO_3$ (3 equiv) was used as the base instead of TBAF.
[d] DMF (1 mL) was added.
[e] Under argon.
[f] Under $O_2$ (1 atm) instead of air.

*N*,*N*-dimethylglycine (**L3**), L-proline (**L4**), ethylenediamine (**L5**), and diazabutadienes **L6**–**L12**, were examined to improve the catalytic efficacy (Table 1, entries 5–14). We found that diazabutadienes **L6**–**L12** as the ligands were superior to the earlier reported effective ligands, such as *N*,*N*-dimethylglycine hydrochloride (**L7**),[8c] L-proline (**L4**),[8c] and ethylenediamine (**L5**),[8d] in terms of reaction rate and yield. Among the diazabutadienes **L6**–**L12**, 1,4-diphenyl-1,4-diazabuta-1,3-diene (DAB-Ph, **L6**) was the most efficient ligand based on yield (Table 1, entries 8–14). The use of other copper sources, such as copper(I) iodide and copper(II) oxide, were also tested in air as the catalyst and they were less effective than copper(II) acetate (Table 1, entries 8, 15, and 16). To our surprise, the yield of **3** decreased sharply to 28% when *N*,*N*-dimethylformamide (1 mL), the previously reported solvent,[8a] was added (Table 1, entry 17). It is noteworthy that argon has a deleterious effect on the reaction mediated by copper(II) acetate (Table 1, entries 8 and 18). Under argon, the yield of **3** was reduced to 60% (Table 1, entry 18). The effect of oxygen was also examined; results identical to those in air were observed when the reaction was carried out under an oxygen atmosphere (Table 1, entry 19).

With the optimized reaction conditions in hand, we were keen to explore the range of substrates, including aryl halides and terminal alkynes, that could be used in the coupling protocol. As shown in Table 2, the copper(II) acetate/1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**) catalytic system proved to be exceptionally active for the Sonogashira reaction of various aryl iodides **1a**–**f** with alkynes. In the presence of copper(II) acetate (10 mol%), 1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**, 20 mol%), and tetrabutylammonium fluoride (3 equiv), substrate **1a** was treated with alkynes **2b** and **2c**, respectively, to afford the corresponding products in good yields (Table, entries 1 and 2), but with alkyne **2d** bearing an unprotected hydroxy group, the reaction was unsuccessful (Table 2, entry 3). The other aryl iodides **1b**–**f** were coupled with alkynes **2a** and **2b** smoothly in good to excellent yields under the same conditions (Table 2, entries 4–10). However, the efficiency of copper(II) acetate/1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**) decreased to some extent for the coupling of aryl bromides **1g**–**k** (Table 2, entries 11–17). For example, only a 43% yield of the desired product **8** was isolated after 19 hours when 1-bromo-4-nitrobenzene (**1g**) was reacted with phenylacetylene (**2a**), copper(II) acetate (10 mol%), 1,4-diphenyl-1,4-diazabuta-1,3-diene (20 mol%), and tetrabutylammonium fluoride (3 equiv) (Table 2, entry 11). We were happy to observe that tetrabutylammonium bromide could improve the reaction. The yield of **8** was enhanced to 69% when tetrabutylammonium bromide (1 equiv) was added (Table 2, entry 12). Other bromides **1h** and **1i** underwent the reaction smoothly to provide moderate yields in the present of tetrabutylammonium bromide (Table 2, entries 14 and 15). It was found that the these reaction conditions were less effective for the reaction of substrates **1j** and **1k**, which gave low yields of the corresponding desired products even in the presence of tetrabutylammonium bromide (Table 2, entries 17 and 19). However, satisfactory yields were obtained when the reactions of **1i–k** were conducted in the presence of 50 mol% of copper(II) acetate and 100 mol% of 1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**) at 140–145 °C (Table 2, entries 16, 18, and 20).

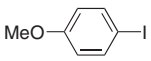
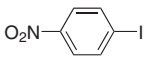
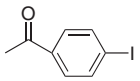
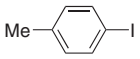
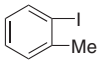
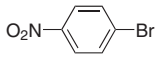
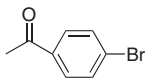
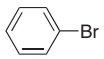
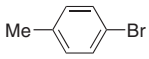
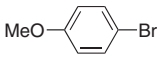
It was interesting to find that the Sonogashira reaction and deprotection occurred in one pot between aryl iodides and prop-2-ynyl acetate (**2d**) to produce the corresponding alk-2-yn-1-ols in good yields (Scheme 1).




**Scheme 1**

It is well known that copper(II) acetate can mediate the Glaser coupling of terminal alkynes to afford diynes, and this reaction often requires the presence of oxygen.[10] To our surprise, zero or low yields of diynes were observed under the conditions used. Thus, some control reactions were carried out to explore the mechanism of the copper-catalyzed Sonogashira cross-coupling (Table 3). Several conclusions can be drawn, including: (1) The addition of 1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**) could suppress the occurrence of the oxidative homocoupling of terminal alkynes. Without a ligand present, using copper(II) acetate as the catalyst and tetrabutylammonium fluoride as the base, the target product **3** was produced in 43% yield together with the homocoupling product **4** in 53% yield (Table 3, entry 1), whereas the use of 1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**) (20 mol%) shifted the selectivity toward the cross-coupling reaction providing **3** in 86% yield with no homocoupling product **4** formed (Table 3, entry 2). (2) Argon in place of air suppressed the copper(II) acetate catalyzed reaction, but favored the copper(I) iodide catalyzed procedure (Table 3, entries 2–5). In other words, oxygen can promote the copper(II) acetate catalyzed Sonogashira protocol. The yield of **3** was reduced from 86% (in air) to 60% (under argon) using copper(II) acetate/1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**) as the catalytic system (Table 3, entries 2 and 3). By contrast, the yield of **3** increased from 45% (in air) to 65% (under argon) and the yield of **4** decreased when copper(I) iodide was used in place of copper(II) acetate (Table 3, entries 4 and 5). (3) Copper(II) acetate is not a good catalyst for the homocoupling reaction under the optimized conditions. In the absence of **1a**, alkyne **2a** was consumed completely in 15 hours [$Cu(OAc)_2$ (10 mol%), DAB-Ph (**L6**) (20 mol%), TBAF (3 equiv), 130–135 °C] to afford **4** in 27% yield (Table 3, entry 6). The yield of **4** was enhanced to 40% when *N*,*N*-dimethylformamide (2 mL) was added (Table 3, entry 8). We found that the ligand 1,4-diphenyl-1,4-diazabuta-1,3-diene (**L6**) has no influence on the homocoupling reaction (Table 3, entries 6 and 7). Employing copper(II) acetate and tetrabutylammonium

**Table 2** Copper(II) Acetate/1,4-Diphenyl-1,4-diazabuta-1,3-diene (**L6**) Catalyzed Sonogashira Cross-Coupling of Aryl Halides with Alkynes[a]

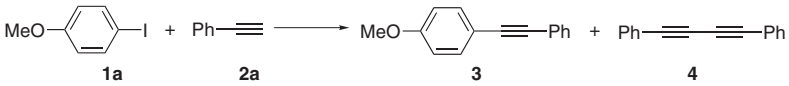
| Entry | Aryl halide | | Alkyne | | Time (h) | Product | Yield[b] (%) |
|---|---|---|---|---|---|---|---|
| 1 |  | **1a** | HC≡C(CH$_2$)$_7$Me | **2b** | 14 | **5** | 87 |
| 2 | | **1a** | HC≡CCH$_2$OTHP | **2c** | 14 | **6** | 84 |
| 3 | | **1a** | HC≡CCH$_2$OH | **2d** | 14 | **7** | trace |
| 4 |  | **1b** | HC≡CPh | **2a** | 14 | **8** | 98 |
| 5 | | **1b** | HC≡C(CH$_2$)$_7$Me | **2b** | 14 | **9** | 95 |
| 6 |  | **1c** | HC≡CPh | **2a** | 16 | **10** | 70 |
| 7 |  | **1d** | HC≡CPh | **2a** | 14 | **11** | 85 |
| 8 |  | **1e** | HC≡CPh | **2a** | 14 | **12** | 93 |
| 9 | | **1e** | HC≡C(CH$_2$)$_7$Me | **2b** | 14 | **13** | 91 |
| 10 |  | **1f** | HC≡CPh | **2a** | 14 | **14** | 85 |
| 11 |  | **1g** | HC≡CPh | **2a** | 19 | **8** | 43 |
| 12[c] | | **1g** | HC≡CPh | **2a** | 19 | **8** | 69 |
| 13[c] | | **1g** | HC≡C(CH$_2$)$_7$Me | **2b** | 19 | **9** | 58 |
| 14[c] |  | **1h** | HC≡CPh | **2a** | 19 | **10** | 72 |
| 15[c] |  | **1i** | HC≡CPh | **2a** | 20 | **9** | 57 |
| 16[cd] | | **1i** | HC≡CPh | **2a** | 26 | **9** | 72 |
| 17[c] |  | **1j** | HC≡CPh | **2a** | 19 | **12** | 32 |
| 18[cd] | | **1j** | HC≡CPh | **2a** | 24 | **12** | 70 |
| 19[c] |  | **1k** | HC≡CPh | **2a** | 23 | **3** | 21 |
| 20[cd] | | **1k** | HC≡CPh | **2a** | 23 | **3** | 40 |

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.65 mmol), Cu(OAc)$_2$·H$_2$O (10 mol%), DAB-Ph (**L6**) (20 mol%), TBAF (3 equiv), 130–135 °C.
[b] Isolated yield.
[c] TBAB (1 equiv).
[d] Cu(OAc)$_2$·2 H$_2$O (50 mol%), DAB-Ph (**L6**) (100 mol%), 140–145 °C.

fluoride with methanol as the medium resulted in the completed consumption of **2a** in three hours but gave **4** in only 6% yield (Table 3, entry 9). Under the same conditions, but using sodium acetate as the base, **4** was obtained in 18% yield (Table 3, entry 10). (4) *N*,*N*-Dimethylformamide as the medium disfavored the target reaction. In *N*,*N*-dimethylformamide, the yield of **3** decreased sharply to 28%, while **4** was obtained in 29% yield (Table 3, entries 2 and 11).

To elucidate the results, a working mechanism was proposed for this copper(II) acetate catalyzed Sonogashira cross-coupling reaction, based on the reported mechanism proposed by Miura[8a] and Rothenberg[8b] (Scheme 2).[2,7–9] Firstly, complexation of copper(II) acetate with the ligand led to the formation of a four-centered transition state **16**, which was observed by Castro and Stephens.[12] Intermediate **16** then reacted with readily with an alkyne with the aid of a base to yield intermediate **17**, and this was fol-

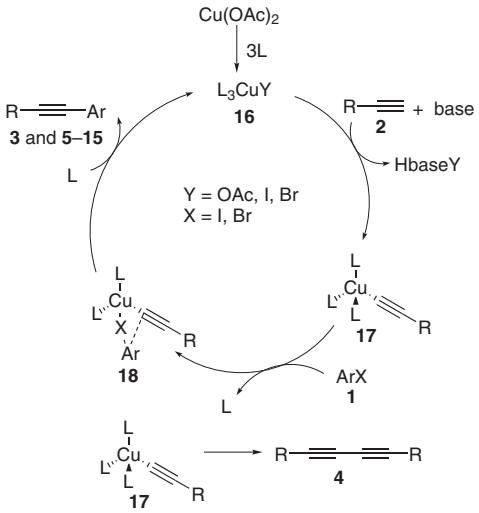
**Table 3** Control Reactions of 1-Iodo-4-methoxybenzene (**1a**) with Phenylacetylene (**2a**)[a]




| Entry | [Cu] | Ligand | Solvent | Time (h) | Yield[bc] (%) | |
|---|---|---|---|---|---|---|
| | | | | | **3** | **4** |
| 1 | $Cu(OAc)_2$ | – | neat | 21 | 43 | 53 |
| 2 | $Cu(OAc)_2$ | **L6** | neat | 14 | 86 | trace |
| 3[d] | $Cu(OAc)_2$ | **L6** | neat | 14 | 60 | trace |
| 4 | CuI | **L6** | neat | 20 | 45 | 26 |
| 5[d] | CuI | **L6** | neat | 18 | 65 | 14 |
| 6[e] | $Cu(OAc)_2$ | **L6** | neat | 15 | – | 27 |
| 7[e] | $Cu(OAc)_2$ | – | neat | 3 | – | 30 |
| 8[e] | $Cu(OAc)_2$ | **L6** | DMF | 15 | – | 40 |
| 9[e] | $Cu(OAc)_2$ | – | MeOH | 3 | – | 6 |
| 10[ef] | $Cu(OAc)_2$ | – | MeOH | 3 | – | 18 |
| 11 | $Cu(OAc)_2$ | **L6** | DMF | 15 | 28 | 29 |

[a] Under otherwise indicated, the reaction conditions were as follows: **1a** (0.5 mmol), **2a** (0.65 mmol), [Cu] (10 mol%), DAB-Ph (**L6**) (20 mol%), TBAF (3 equiv), air, 130–135 °C.
[b] Isolated yield.
[c] Yield of **4** based on the amount of **2a**.
[d] Under argon.
[e] Without **1a**.
[f] NaOAc (3 equiv) was used instead of TBAF.

lowed by the oxidative addition of **17** to ArX to afford intermediate **18**. The subsequent reductive elimination of **18** took place to produce the desired product and regenerate the active copper species **16**. On the other hand, the homocoupling of terminal alkyne could be catalyzed by **17** to afford the diyne **4**.[10] Further study to obtain a more accurate mechanism for the reaction is underway.




**Scheme 2**

In summary, we have demonstrated an inexpensive copper(II) acetate/1,4-diphenyl-1,4-diazabuta-1,3-diene system for the Sonogashira-type, cross-coupling reaction. The system is effective for aryl iodides and activated aryl bromides, and emerges as an attractive alternative to the palladium/ligand catalyst systems. It is noteworthy that the reaction is performed under aerobic and solvent-free conditions. Further mechanistic and reactive studies of this system in other cross-coupling transformations are in progress.

NMR spectroscopy was performed on Bruker AMX-300 or 400 spectrometers, operating at 300 MHz ($^1$H NMR) and 75 MHz ($^{13}$C NMR) or 400 MHz ($^1$H NMR) and 100 MHz ($^{13}$C NMR). TMS was used an internal standard.

**Copper(I) Iodide/1,4-Diphenyl-1,4-diazabuta-1,3-diene Catalyzed Sonogashira Cross-Coupling Reactions; General Procedure**

A mixture of aryl halide **1** (0.5 mmol), alkyne **2** (0.65 mmol), $Cu(OAc)_2$ (10 mol%), DAB-Ph (**L6**, 20 mol%), and TBAF (3 equiv) was stirred at 130–135 °C for the desired time until complete consumption of starting material as monitored by TLC. The mixture was then dissolved in EtOAc (10 mL), filtered, washed with $H_2O$ (3 × 5 mL), extracted with $Et_2O$ (5 × 10 mL) and evaporated. The residue was purified by flash column chromatography (hexane or hexane–EtOAc) to afford the product.

**1-Methoxy-4-(2-phenylethynyl)benzene (3)[8c]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.51 (m, 2 H), 7.48 (d, *J* = 9.0 Hz, 2 H), 7.34–7.32 (m, 3 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

LRMS (EI, 20 eV): *m*/*z* (%) = 208 ($M^+$, 100).

**1,4-Diphenylbuta-1,3-diyne (4)[8c]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.4 Hz, 4 H), 7.38–7.34 (m, 6 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 132.8, 129.6, 128.8, 122.1, 81.9, 74.2.

LRMS (EI, 20 eV): *m*/*z* (%) = 202 ($M^+$, 100).

**1-(Dec-1-ynyl)-4-methoxybenzene (5)[4]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 3.80 (s, 3 H), 2.38 (t, *J* = 7.6 Hz, 2 H), 1.61–1.57 (m, 2 H), 1.45–1.40 (m, 2 H), 1.31–1.24 (m, 8 H), 0.88 (t, *J* = 6.4 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.9, 132.8, 116.1, 113.7, 88.8, 80.1, 55.2, 31.8, 29.2, 29.1, 28.9, 28.8, 22.7, 19.4, 14.1.

LRMS (EI, 20 eV): *m*/*z* (%) = 244 ($M^+$, 100).

**2-[3-(4-Methoxyphenyl)prop-2-ynyloxy]tetrahydro-2*H*-pyran (6)[8c]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.8 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 4.90 (t, *J* = 3.2 Hz, 1 H), 4.53–4.22 (m, 2 H), 3.89 (t, *J* = 7.2 Hz, 1 H), 3.80 (s, 3 H), 3.58–3.54 (m, 1 H), 1.76–1.54 (m, 6 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 159.6, 133.3, 114.8, 113.8, 96.8, 85.7, 83.6, 62.0, 55.2, 54.8, 30.3, 25.4, 19.1.

LRMS (EI, 20 eV): *m*/*z* (%) = 246 ($M^+$, 100).

**3-(4-Methoxyphenyl)prop-2-yn-1-ol (7)[4i]**
$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.8 Hz, 2 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 4.49 (s, 2 H), 3.82 (s, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 159.7, 133.2, 114.5, 113.9, 85.8, 85.6, 55.3, 51.7.

LRMS (EI, 20 eV): *m*/*z* (%) = 162 ($M^+$, 100), 145 ($M^+$ – OH, 33).

**1-Nitro-4-(phenylethynyl)benzene (8)[8c]**
$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.8 Hz, 2 H), 7.65 (d, *J* = 8.8 Hz, 2 H), 7.58–7.54 (m, 2 H), 7.40–7.38 (m, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 141.3, 132.6, 132.2, 130.6, 129.6, 128.8, 124.0, 122.5, 95.0, 87.9.

LRMS (EI, 20 eV): *m*/*z* (%) = 223 ($M^+$, 100).

**1-(Dec-1-ynyl)-4-nitrobenzene (9)[4]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.8 Hz, 2 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 2.44 (t, *J* = 7.2 Hz, 2 H), 1.74–1.59 (m, 2 H), 1.47–1.43 (m, 2 H), 1.31–1.26 (m, 8 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 132.6, 131.6, 123.8, 118.5, 97.2, 79.6, 32.2, 29.5, 29.4, 29.3, 28.7, 23.0, 19.9, 14.4.

LRMS (EI, 20 eV): *m*/*z* (%) = 259 ($M^+$, 100).

**4-(Phenylethynyl)acetophenone (10)[2]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.8 Hz, 2 H), 7.61 (d, *J* = 8.8 Hz, 2 H), 7.57–7.55 (m, 2 H), 7.38 (t, *J* = 3.2 Hz, 3 H), 2.63 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.4, 136.1, 131.8, 131.7, 128.8, 128.4, 128.3, 122.6, 92.7, 88.6, 26.7.

LRMS (EI, 20 eV): *m*/*z* (%) = 220 ($M^+$, 100).

**Diphenylacetylene (11)[8c]**
$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.51 (m, 4 H), 7.39–7.26 (m, 6 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 132.0, 128.7, 128.6, 123.7, 89.7.

LRMS (EI, 20 eV): *m*/*z* (%) = 178 ($M^+$, 100).

**4-(Phenylethynyl)toluene (12)[8c]**
$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.50 (m, 2 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 7.35–7.31 (m, 3 H), 7.15 (d, *J* = 7.8 Hz, 2 H), 2.36 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 138.7, 132.9, 131.9, 129.6, 129.5, 128.8, 128.7, 128.4, 89.1, 83.4, 21.9.

LRMS (EI, 20 eV): *m*/*z* (%) = 192 ($M^+$, 100).

**4-(Dec-1-ynyl)toluene (13)[4]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 2.38 (t, *J* = 7.2 Hz, 2 H), 2.32 (s, 3 H), 1.61–1.55 (m, 2 H), 1.46–1.42 (m, 2 H), 1.31–1.29 (m, 8 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 137.4, 131.4, 128.9, 121.0, 89.6, 80.6, 31.9, 29.2, 29.1, 28.9, 28.8, 23.7, 21.4, 18.4, 14.1.

LRMS (EI, 20 eV): *m*/*z* (%) = 228 ($M^+$, 100).

**2-(Phenylethynyl)toluene (14)[4]**
$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.52 (m, 3 H), 7.35–7.33 (m, 4 H), 7.23–7.22 (m, 2 H), 2.52 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 140.2, 132.6, 131.9, 131.6, 129.5, 129.2, 128.4, 128.3, 128.2, 125.6, 88.4, 81.7, 20.7.

LRMS (EI, 20 eV): *m*/*z* (%) = 192 ($M^+$, 100).

**3-(4-Nitrophenyl)prop-2-yn-1-ol (15)[4i]**
$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.8 Hz, 2 H), 7.58 (d, *J* = 8.8 Hz, 2 H), 4.54 (s, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 147.3, 132.4, 129.4, 123.6, 92.5, 83.8, 51.5.

LRMS (EI, 20 eV): *m*/*z* (%) = 177 ($M^+$, 100), 160 ($M^+$ – OH, 30).

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