Sonogashira Cross-Coupling Using Carbon Aerogel Doped with Palladium Nanoparticles; A Recoverable and Reusable Catalyst

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Abstract: The Sonogashira cross coupling of aryl iodides with terminal alkynes has been carried out in the presence of carbon aerogels doped with metallic palladium nanoparticles. Coupling products have been isolated in excellent yields and the catalyst system can be easily recovered in the presence of air without any particular precautions and reused several times.

Key words: palladium, nanoparticles, Sonogashira cross coupling, carbon aerogels, catalysis

The palladium-catalyzed cross coupling of terminal alkynes with aryl and vinyl halides or triflates in the presence of a copper salt as co-catalyst is one of the most powerful tools for the formation of C–C bonds. This reaction, known as the Sonogashira cross coupling,[2] allows alkynylation to be performed under milder conditions than those typical of Heck[3] and Cassar[4] protocols and it has found a variety of applications ranging from the preparation of fine chemicals to the synthesis of biologically active substances.

Since its discovery, a great deal of work has been done to modify the original protocol so as to include an even wider range of reactants as well as to limit one of the major drawbacks of this process in industrial applications: the utilization of two metals that hinder the recovery and reutilization of the expensive palladium catalyst (its recovery would be the best way to overcome cost-related problems). As to the latter point, interesting results have been achieved by enhancing the catalyst efficacy by employing more efficient phosphines.[2d] However, these phosphines are not readily available and some limits to their use in large-scale applications still remain.

A subject that has attracted the attention of several research groups is the utilization of solid-supported palladium catalysts.[2d,f] Indeed, in addition to facilitating the recovery and reutilization of palladium, the use of solid-supported palladium catalysts could also reduce the palladium contamination of the isolated product, a significant problem for the pharmaceutical industry.[5]

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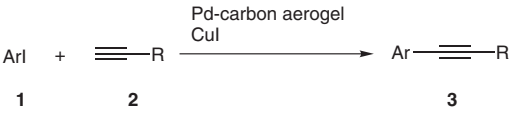
In this context, we decided to investigate the utilization of carbon aerogels doped with palladium nanoparticles as catalysts in the Sonogashira reaction (Scheme 1). Aerogels[6] represent a new class of porous solids, obtained via sol-gel processes coupled with supercritical drying of wet gels, which have been shown to exhibit a great potential for the preparation of heterogeneous catalysts.[7] Herein we report the results of this study.



Scheme 1

Carbon aerogels doped with metallic palladium nanoparticles were synthesized as described previously.[8] Before their utilization, the catalysts were washed with *N*,*N*-dimethylformamide. A sample of palladium-carbon aerogel containing 46% of palladium in 4 mL of *N*,*N*-dimethylformamide was heated at 120 °C for two days and then recovered by decantation. The procedure was repeated three times.

The reaction of 4-iodoacetophenone with hept-1-yne in the presence of 6 mol% of palladium-carbon aerogel, diisopropylamine (1.5 equiv) in *N*,*N*-dimethylformamide at 100 °C was initially tested. Only traces of the cross-coupling derivative **3a** were formed after 24 hours under these conditions. When the same reaction was carried out in the presence of copper(I) iodide (12 mol%), **3a** was isolated in 90% yield after 24 hours. However, when 4-iodoanisole, a model of electron-rich aryl iodides, was subjected to the same conditions, it produced only trace amounts of the desired cross-coupling derivative **3b** after 48 hours. After some experimentation, we found that the alkynylation of 4-iodoanisole proceeded smoothly upon addition of 12 mol% of triphenylphosphine and **3b** was isolated in 87% yield after 23 hours.

The remarkable effect of the added phosphine ligand might be accounted for by assuming that a higher amount of palladium might be dissolved by coordination. However, sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) analysis indicated the level of

palladium in *N*,*N*-dimethylformamide, after decanting, to be essentially the same with and without triphenylphosphine (6–9 ppm). This behavior has not been investigated and will not be commented upon further.

Copper(I) iodide and triphenylphosphine were then used as the reaction was extended to other aryl iodides and terminal alkynes. Several examples of palladium-carbon aerogel-catalyzed Sonogashira cross-coupling reactions are listed in Table 1. A variety of electron-rich and electron-poor aryl iodides **1** and terminal alkynes **2** reacted smoothly under these conditions to give the corresponding cross-coupling derivatives in excellent yields.

We also investigated the recyclability of the palladium catalyst. The results of this study, performed with 3-iodoanisole and hept-1-yne using a sample containing 35.6% of palladium, are summarized in Figure 1.

The upper limit of utilization of the palladium-carbon aerogel catalyst was not determined. It was recovered (simply decanting the solution and mechanically separating the palladium-carbon aerogel from the salts in the presence of air and without any particular precaution) and reused several times. A loss of activity was observed after the second run. Run 3 gave the coupling product in 63% yield. However, subjecting the sample of palladium-carbon aerogel used in the coupling reactions to the same washing procedure utilized at the beginning of the recycling process (DMF, 120 °C, 2 d) regenerated its activity. The same treatment was repeated after runs 6 and 12.

Furthermore, no appreciable leaching of palladium was observed. Indeed, after fifteen cycles only a slight variation in the total amount of palladium was observed (within experimental error; 35.3% in the initial sample and 32.1% in the sample recovered after 15 cycles) and still in the form of a palladium(0) species, as shown by an X-ray diffraction (XRD) analysis (Figure 2). A decrease of the surface area was observed by comparison between the BET parameters of the fresh aerogel and the used one, after fifteen cycles (from 422 to 265 $m^2 \cdot g^{-1}$). This is related to the collapse of the smallest pores (mostly micropores) due to the air manipulation (also supported by the increase of the average pore size). However, no decrease in its catalytic activity was observed.

Table 1 The Sonogashira Cross Coupling of Aryl Iodides **1** and Alk-1-ynes **2** Catalyzed by Palladium-Carbon Aerogel[a]

Entry	Ar	R	Time (h)	Product	Yield[b] (%)
1	4-AcC_6H_4	$(CH_2)_4Me$	8	**3a**	97[c]
2	4-$MeOC_6H_4$	$(CH_2)_4Me$	23	**3b**	87
3	3-$MeOC_6H_4$	$(CH_2)_4Me$	16	**3c**	96
4	4-$EtO_2CC_6H_4$	$(CH_2)_4Me$	14	**3d**	98
5	3-O_2N-4-MeC_6H_3	$(CH_2)_4Me$	16	**3e**	99[c]
6	4-AcC_6H_4	Ph	6	**3f**	99
7	3-$MeOC_6H_4$	Ph	7	**3g**	92
8	4-$MeOC_6H_4$	Ph	20	**3h**	97
9	4-$EtO_2CC_6H_4$	Ph	6	**3i**	99
10	3-O_2N-4-MeC_6H_3	Ph	6	**3j**	95
11	4-AcC_6H_4	CH_2OH	16	**3k**	96
12	3-$MeOC_6H_4$	CH_2OH	18	**3l**	94
13	4-$MeOC_6H_4$	CH_2OH	28	**3m**	98
14	4-$EtO_2CC_6H_4$	CH_2OH	16	**3n**	97
15	3-O_2N-4-MeC_6H_3	CH_2OH	16	**3o**	92

[a] Reactions were carried out under argon on a 0.79 mmol scale at 100 °C using: ArI (1 equiv), alk-1-yne (1.5 equiv), 46% Pd-C aerogel (0.06 equiv), CuI (0.12 equiv), Ph_3P (0.12 equiv), *i*-Pr_2NH (1.5 equiv), deoxygenated DMF (0.5 mL).
[b] Yields are given for isolated products.
[c] Same results were obtained using 0.03 equiv of 46% Pd-C aerogel.

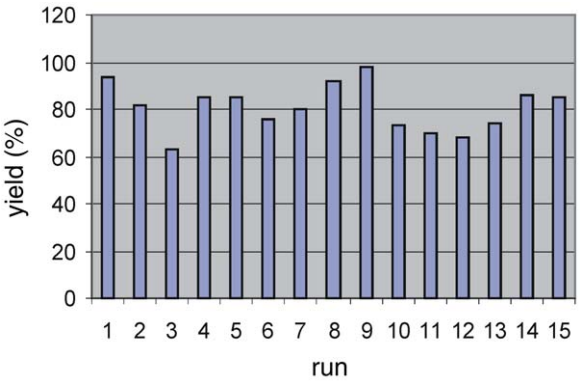


Figure 1 Recycling studies for the Sonogashira cross coupling of 3-iodoanisole and hept-1-yne in the presence of palladium-carbon aerogel as catalyst. Reactions were carried out under standard conditions; yields are given for isolated products.

In conclusion, we have shown that carbon aerogels doped with metallic palladium nanoparticles represent an efficient and ready-to-use catalyst for the Sonogashira cross-coupling reaction. The catalyst can be easily recovered in the presence of air, without any particular precautions and reused several times.

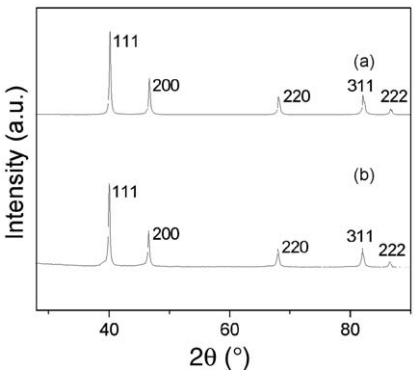


Figure 2 XRD patterns of: (a) original palladium-carbon aerogel and (b) recovered palladium-carbon aerogel after 15 cycles.

Melting points were determined with a Büchi B-545 apparatus and are uncorrected. All reagents and solvents are commercially available and were used as purchased, without further purification. Reaction products were purified on axially compressed columns, packed with 25–40 μm silica gel (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluted with *n*-hexane–EtOAc mixtures. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100.6 MHz) were recorded with a Bruker Avance 400 spectrometer. IR spectra were recorded with a Jasco FT/IR-430 spectrophotometer. Mass spectra were recorded with a Shimadzu GC-MS QP-2010S spectrometer.

1-(3-Methoxyphenyl)hept-1-yne (3c); Typical Procedure

In a 10-mL closed-cap flask containing 46% Pd-C aerogel (11 mg, 0.047 mmol) were placed CuI (19 mg, 0.1 mmol), Ph_3P (25 mg, 0.1 mmol), 3-iodoanisole (189 mg, 0.79 mmol), *i*-Pr_2NH (0.17 mL, 1.2 mmol), hept-1-yne (0.16 mL, 1.2 mmol), and previously degassed DMF (0.5 mL) under argon. To avoid the fragmentation of the catalyst, the reactor was orbitally stirred at 600 rpm using a Synthesis 1 Heidolph apparatus at 100 °C for 16 h. After cooling, the soln was removed by means of a Pasteur pipet and the catalyst was washed with DMF (3 × 0.3 mL). The combined organic extracts were diluted in Et_2O (100 mL), washed with brine (3 × 30 mL), dried (Na_2SO_4), and evaporated at reduced pressure. The residue (a yellow oil) was purified by high pressure column chromatography (silica gel, *n*-hexane–EtOAc, 99.5:0.5) to give **3c** as a yellow oil; yield: 153 mg (96%).

IR (neat): 2927, 2228, 1598, 1575, 1486, 1463, 1287, 1045, 780, 680 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.22 (t, *J* = 7.8 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.98 (br s, 1 H), 6.86 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 3.82 (s, 3 H), 2.44 (d, *J* = 7.2 Hz, 2 H), 1.64 (m, 2 H), 1.48 (m, 2 H), 1.41 (m, 2 H), 0.99 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100.3 MHz, $CDCl_3$): δ = 159.3, 129.2, 125.1, 124.1, 116.4, 114.0, 90.4, 80.5, 51.2, 31.2, 28.5, 22.3, 19.4, 14.0.

MS: *m*/*z* (%) = 202 (100, M$^+$), 145 (81), 115 (73), 147 (69).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found C, 83.03; H, 8.95.

Recycling Procedure

After each run, the Pd-C aerogel was recovered by decanting the soln and separating the catalyst system mechanically from the salts in the presence of air, without any particular precaution. It was simply picked up with a spatula, washed with DMF (3 × 0.3 mL), MeCN (5 × 1 mL), MeOH (5 × 1 mL), and DMF (0.3 mL), and immersed in DMF to keep it wet until subsequent utilization. In case of loss of activity, the Pd-C aerogel can be reactivated by heating it in DMF at 120 °C for 2 d.

4-(Hept-1-ynyl)acetophenone (3a)

Oil.

IR (neat): 2926, 2230, 1684, 1260, 825 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.82 (d, *J* = 8.2 Hz, 2 H), 7.43 (d, *J* = 8.2 Hz, 2 H), 2.59 (s, 3 H), 2.42 (t, *J* = 7.2 Hz, 2 H), 1.60 (p, *J* = 7.2 Hz, 2 H), 1.40–1.30 (m, 4 H), 0.90 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 197.4, 135.7, 131.7, 129.2, 128.2, 94.5, 80.1, 31.1, 28.3, 26.6, 22.3, 19.5, 14.0.

MS (EI, 70 eV): *m*/*z* (%) = 43 (100), 129 (17), 199 (16), 41 (15), 114 (10), 214 (M$^+$, 9).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found C, 84.13; H, 8.46.

1-(4-Methoxyphenyl)hept-1-yne (3b)

Oil.

IR (neat): 2926, 2200, 1603, 1510, 1245, 834 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.84 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 2.4 Hz, 2 H), 3.81 (s, 3 H), 2.42 (t, *J* = 7.2 Hz, 2 H), 1.62 (p, *J* = 7.2 Hz, 2 H), 1.41–1.29 (m, 4 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 159.0, 132.9, 116.3, 113.8, 88.8, 80.2, 55.2, 31.2, 28.6, 22.3, 19.4, 14.0.

MS (EI, 70 eV): *m*/*z* (%) = 45 (100), 147 (55), 41 (50), 202 (M$^+$, 47).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found C, 83.20; H, 8.99.

Ethyl 4-(Hept-1-ynyl)benzoate (3d)

Oil.

IR (neat): 2930, 1710, 2225, 1250, 830 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.95 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 2.41 (t, *J* = 7.2 Hz, 2 H), 1.61 (p, *J* = 7.2 Hz, 2 H), 1.43–1.36 (m, 4 H), 1.37 (t, *J* = 6.8 Hz, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 166.0, 131.3, 129.3, 129.1, 128.8, 93.8, 80.1, 60.9, 31.1, 28.3, 22.2, 19.4, 14.2, 13.9,

MS (EI, 70 eV): *m*/*z* (%) = 129 (100), 117 (65), 41 (62), 143 (50), 115 (47), 128 (46), 244 (M$^+$, 36).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found C, 78.57; H, 8.27.

1-(4-Methyl-3-nitrophenyl)hept-1-yne (3e)

Oil.

IR (neat): 2930, 2230, 1530, 1346, 895, 826 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.97 (s, 1 H), 7.49 (d, *J* = 7.8 Hz, 1 H), 7.24 (d, *J* = 7.8 Hz, 1 H), 2.57 (s, 3 H), 2.40 (t, *J* = 7.2 Hz, 2 H), 1.61 (p, *J* = 7.2 Hz, 2 H), 1.45–1.31 (m, 4 H), 0.93 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 149.0, 135.6, 132.6, 132.5, 127.4, 123.4, 92.7, 78.3, 31.1, 28.2, 20.20, 22.2, 19.3, 13.9.

MS (EI, 70 eV): *m*/*z* (%) = 43 (100), 129 (17), 199 (16), 214 (14), 231 (M$^+$, 3).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.78; H, 7.40; N, 6.04.

4-(Phenylethynyl)acetophenone (3f)

Mp 96–7 °C.

IR (KBr): 2992, 2217, 1677, 1262, 830, 750, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.95 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.57 (m, 2 H), 7.39 (m, 3 H), 2.62 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 196.8, 135.7, 131.3, 131.2, 128.3, 127.98, 127.8, 127.7, 122.2, 92.3, 88.2, 26.1.

MS (EI, 70 eV): *m*/*z* (%) = 205 (100), 220 (M$^+$, 76), 176 (50), 43 (46).

Anal. Calcd for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found C, 87.14; H, 5.51.

1-(3-Methoxyphenyl)-2-phenylacetylene (3g)

Mp 74–75 °C.

IR (KBr): 2930, 2250, 1595, 1229, 865, 762, 684 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.59 (m, 2 H), 7.39 (m, 3 H), 7.31 (d, *J* = 8.0 Hz, 1 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 7.12 (m, 1 H), 6.94 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 158.9, 131.2, 128.9, 127.9, 127.8, 123.8, 123.7, 122.7, 115.9, 114.5, 88.9, 88.7, 54.8.

MS (EI, 70 eV): *m*/*z* (%) = 208 (M^+, 100), 178 (23), 165 (22), 139 (9).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found C, 86.59; H, 5.80.

1-(4-Methoxyphenyl)-2-phenylacetylene (3h)
Mp 57–59 °C.

IR (KBr): 2930, 2211, 1510, 1244, 833, 750, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.58 (m, 2 H), 7.53 (d, *J* = 8.8 Hz, 2 H), 7.37 (m, 3 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 159.2, 132.6, 131.0, 127.9, 127.5, 123.2, 114.9, 113.6, 89.0, 87.6, 54.8.

MS (EI, 70 eV): *m*/*z* (%) = 208 (M^+, 100), 193 (44), 165 (37), 139 (12).

Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found C, 86.44; H, 5.79.

Ethyl 4-(Phenylethynyl)benzoate (3i)
Mp 72–73 °C.

IR (KBr): 2984, 2214, 1710, 1262, 850, 750, 688 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.58 (m, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.38 (m, 3 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 1.43 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 166.1, 131.3, 131.0, 129.3, 129.0, 128.3, 128.0, 127.4, 122.2, 91.8, 88.2, 60.7, 13.8.

MS (EI, 70 eV): *m*/*z* (%) = 250 (M^+, 100), 205 (88), 176 (47), 222 (33).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found C, 81.64; H, 5.62.

1-(4-Methyl-3-nitrophenyl)-2-phenylacetylene (3j)
Mp 106–107 °C.

IR (KBr): 2995, 2214, 1525, 1350, 826, 761, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.14 (s, 1 H), 7.64 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1 H), 7.56 (m, 2 H), 7.40 (m, *J* = 3.2 Hz, 3 H), 7.34 (d, *J* = 8 Hz, 1 H), 2.64 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 148.6, 135.0, 133.0, 132.4, 131.2, 128.4, 128.0, 127.0, 122.1, 121.9, 90.8, 86.4, 19.9.

MS (EI, 70 eV): *m*/*z* (%) = 237 (M^+, 100), 189 (66), 220 (52), 165 (50).

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found C, 75.86; H, 4.68; N, 5.92.

4-(3-Hydroxyprop-1-ynyl)acetophenone (3k)
Mp 81–82 °C.

IR (KBr): 3350, 2900, 2250, 1662, 1270, 820 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.82 (d, *J* = 7.2 Hz, 2 H), 7.43 (d, *J* = 7.2 Hz, 2 H), 4.51 (s, 2 H), 3.40 (s, 1 H), 2.55 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 197.6, 135.7, 131.2, 127.7, 127.2, 90.6, 84.0, 50.8, 26.1.

MS (EI, 70 eV): *m*/*z* (%) = 43 (100), 159 (88), 77 (71), 174 (M^+, 50), 131 (50).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found C, 75.90; H, 5.80.

3-(3-Methoxyphenyl)prop-2-ynol (3l)
Oil.

IR (neat): 3370, 2936, 2227, 1600, 1050, 850 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.21 (dd, J_1 = 8.4 Hz, J_2 = 7.6 Hz, 1 H). 7.04 (d, *J* = 7.6 Hz, 1 H), 6.99 (s, 1 H), 6.88 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H), 4.51 (s, 2 H), 3.82 (s, 3 H), 2.96 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 158.7, 128.9, 123.8, 123.1, 116.1, 114.5, 86.8, 84.9, 54.8, 50.9.

MS (EI, 70 eV): *m*/*z* (%) = 162 (M^+, 100), 91(64), 63 (32), 104 (31), 78 (30), 145 (13).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found C, 74.13; H, 6.22.

3-(4-Methoxyphenyl)prop-2-ynol (3m)
Oil.

IR (neat): 3334, 2926, 2235, 1600, 1247, 826 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.37 (d, *J* = 8.8 Hz, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 4.49 (s, 2 H), 3.78 (s, 3 H), 2.92 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 159.2, 132.7, 114.2, 113.5, 85.6, 85.0, 54.8, 50.9.

MS (EI, 70 eV): *m*/*z* (%) = 162 (M^+, 100), 91 (50), 131 (39), 145 (38).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found C, 73.97; H, 6.23.

Ethyl 4-(3-Hydroxyprop-1-ynyl)benzoate (3n)
Mp 63–64 °C.

IR (KBr): 3462, 2992, 2150, 1699, 1288, 1015, 855, 778 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 4.51 (s, 2 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 3.17 (s, 1 H), 1.36 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 165.7, 131.0, 129.4, 128.9, 126.80, 90.0, 84.1, 60.8, 50.8, 13.1.

MS (EI, 70 eV): *m*/*z* (%) = 131 (100), 77 (58), 103 (48), 159 (44), 204 (M^+, 30).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found C, 70.46; H, 5.94.

3-(4-Methyl-3-nitrophenyl)prop-2-ynol (3o)
Oil.

IR (neat): 3363, 2928, 2237, 1526, 1350, 1033, 882, 834, 800 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.95 (d, *J* = 1.2 Hz, 1 H), 7.49 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1 H), 7.24 (d, *J* = 7.6 Hz, 1 H), 4.50 (s, 2 H), 2.94 (s, 1 H), 2.55 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 148.4, 135.2, 133.3, 132.3, 127.0, 121.3, 88.8, 82.5, 50.7, 19.8.

MS (EI, 70 eV): *m*/*z* (%) = 115 (100), 91 (87), 174 (70), 191 (M^+, 53).

Anal. Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found C, 62.76; H, 4.72; N, 7.30.

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