Ligand-Free Copper Oxide Nanoparticle-Catalyzed Sonogashira Coupling Reaction

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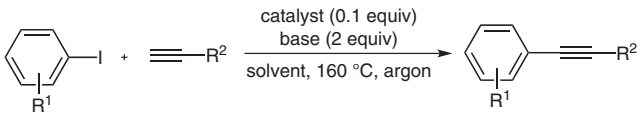
Abstract: The catalytic Sonogashira coupling reaction of terminal alkynes and aryl halides is developed using copper(II) oxide nanoparticles as catalyst in dimethyl sulfoxide. The procedure is experimentally simple, general, efficient, and free from addition of external cocatalysts or chelating ligands.

Key words: copper(II) oxide nanoparticles, Sonogashira coupling, ligand-free, nano catalyst

The catalytic coupling reaction of terminal alkynes with aryl or vinyl halides is named as Sonogashira coupling, which is typically performed with a palladium catalyst, a copper(I) cocatalyst, and an amine base under anhydrous and anaerobic conditions.[1] However, palladium complexes, the most commonly used catalysts for the Sonogashira-type cross-coupling reaction, are considerably expensive, which limits their application in industry.[1,2] Recently, much attention has been attracted to the use of copper complexes as the catalysts for the Sonogashira-type cross-coupling of aryl halides with terminal alkynes.[3] It was shown that copper halides chelated by many ligands such as triphenylphosphine,[3a,b] 1,10-phenanthroline,[3c,d] *N,N*-dimethylglycine,[3e] ethylenediamine,[3f] 2-aminopyrimidine-4,6-diol,[3g] and tertiary amines[3h,i] are effective catalysts in Sonogashira reaction. It is known that nanomaterials containing high surface area and reactive morphologies have been studied as effective catalysts for many organic syntheses due to the advantages of high atom efficiency, simplified isolation of product, and easy recovery and recyclability of the catalysts.[4] Since the copper(II) oxide nanoparticles are readily accessible, air-stable, recyclable, and free from addition of external chelating ligands, a couple of literature have reported the intermolecular cross-coupling reactions of aryl iodides with nitrogen, oxygen, sulfur, and selenide nucleophiles using copper(II) oxide nanoparticles under ligand-free conditions.[5] However, there are few successful examples of ligand-free copper nanoparticle-catalyzed cross Sonogashira coupling between aryl halides and terminal alkynes so far, except the article reported by Rothenberg.[6] For instance, Miura and co-workers have reported this reaction using the copper(I) oxide/triphenylphosphine catalytic system, however, a rather low yield of the Sonogashira product was given after 20 hours even in the reaction of iodobenzene with phenylacetylene at 120 °C.[3a] Li also reported the combination of the octahedral copper(I) oxide nanoparticles with triphenylphosphine and TBAB as an efficient and reusable system for the Sonogashira-type cross-coupling reaction under solventless conditions.[7] Recently, the copper nanocluster-catalyzed Sonogashira reaction was developed by Rothenberg in high yields.[8] From the point of economy and environment, the development of some efficient copper catalytic systems for Sonogashira reaction of a wide range of aryl and alkyl halides are still challenging. Herein, we wish to demonstrate the use of a simplest copper catalyst system for Sonogashira coupling of aryl halides and teminal alkynes (Scheme 1).



Scheme 1 Ligand-free nano-CuO-catalyzed Sonogashira coupling between aryl halides and terminal alkynes

We initiated our investigation of Sonogashira reaction between iodobenzene (**1a**) (1.2 equiv) and phenylacetylene (**2a**) (1 equiv) using 10 mol% of copper(II) oxide nanoparticle as catalyst. The first result was quite inspiring to note that 44% yield of **3aa** was obtained when the reaction was performed for 12 hours in the presence of 2 equivalents of potassium hydroxide as base in dimethyl sulfoxide at 160 °C (Table 1, entry 1).[9] Next, some other bases and solvents were examined in the presence of catalytic nano copper(II) oxide (Table 1, entries 2–5). Potassium carbonate was shown to be the best base in dimethyl sulfoxide giving 88% yield of the product (Table 1, entry 3), while cesium carbonate resulted in a yield of 43% as compared with potassium hydroxide (Table 1, entry 2). Other solvents gave no marked improvement compared with dimethyl sulfoxide when the base potassium carbonate was kept constant. For instance, only 15% of yield was realized when *N*,*N*-dimethylformamide was chosen as solvent (Table 1, entry 4), although *N*-methyl-2-pyrrolidinone could afford around 84% yield (Table 1, entry 5).

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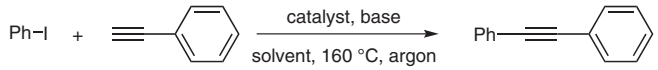
Other nano metal oxides, like nano-Fe_2O_3, nano-NiO, and nano-In_2O_3, could only produce trace amount of Sonogashira product under the same conditions (Table 1, entries 6–8). It was found that the yield of product dropped when the amount of nano-CuO catalyst was decreased (Table 1, entries 11). Interestingly, the normal commercial granules-CuO could not catalyze this type of Sonogashira reaction well, which proves that nanoparticles were involved in the reaction (Table 1, entries 12). With these data in hand, the reaction temperature and molar ratio of two reactants were optimized finally. It was found that lower temperatures below 160 °C significantly reduced the yields of this reaction (Table 1, entries 9, 10). A high temperature of up to 160 °C is a key factor, which is required to fully excite the catalytic activity of copper(II) oxide nanoparticles in the coupling reaction. Meanwhile, the yield of product **3aa** was improved up to 97% when the molar ratio between **1a** and **2a** was increased from 1.2 to 1.5 (Table 1, entry 13). In addition, the TEM analysis of the CuO nanoparticles, before and after reactions under the condition (Table 1, entry 13) showed that after the reaction, the morphology of CuO nanoparticles have been changed and most CuO nanoparticles were aggregated (Figure 1). This change of morphology was similar with the change of nano palladium in the catalytic Suzuki reaction.[10]

Based on the above-mentioned optimal conditions, a variety of substrates were examined in the coupling reaction and the results are listed in Table 2. It was shown that almost all the combinations of different alkynes and aryl iodides afforded high to excellent yields of target Sonogashira products. And the substrate scope for aryl iodides was wide enough for 1-iodo-3-methylbenzene or 1-iodo-4-methylbenzene, electron-efficient 1-iodo-3-methoxybenzene and electron-deficient 1-iodo-4-nitrobenzene as well. It was also found that satisfactory yield was obtained using aliphatic alkyne as substrate (Table 2, entry 20).

In summary, we have developed an experimentally simple and general procedure for the Sonogashira coupling reaction of terminal alkynes with aryl halides in dimethyl sulfoxide catalyzed by nano-CuO in excellent and high yields. Except for the solvent dimethyl sulfoxide and catalytic amount of nano-CuO, no other ligands or cocatalysts were required for the reaction to proceed smoothly. It was thus proven that copper(II) oxide nanoparticles were effective catalyst for the Sonogashira coupling reaction studied.

Table 1 Optimization of Nanocatalyst, Solvent, Base, and Temperature in the Sonogashira Reaction between Iodobenzene (**1a**) and Phenylacetylene (**2a**)[a]



1a **2a** **3aa**

Entry	Solvent	Base	Catalyst	Temp (°C)	Yield (%)[b]
1	DMSO	KOH	nano-CuO	160	44
2	DMSO	Cs_2CO_3	nano-CuO	160	43
3	DMSO	K_2CO_3	nano-CuO	160	88
4	DMF	K_2CO_3	nano-CuO	160	15
5	NMP	K_2CO_3	nano-CuO	160	84
6	DMSO	K_2CO_3	nano-Fe_2O_3	160	12
7	DMSO	K_2CO_3	nano-NiO	160	10
8	DMSO	K_2CO_3	nano-In_2O_3	160	13
9	DMSO	K_2CO_3	nano-CuO	120	11
10	DMSO	K_2CO_3	nano-CuO	145	55
11[c]	DMSO	K_2CO_3	nano-CuO	160	42
12	DMSO	K_2CO_3	CuO	160	23
13[d]	DMSO	K_2CO_3	nano-CuO	160	97

[a] Reaction conditions: aryl iodide (1.2 mmol), phenylacetylene (1.0 mmol), catalyst (0.1 mmol), solvent (2 mL), base (2 mmol), 160 °C, 12 h under argon.
[b] Isolated yield.
[c] Nano-CuO, 0.05 mmol.
[d] Aryl iodide (1.5 mmol), phenylacetylene (1.0 mmol).

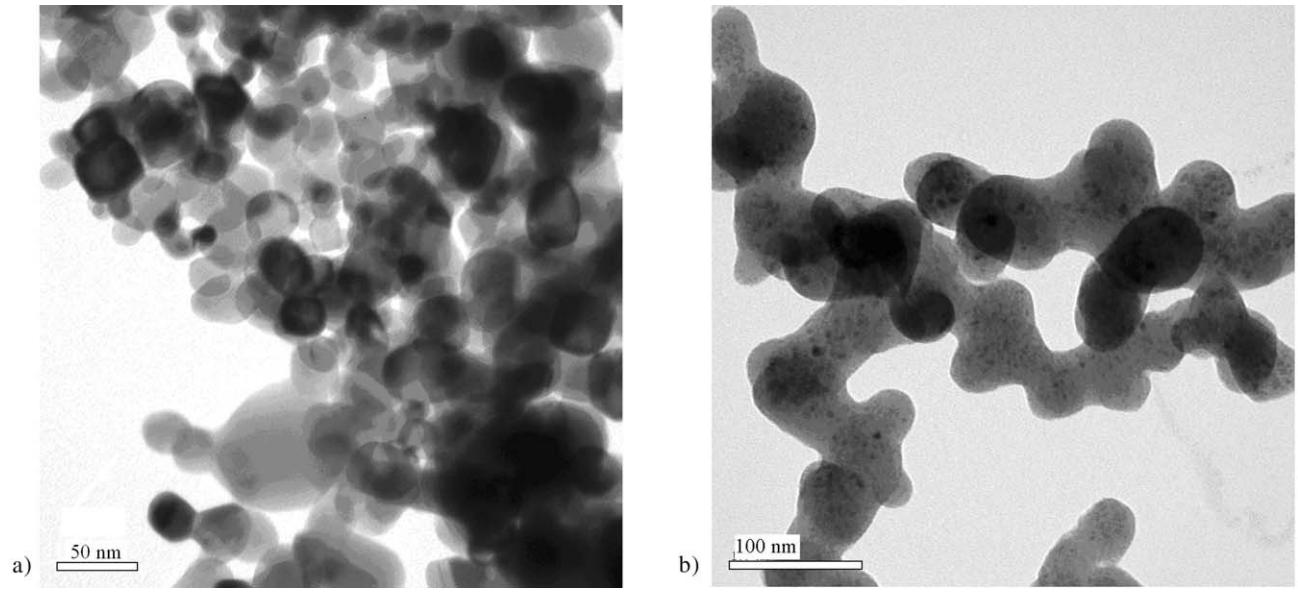
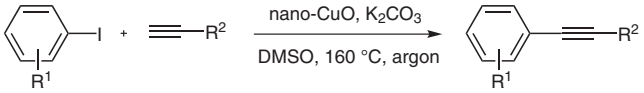


Figure 1 TEM images of (a) commercial CuO nanoparticles from Sigma-Aldrich and (b) CuO nanoparticles after the reaction

Table 2 Combinatorial Synthesis of Unsymmetric Diaryl-Substituted Ethyne via Efficient Sonogashira Coupling Reaction Catalyzed by Copper(II) Oxide Nanoparticles[a]



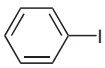
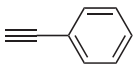
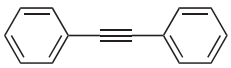
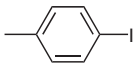
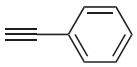
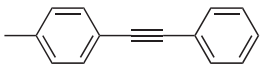
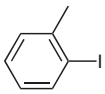
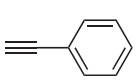
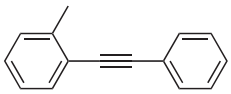
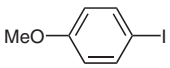
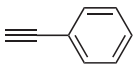
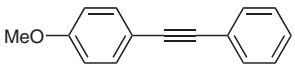
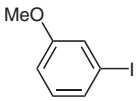
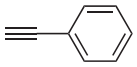
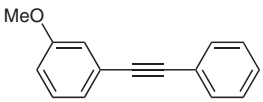
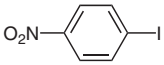
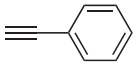
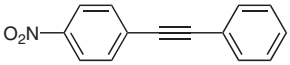
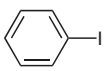
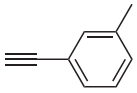
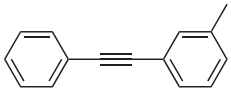
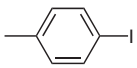
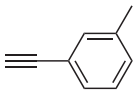
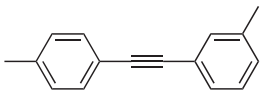
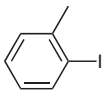
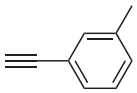
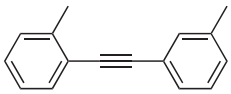
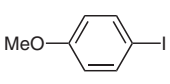
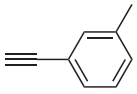
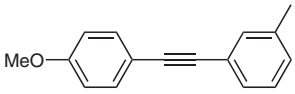
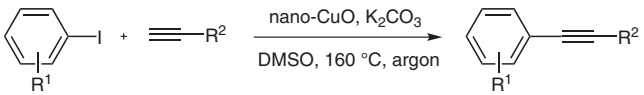
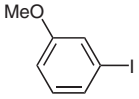
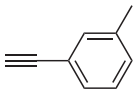
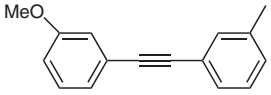
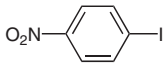
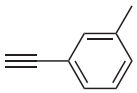
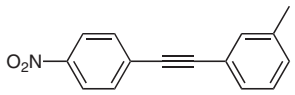
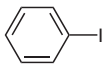
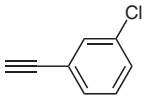
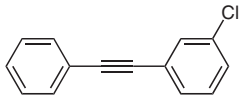
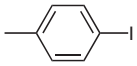
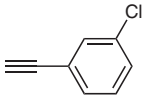
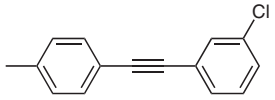
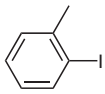
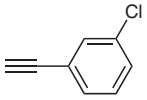
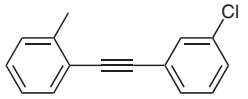
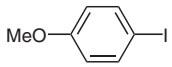
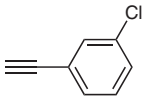
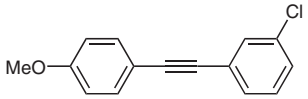
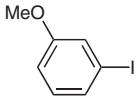
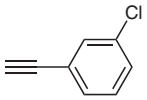
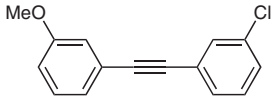
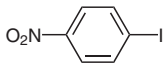
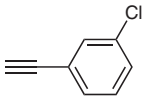
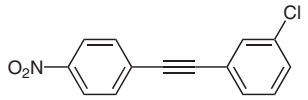
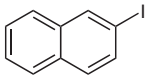
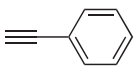
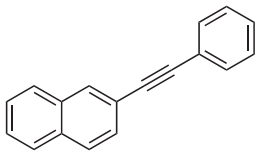
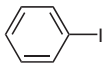
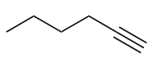
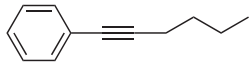
Entry	Aryl iodide	Alkyne	Product	Yield (%)[b]
1				97
2				96
3				97
4				74
5				78
6				80
7				91
8				95
9				99
10				95

Table 2 Combinatorial Synthesis of Unsymmetric Diaryl-Substituted Ethyne via Efficient Sonogashira Coupling Reaction Catalyzed by Copper(II) Oxide Nanoparticles[a] (continued)



Entry	Aryl iodide	Alkyne	Product	Yield (%)[b]
11				90
12				72
13				77
14				75
15				95
16				65
17				86
18				60
19				82
20				88

[a] Reaction conditions: aryl iodide (1.5 mmol), phenylacetylene (1.0 mmol), nano-CuO (0.1 mmol), DMSO (2 mL), K_2CO_3 (2 mmol), 160 °C, 12 h under argon.
[b] Isolated yield.

^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker AVANCE 600 spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were recorded with a Bruker Tensor 27 FT-IR spectrophotometer using KBr pellets. GC-MS was performed on a Finnigan Trace DSQ chromatograph. The morphology of CuO nanoparticles was tested by TEM, Tecnai-12 Philip Apparatus Co., United States. The nano-CuO was purchased from Sigma-Aldrich and the size of CuO was less than 50 nm. Petroleum ether used refers to the fraction boiling in the range of 60–90 °C.

Sonogashira Coupling Reaction with the Aid of CuO Nanoparticles; General Procedure

A mixture of aryl halide (1.5 mmol), alkyne (1.0 mmol), CuO nanoparticles (0.1 equiv), K_2CO_3 (2 equiv), and DMSO (2 mL) in a Schlenk tube was stirred under an argon atmosphere at 160 °C. The progress of the reaction was monitored by TLC (EtOAc–PE 1:100 or pure PE). After completion of the reaction, the reaction mixture was treated with H_2O (5 mL) and EtOAc (8 mL). The organic and aqueous layers were then separated, and the aqueous layer was extracted with EtOAc (5 × 3 mL). The combined organic extracts were dried (Na_2SO_4), then filtered, and evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether or petroleum ether–EtOAc) to afford the corresponding coupling products.

1, 2-Diphenylethyne
IR (KBr): 2927, 1493, 753, 685 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.31–7.35 (m, 6 H), 7.46 (d, *J* = 7.6 Hz, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 89.3, 123.2, 128.2, 128.3, 131.6.

MS (ES): *m*/*z* = 178 $[M]^+$.

1-Methyl-4-(2-phenylethynyl)benzene
IR (KBr): 3040, 2918, 2211, 1591, 1508, 817, 754 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 7.14 (d, *J* = 7.5 Hz, 2 H), 7.32 (t, *J* = 5.9 Hz, 3 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.51 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.4, 87.7, 88.5, 119.2, 122.5, 127.0, 127.2, 128.0, 130.5, 130.5, 137.3.

MS (ES): *m*/*z* = 191 $[M]^+$.

1-Methyl-2-(2-phenylethynyl)benzene
IR (KBr): 3061, 3026, 2919, 2214, 1599, 1493, 754, 698 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.51 (s, 3 H), 7.15 (s, 1 H), 7.22 (t, *J* = 6.4 Hz, 2 H), 7.31–7.35 (m, 3 H), 7.49 (d, *J* = 7.5 Hz, 1 H), 7.53 (d, *J* = 7.1 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.7, 88.3, 93.3, 123.1, 123.6, 125.5, 128.1, 128.3, 128.3, 129.4, 131.5, 131.8, 140.2.

MS (ES): *m*/*z* = 192 $[M]^+$.

1-Methoxy-4-(2-phenylethynyl)benzene
IR (KBr): 2910, 2212, 1597, 1507, 1104, 830 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 3.74 (s, 3 H), 6.80 (d, *J* = 8.2 Hz, 2 H), 7.23–7.26 (m, 3 H), 7.40 (d, *J* = 8.1 Hz, 2 H), 7.44 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.2, 88.0, 89.3, 113.9, 115.3, 123.5, 127.9, 128.2, 131.3, 133.0, 159.5.

MS (ES): *m*/*z* = 208 $[M]^+$.

1-Methoxy-3-(2-phenylethynyl)benzene
IR (KBr): 2956, 1587, 1489, 1229, 1075, 794, 763 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 7.06 (s, 1 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 5.4 Hz, 1 H), 7.34 (d, *J* = 5.8 Hz, 3 H), 7.53 (d, *J* = 6.4 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.2, 89.1, 89.2, 114.9, 116.3, 123.1, 124.1, 124.2, 128.3, 128.3, 129.4, 131.6, 159.3.

MS (ES): *m*/*z* = 208 $[M]^+$.

1-Nitro-4-(2-phenylethynyl)benzene
IR (KBr): 2963, 2210, 1589, 1510, 1343, 856, 759 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.39 (s, 3 H), 7.56 (s, 2 H), 7.66 (d, *J* = 7.8 Hz, 2 H), 8.22 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 87.5, 94.6, 122.0, 123.6, 128.5, 129.2, 130.2, 131.8, 132.2, 146.9.

MS (ES): *m*/*z* = 223 $[M]^+$.

1-Methyl-3-(2-phenylethynyl)benzene
IR (KBr): 3052, 2920, 2208, 1600, 1493, 784, 754 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 7.10 (d, *J* = 7.0 Hz, 1 H), 7.22 (t, *J* = 8.5 Hz, 2 H), 7.32 (s, 4 H), 7.52 (d, *J* = 6.0 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.2, 89.0, 89.6, 123.1, 123.4, 128.1, 128.2, 128.3, 128.7, 129.1.

MS (ES): *m*/*z* = 192 $[M]^+$.

2-*m*-Tolyl-1-*p*-tolylethyne
IR (KBr): 3031, 2915, 1589, 1509, 816, 783 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.35 (d, *J* = 9.3 Hz, 6 H), 7.14 (t, *J* = 8.7 Hz, 3 H), 7.23 (t, *J* = 9.0 Hz, 1 H), 7.32 (d, *J* = 7.4 Hz, 1 H), 7.35 (s, 1 H), 7.41 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.2, 21.5, 88.8, 89.2, 120.2, 123.2, 128.2, 128.6, 128.9, 129.0, 131.4, 132.1, 137.9, 138.2.

MS (ES): *m*/*z* = 206 $[M]^+$.

2-*m*-Tolyl-1-*o*-tolylethyne
IR (KBr): 3025, 1591, 1486, 785, 754 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 2.51 (s, 3 H), 7.13–7.17 (m, 2 H), 7.23 (d, *J* = 8.8 Hz, 3 H), 7.35 (t, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 7.4 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.7, 20.2, 86.9, 92.4, 122.0, 122.3, 124.5, 127.1, 127.2, 127.5, 128.0, 128.4, 130.7, 131.0, 136.9, 139.1.

MS (ES): *m*/*z* = 206 $[M]^+$.

1-[2-(4-Methoxyphenyl)ethynyl]-3-methylbenzene
IR (KBr): 2961, 1597, 1508, 1173, 884, 791 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 3.82 (s, 3 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 7.4 Hz, 1 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 7.32 (d, *J* = 7.5 Hz, 1 H), 7.34 (s, 1 H), 7.46 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.2, 55.2, 88.2, 89.0, 113.9, 115.4, 123.3, 128.2, 128.5, 128.8, 132.0, 133.0, 137.9, 159.5.

MS (ES): *m*/*z* = 222 $[M]^+$.

1-[2-(3-Methoxyphenyl)ethynyl]-3-methylbenzene
IR (KBr): 3004, 2950, 2837, 2208, 1595, 1485, 1241, 782, 687 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 3.82 (s, 3 H), 6.89 (d, *J* = 8.3 Hz, 1 H), 7.05 (s, 1 H), 7.11–7.15 (m, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 7.5 Hz, 1 H), 7.36 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.2, 55.2, 88.9, 89.3, 114.8, 116.2, 122.9, 124.1, 124.3, 128.2, 128.7, 129.2, 129.3, 132.2, 138.0, 159.3.

MS (ES): *m*/*z* = 222 $[M]^+$.

1-Methyl-3-[2-(4-nitrophenyl)ethynyl]benzene
IR (KBr): 2964, 2202, 1590, 1510, 1340, 850, 796 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.21 (d, *J* = 7.6 Hz, 1 H), 7.28 (t, *J* = 7.6 Hz, 1 H), 7.37 (t, *J* = 10.1 Hz, 2 H), 7.65 (d, *J* = 8.2 Hz, 2 H), 8.21 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.2, 87.2, 94.9, 121.8, 123.6, 128.4, 128.9, 130.1, 130.3, 132.2, 132.3, 138.2, 146.8.

MS (ES): *m*/*z* = 237 $[M]^+$.

1-Chloro-3-(2-phenylethynyl)benzene
IR (KBr): 3064, 2223, 1593, 1490, 783, 751 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.24–7.31 (m, 2 H), 7.35 (s, 3 H), 7.40 (d, *J* = 7.3 Hz, 1 H), 7.52 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 87.9, 90.5, 122.7, 125.0, 128.4, 128.4, 128.6, 129.5, 129.7, 131.4, 131.6, 134.1.

MS (ES): *m*/*z* = 212 $[M]^+$.

1-Chloro-3-(2-*p*-tolylethynyl)benzene
IR (KBr): 2921, 1588, 1465, 816, 788, 710 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 7.16 (d, *J* = 7.4 Hz, 2 H), 7.24–7.29 (m, 2 H), 7.38–7.42 (m, 3 H), 7.50 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.5, 87.3, 90.7, 119.6, 125.2, 128.2, 129.1, 129.5, 129.6, 131.3, 131.5, 134.1, 138.8.

MS (ES): *m*/*z* = 226 $[M]^+$.

1-[2-(3-Chlorophenyl)ethynyl]-2-methylbenzene
IR (KBr): 3063, 1555, 1450, 876, 750, 714 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.50 (s, 3 H), 7.18 (t, *J* = 7.2 Hz, 1 H), 7.24 (d, *J* = 5.9 Hz, 2 H), 7.26–7.31 (m, 2 H), 7.40 (d, *J* = 7.2 Hz, 1 H), 7.49 (d, *J* = 7.5 Hz, 1 H), 7.51 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.7, 89.5, 91.8, 122.4, 125.2, 125.6, 128.3, 128.6, 129.5, 129.5, 129.6, 131.3, 131.9, 134.1, 140.3.

MS (ES): *m*/*z* = 226 $[M]^+$.

1-Chloro-3-[2-(4-methoxyphenyl)ethynyl]benzene
IR (KBr): 2961, 2220, 1591, 1506, 1174, 885, 829, 790 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.88 (d, *J* = 7.7 Hz, 2 H), 7.24–7.28 (m, 2 H), 7.38 (d, *J* = 7.0 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 2 H), 7.49 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.3, 86.7, 90.6, 114.0, 114.8, 125.3, 128.1, 129.5, 129.5, 131.2, 133.1, 134.1, 159.8.

MS (ES): *m*/*z* = 242 $[M]^+$.

1-Chloro-3-[2-(3-methoxyphenyl)ethynyl]benzene
IR (KBr): 2985, 2225, 1569, 1483, 1125, 926, 871, 784 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.90–6.91 (d, *J* = 8.2 Hz, 2 H), 7.05 (s, 1 H), 7.12 (d, *J* = 7.4 Hz, 1 H), 7.25–7.31 (m, 3 H), 7.41 (d, *J* = 7.2 Hz, 1 H), 7.52 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.3, 87.7, 90.4, 115.2, 116.3, 123.7, 124.2, 124.9, 128.5, 129.4, 129.5, 129.7, 131.4, 134.1, 159.3.

MS (ES): *m*/*z* = 241 $[M]^+$.

1-Chloro-3-[2-(4-nitrophenyl)ethynyl]benzene
IR (KBr): 3067, 2217, 1647, 1593, 1513, 883, 794, 748 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 (t, *J* = 7.7 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.44, (d, *J* = 7.5 Hz, 1 H), 7.55 (s, 1 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 8.23 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 88.4, 92.9, 123.6, 123.8, 129.5, 129.6, 129.7, 129.9, 131.6, 132.3, 134.4, 147.2.

MS (ES): *m*/*z* = 257 $[M]^+$.

2-(2-Phenylethynyl)naphthalene
IR (KBr): 3054, 1596, 1494, 748 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.2 Hz, 3 H), 7.48 (d, *J* = 2.7 Hz, 2 H), 7.57 (d, *J* = 7.2 Hz, 3 H), 7.80 (s, 3 H), 8.04 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 89.7, 89.8, 120.6, 123.4, 126.5, 126.6, 127.8, 128.0, 128.3, 128.3, 128.4, 131.4, 131.7, 132.8, 133.1.

MS (ES): *m*/*z* = 228 $[M]^+$.

1-(Hex-1-ynyl)benzene
IR (KBr): 3059, 2931, 2867, 2232, 1489, 1450, 1378, 1238, 754, 691 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 6.2 Hz, 3 H), 1.49 (t, *J* = 5.7 Hz, 2 H), 1.59 (d, *J* = 6.3 Hz, 2 H), 2.41 (d, *J* = 6.0 Hz, 2 H), 7.25 (d, *J* = 6.0 Hz. 3 H), 7.38 (d, *J* = 5.5 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.6, 19.1, 22.0, 30.9, 80.6, 90.4, 124.2, 127.4, 128.1, 131.5.

MS (ES): *m*/*z* = 158 $[M]^+$.

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