Graphical Abstract

Agarose Functionalized Phosphorus Ligand for Stabilization of Small-Sized Palladium and Copper Nanoparticles: Efficient Heterogeneous Catalyst for Sonogashira Reaction

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ABSTRACT

Mono-dispersed and small-sized bimetallic copper and palladium nanoparticles were successfully supported on phosphinite functionalized agarose biopolymer. The new material was characterized using various techniques such as solid state UV-Vis and FT-IR spectroscopies, SEM, EDX, TGA, HRTEM, SAED, EDX-Map, and nitrogen adsorption-desorption analysis. The heterogeneous and recyclable catalyst has been used in Sonogashira coupling reaction of aryl iodides at room temperature and aryl bromides at 50 °C under low palladium loading conditions (0.05 mol%).

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1. Introduction

The design and preparation of new heterogeneous palladium catalysts has attracted attention because the recovery of expensive palladium catalysts is important from an economic and green chemistry standpoint.¹ Different inorganic materials as a solid supports were employed for heterogenization of palladium catalysts in various coupling reactions.¹ However, naturally occurring organic solids which are degradable, cheap, available and abundant in nature are good alternative to inorganic solid supports.² Palladium catalyzed Sonogashira coupling reaction, which is a reaction of vinyl or aryl halides or triflates with terminal alkynes is one of the most powerful approaches for the construction of aryl-alkynes and conjugated enynes in the presence or absence of a copper(I) co-catalyst.³ The enyne products have extensive applications in natural products, agriculture and pharmaceutical industries.^{4,5} Despite numerous reports on copper-free Sonogashira coupling reactions,⁶ it has been demonstrated that addition of copper under oxygen free conditions leads to increase in efficiency of Sonogashira coupling reaction.⁶ Furthermore, some attempts have been made to carry out Sonogashira reaction in the absence of palladium using other transition metals such as iron,⁷ copper^{8,9} and gold¹⁰ catalysts. However, in most of these cases, results are limited to use of aryl iodides and activated bromides under high reaction temperature ($\geq 130^\circ\text{C}$) and catalyst loading.

In recent years much attention has been paid to the use of bimetallic nanoparticles consisting of two different metal elements as heterogeneous catalysts.¹¹ Presence of two metals in the catalyst causes exhibition of superior catalytic activity and selectivity compared to their monometallic analogues. Due to the abundant catalytic applications of palladium catalysts, among the different types of bimetallic catalysts, palladium based bimetallic catalysts are designated as promising catalysts in different organic transformations.¹² For instance, Pd/Ni,¹³ Pd/Au,¹⁴ Pd/Pt,¹⁵ and Pd/Cu¹⁶ have been introduced as efficient bimetallic materials in different applications.

Recently we have reported agarose as bioorganic and degradable polymer for stabilization of palladium or copper nanoparticles and their applications in different coupling reactions.¹⁷ Among the different ligands for stabilization of palladium catalysts, functional groups containing phosphorus atoms are excellent ligands for stabilization of palladium species during coupling reactions.¹⁸ Herein, we wish to report bimetallic copper and palladium nanoparticles supported on phosphorus functionalized agarose as an efficient catalyst in Sonogashira coupling reaction under mild reaction conditions.

2. Results and Discussion

Agarose supported copper nanoparticles (CuNPs@Agarose) were prepared according to our previous report.^{17a} Phosphorus functionalized CuNPs@Agarose was obtained from the reaction of CuNPs@Agarose and chlorodiphenylphosphine (PPh_2Cl) in dry toluene. The amount of active phosphorus was determined by reacting phosphorus functionalized CuNPs@Agarose with an excess of molecular iodine in refluxing acetonitrile until the consumption of I_2 was stopped. On the basis of titration of unreacted iodine by sodium thiosulfate, the phosphorus content of compound was determined to be 1.9 mmol g^{-1} . The final catalyst containing palladium and copper nanoparticles which is referred as PdCu@Phos.Agarose throughout the text of this article, was easily prepared by treating phosphorus functionalized CuNPs@Agarose with $\text{Pd}(\text{OAc})_2$ in CH_2Cl_2 . Using ICP analysis,

the content of palladium and copper in the final material was found to be 0.03 and 0.5 mmol g^{-1} respectively.

A SEM image of the PdCu@Phos.Agarose showed the presence of large sheets of agarose in micro scale dimension (Figure 1). Furthermore, elemental maps study of this image confirms existence of Pd, Cu, C, and P elements in the structure (Figure , S).

Figure 1. a) SEM image of the PdCu@Phos.Agarose; b) EDX-Map image of PdCu@Phos.Agarose

In addition, energy-dispersive X-ray spectroscopy (EDS) analysis of material confirmed presence of palladium, copper and phosphorus species in the PdCu@Phos.Agarose structure (Figure 2).

Figure 2. EDX image of the PdCu@Phos.Agarose

Thermogravimetric analysis of the catalyst showed three determined weight loss (Figure 3). The first weight loss is related to water and physically absorbed solvents. The second and third steps were may related to the phosphinite removal and decomposition of the agarose biopolymer respectively.

Figure 3. Thermogravimetric diagram of the catalyst.

The reduction and formation of copper and palladium nanoparticles in PdCu@Phos.Agarose was confirmed by solid-state UV-Vis spectroscopy, in which the peaks at 310 and 420 nm related to CuBr and Pd(OAc)₂ respectively,¹⁹ disappeared upon formation of the PdCu@Phos.Agarose. (Figure 4).

Figure 4. DRS-UV-Vis spectra of Pd(OAc)₂, CuBr and PdCu@Phos.Agarose nanocatalyst.

HRTEM image of PdCu@Phos.Agarose showed presence of supported mono dispersed and uniform nanoparticles in the structure of material (Figure 5a-c). According to the particle size distribution plot obtained from TEM measurements, average sizes of nanoparticles were determined in 5-7 nm (Figure 2, SI). Figure 5d shows the selected area diffraction pattern (SAED) analysis with prominent ring pattern corresponding to Cu and Pd. The diffraction pattern shows prominent rings with interplanar spacing values of 0.20, 0.15 and 0.13 nm corresponding to (111), (200) and (220) planes respectively for Cu with fcc structure (JCPDS no. 04-0836). Similarly, *d*-spacing values, 0.25 and 0.14 nm corresponds to (111) and (220) planes of *fcc*-Pd (JCPDS no. 46-1043) respectively. Additional ring patterns corresponding to Cu₃Pd alloy planes with *d*-spacing values of 0.32 and 0.26 nm corresponding to (101) and (110) planes respectively. The Cu₃Pd alloy form exists as a tetragonal structure, confirming the formation of an additional secondary phase.

Figure 5. (a-c) Representative HRTEM images and (d) SAED pattern of PdCu@Phos.Agarose.

Adsorption and desorption isotherms of nitrogen of the PdCu@Phos.Agarose sample showed the typical type III isotherm with an H3 hysteresis loop which is typical for polymeric structures²⁰ as defined by IUPAC nomenclature and indicated that polymeric structure were preserved during the synthesis (Figure 6). The result also indicated BET surface area of 26 m²/g, pore volume of 0.35 cm³/g and pore diameter of 3.2 nm.

Figure 6. The nitrogen adsorption-desorption isotherm of the PdCu@Phos.Agarose.

XRD studies of PdCu@Phos.Agarose are shown in Figure 7. The analysis shows the presence of crystalline peaks along with high amorphous organic background. The diffracted peaks observed at 2θ value of 24°, 34°, 36° and 39° corresponds to the lattice plane (101), (110), (110), and (110) respectively of Cu₃Pd (JCPDS no.07-0138) which matches well with the SAED pattern as shown in Figure 5d.²¹ Further, low intense peaks at 2θ value of 55°, 58° and 60° matches to the (207) planes of Cu₃Pd (JCPDS no.07-0138). Similarly, the crystalline peak occurring at 2θ value

of 41° corresponds to the lattice plane (110) of CuPd (JCPDS no. 48-1551).²² Apart from the complex structure, individual peaks of Cu and Pd were observed at 2θ value of 43° and 68° corresponds to (111) and (220) planes matching well with the SAED pattern respectively.

Figure 7. X-Ray diffractogram of PdCu@Phos.Agarose

The X-ray photoelectron spectroscopy (XPS) spectra of the region corresponding to the binding energy range of 335-342 eV related to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ was studied. The results showed the presence of two intensive doublets at 335.5 and 340.7 eV related to Pd(0) and peaks at 337 and 342.5 eV related to Pd(II) species. (Figure 8a).²³ Moreover, in the XPS spectra, the binding energy of Cu $2p_{3/2}$ centered at 932.1 and 934.8 eV were observed that indicate the presence of both metallic Cu and Cu₂O species (Figure 8b).²⁴

Table 1 Screening of different reaction conditions for the reaction of iodobenzene with phenylacetylene.^a

Entry	Solvent	Base	Temp. (°C)	Pd (mol %)	Yield (%) ^b
1	DMF	Et ₃ N	50	0.05	2
2	DMF	Piperidine	50	0.035	6
3	DMF	Piperidine	50	0.05	30
4	DMSO	Piperidine	50	0.035	70
5	DMSO	Piperidine	50	0.05	85

Figure 8. a) XPS spectrum of PdCu@Phos.Agarose in the Pd 3d region and b) in the Cu 2p region

Furthermore, the high-resolution of P 2p XPS spectrum is shown in Figure 9 which reveals the presence of spin-orbit peaks related P-C bond at 132.3 eV and P-O bond at 133.5 eV in prepared PdCu@Phos.Agarose.²⁵

Figure 9. XPS spectrum of PdCu@Phos.Agarose in the P 2p region

The catalytic application of new PdCu@Phos.Agarose was assessed in Sonogashira coupling reaction of aryl halides. Initially, reaction of iodobenzene with phenylacetylene was selected as a model reaction and effect of different factors such as solvent, base and catalyst amount was investigated (Tables S1 and 1). Results indicated that using H₂O or mixture of H₂O-DMF as solvent in the presence of different bases at 50 °C afford low yields for the reaction (Table S1, entries 1-12). This lack of reactivity is may related to poor solubility of substrates in aqueous media. Using THF or mixture of THF-H₂O did not improve the reaction yield (Table S1, entries 13-15). Study of the reaction in dipolar solvents such as DMF, DMSO and *N,N*-dimethylacetamide (DMA) in the presence of organic bases piperidine and 1,4-diazabicyclo[2.2.2]octane (DABCO) increased reaction yields (Table 1). However, the best yield was obtained using DMA as a solvent and DABCO as a base using 0.05 mol% Pd at 50 °C (Table 1, entry 11). It is worth mentioning that performing reaction at room temperature (30 °C) caused a 4% reduction in the reaction yield; therefore this was selected as the optimized reaction temperature (Table 1, entry 12).

6	DMSO	Piperidine	30	0.05	53
7	DMSO	DABCO	30	0.05	58
8	DMSO	<i>t</i> -BuOK	30	0.05	37
9	DMSO	K ₂ CO ₃	30	0.05	8
10	DMA	Piperidine	50	0.05	30
11	DMA	DABCO	50	0.05	91 ^c
12	DMA	DABCO	30	0.05	87 ^c
13	DMA	DBU	30	0.05	4
14	DMA	K ₃ PO ₄ ·3H ₂ O	30	0.05	38
15	DMA	Piperidine	30	0.05	7
16	DMA	Cs ₂ CO ₃	30	0.05	4
17	DMA	Et ₃ N	30	0.05	2
18	DMA	<i>t</i> -BuOK	30	0.05	4
19	DMA	K ₂ CO ₃	30	0.05	33
20	Diglyme	DABCO	30	0.05	40

^a Reactions carried out on a 0.5 mmol scale using 8.5 mg PdCu@Phos.Agarose catalyst (containing 0.05 mol% Pd and 0.8 mol% Cu).

^b GC conversion

^c Isolated yield of product

Having optimized conditions in hand, DMA as a solvent, DABCO as a base, and 0.05 mol% Pd, the substrate scope of the Sonogashira reaction was investigated. Results indicated that aryl iodides containing both electron donating groups as well as electron withdrawing groups reacted well with phenylacetylene and 4-ethynyltoluen and desired alkyne products were obtained in 73-96% isolated yields (Table 2, entries 1-7, 11-12, 16-22). Reactions of 2-iodo-4-nitrotoluene as sterically hindered aryl iodides proceeded well and afford coupling product in 79-82%

isolated yield (Table 2, entries 3, 18). Also, reactions of aryl iodides with propargyl alcohol proceeded very efficient and gave desired alkynes in excellent yields (95-98%) (Table 2, entries 14, 15). However, reactions of aryl bromides under optimized reaction conditions at 30 °C were sluggish therefore; the temperature was raised to 50 °C. The reaction of aryl bromides such as 4-nitrobromobenzene, 4-bromobenzaldehyde, and 5-bromopyrimidinewere performed well and coupling products were obtained in high yields (Table 2, entries 8-10, 23, 24).

Table 2 Sonogashira coupling reaction of structurally different aryl iodides and bromides with alkynes in the presence of the catalyst.^a

Entry	ArX	R	Product	Isolated Yield%
1		Ph	1a	88
2		Ph	1b	97 ^b
3		Ph	1c	80

Tetrahedron

4		Ph	1d		75
5		Ph	1e		95
6		Ph	1f		75
7		Ph	1g		77
8		Ph	1b		72 ^c
9		Ph	1h		97 ^d
10		Ph		1i	83 ^d
11		Ph	1j		95
12		Ph		1k	75
13		HOCH ₂ -	1l		98
14		HOCH ₂ -	1m		95

15		HOCH_2^-	1n	98
16		$4\text{-MeC}_6\text{H}_4^-$	1k	95
17		$4\text{-MeC}_6\text{H}_4^-$	1o	99 ^b
18		$4\text{-MeC}_6\text{H}_4^-$	1p	83
19		$4\text{-MeC}_6\text{H}_4^-$	1q	80
20		$4\text{-MeC}_6\text{H}_4^-$	1r	96
21		$4\text{-MeC}_6\text{H}_4^-$	1s	91
22		$4\text{-MeC}_6\text{H}_4^-$	1t	75
23		$4\text{-MeC}_6\text{H}_4^-$	1u	88 ^d
24		$4\text{-MeC}_6\text{H}_4^-$	1o	73 ^c

^a Isolated yield after column chromatography, reaction carried out using compound aryl halide (0.5 mmol), alkyne (0.75 mmol), DABCO (1 mmol), DMA (2 mL) and catalyst (8.5 mg containing 0.05 mol% Pd and 0.8 mol% Cu).

^b Reaction performed during 8 h

^c Reactions performed at 50 °C

^d Reaction performed using 0.1 mol% catalyst during 48 h

^e Reaction performed using Pd(PPh₃)₂Cl/CuI catalyst

In order to show the practical applicability of the catalyst, we have scaled up the reaction of iodobenzene to 10 mmol with 15 mmol phenylacetylene under optimized reaction conditions. Results indicated that reaction proceed well affording 90% isolated yields at 24 h. Furthermore, the Pd-Cu supported catalyst is stable and recyclable up to three reaction runs, giving an average of 89% isolated yields under the optimized reaction conditions. Leaching of Pd and Cu to reaction mixture after first run was determined by ICP analysis to be 2% and 1.4% respectively.

Thermogravimetric analysis of the catalyst after 3rd run showed stability and existence of organic group in the catalyst structure (Figure 10).

Figure 10. Thermogravimetric analysis of the catalyst after 3rd run

Furthermore TEM image of recycled catalyst showed preserve of nano structure of catalyst with small aggregation of nanoparticles (Figure 11). Particle size distribution plot obtained from TEM measurements showed that the major part of the particles is located between 6-7 nanometers (Figure 3, SI).

Figure 11. TEM image of reused catalyst after 3rd run

In addition, SEM image of recycled catalyst after 3rd run showed preserve of gel-like structure of catalyst during the reaction (Figure 1, supporting information). Furthermore, energy-dispersive X-ray spectroscopy (EDS) analysis of the reused catalyst showed presence of Pd, Cu and P species in the catalyst structure (Figure 4, SI).

Comparison catalytic activity of presented Pd-Cu nanocatalyst with some of other Pd-Cu bimetallic catalysts in Sonogashira coupling reaction of iodobenzene with phenylacetylene are presented in Table 3. The results indicated Pd-Cu nanocatalyst has overall high catalytic activity at low palladium loading and using mild reaction temperature. Also, using monometallic Pd@Phos.Agarose or Cu@Phos.Agarose low yield for the reaction were obtained (Table 3, entries 7 and 8).

Table 3 Comparing catalytic activity of presented PdCu@Phos.Agarose with other Pd/Cu bimetallic catalysts, Pd@Phos.Agarose and Cu@Phos.Agarose in Sonogashira reaction of iodobenzene with phenylacetylene.

Entry	Catalyst	TOF(h ⁻¹)	Pd (mol %)	Cu (mol %)	T (°C)	Yield ^b (%)
1	rGO@Cu ₄₈ Pd ₅₂ ^{16c}	145.31	0.63	0.10	120	93
2	MMT@Pd/Cu ^{16d}	6.06	1	1.15	65	97 ^a
3	Poli-βCD/Pd/Cu-TPP ^{16e}	16.04	0.5	0.70	70	96 ^a

4	Pd/Cu-ARF(II) ^{16h}	43.43	Not reported	2.05	80	85
5	Pd-CuFe ₂ O ₄ @SiO ₂ ¹⁶ⁱ	10.97	0.3	0.27	50	80
6	PdCu@Phos.Agarose	73.33	0.05	0.80	30	88
7	Pd@Phos.Agarose		0.03	--	30	45
8	Cu@Phos.Agarose		--	0.80	30	20

^a In the presence of 2 mol% PPh₃

^b GC conversion

3. Conclusions

In conclusion, in this study we have successfully synthesized and characterized dual palladium and copper nanoparticles supported phosphinite functionalized agarose biopolymer. The catalytic activity of this bimetallic catalyst was assessed in Sonogashira coupling reactions of aryl iodides and bromides under low Pd loading and mild reaction conditions. The protocol is applicable for large-scale operation and the catalyst is recyclable which has been applied in three consecutive runs without noticeable change in its catalytic activity.

4. Experimental section

4.1. General:

All chemicals were purchased from Acros, Sigma-Aldrich, and Merck and used without further purification. ¹H NMR spectra were recorded at 400 MHz and ¹³C NMR were recorded at 100 MHz in CDCl₃ using TMS as internal standard. The scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX) was obtained using Carl Zeiss ΣiGMA instrument. Transmission electron microscopic (TEM) were recorded using (TEM, JEOL 2010, Japan) instrument. Thermogravimetric analysis was conducted from room temperature to 700 °C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. DRS-UV-vis spectra were determined by Perkin-Elmer, Lambda 25 instrument. The content of copper and palladium in the catalyst was determined using atomic absorption spectrometry (Varian). FT-IR spectra were recorded using a Bruker Vector 22 instrument after mixing the samples with KBr.

4.2. Preparation of Agarose-supported copper nanoparticles:

The synthesis of the Agarose containing copper nanoparticles has been introduced by our recent report^{16a} which will briefly be explained in the following paragraphs. 2 g agarose was added to 200 mL distilled water and mixture was stirred for 12 h at 80 °C. In other flask, solution of 0.2 mmol CuBr in 25 mL of H₂O was added to Agarose hydrogel suspension. To the resulting mixture, NaBH₄ (2 mmol) was added and mixture was stirred at 80 °C for 24 h. Then, reaction mixture was cooled down to room temperature, centrifuged and separated solid material extremely dried for 24 h.

4.3. Preparation of phosphorous functionalized CuNPs@Agarose:

Prepared dried CuNPs@Agarose (500 mg) was sonicated in dry toluene (2 mL) for 10 minute. To the resulting mixture chlorodiphenylphosphine (3 mmol, 660 mg) was added drop wise and mixture was stirred at 60 °C for 24 h under argon protection. Then, reaction mixture was cooled down to room temperature, filtered and solid was dried in oven at 60 °C.

4.4. Preparation of palladium nanoparticles deposited on phosphorous functionalized CuNPs@Agarose:

500 mg of material was sonicated in dichloromethane (10 mL) for 10 min. Then, solution of Pd(OAc)₂ (15 mg, 0.06 mmol) in dichloromethane (2 mL) was added and mixture stirred for 24 h at room temperature. The resulting catalyst was separated by filtration and solid washed with dichloromethane (5×5 mL) and dried in oven at 60 °C. The content of palladium and copper in the catalyst were determined by atomic adsorption to be 0.03 mmolg⁻¹ and 0.5 mmolg⁻¹ respectively.

4.5. General procedure for Sonogashira reaction:

Aryl halide (0.5 mmol) and phenylacetylene (0.75 mmol) were added to a flask containing PdCu@Phos.Agarose nanocatalyst (8.5 mg containing 0.05 mol% Pd and 0.8 mol% Cu), DABCO (1 mmol) and N,N-dimethylacetamide (DMA) (2 mL). The mixture was stirred at room temperature for aryl iodides and 50 °C for aryl bromides under argon atmosphere. After completion of the reaction (monitored by GC), water (2 mL) was added to the reaction mixture and crude product extracted with ethyl acetate (3×5 mL). For further purification, the organic solvent was removed under vacuum and the resulting residue was purified by column chromatography on silica gel using hexane and ethyl acetate as eluents.

5. Characterizations of products

1,2-diphenylethyne (1a)^{16d}: White solid, m.p: 63 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.60-7.57 (d, 4H, *J*= 12), 7.43-7.36 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 132.15, 128.89, 128.80, 123.79, 89.91; FT-IR (KBr): 3413, 3062, 2921, 1952, 1630, 1490, 1442, 1161, 916, 754.

1-nitro-4-(phenylethynyl)benzene (1b)²⁶: Yellow solid, m.p: 120-122 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 8.26-8.24 (d, 2H, *J*= 8), 7.71-7.69 (d, 2H, *J*= 8), 7.61-7.58 (m, 2H), 7.43-7.39 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 147.47, 132.79, 132.36, 130.78, 129.80, 129.06, 124.16, 122.60, 95.22, 88.06; FT-IR (KBr): 3046, 2959, 2141, 1730, 1263, 1025, 750, 679.

2-methyl-4-nitro-1-(phenylethynyl)benzene (1c): White solid, m.p: 95-97 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 8.13 (s, 1H), 8.06-8.04 (d, 1H, *J*= 8), 7.64-7.62 (d, 1H, *J*=8), 7.61-7.58 (m, 2H), 7.43-7.40 (m, 3H), 2.63 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 147.39, 142.18, 132.87, 132.25, 130.52, 129.72, 129.05, 124.76, 122.88, 121.33, 99.04, 87.17, 30.24; FT-IR (KBr): 3549, 3413, 3072, 2923, 2200, 1732, 1589, 1388, 1079, 799, 752.

1-methoxy-4-(phenylethynyl)benzene (1d)²⁷: White solid, m.p: 65-67 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.57-7.55 (d, 2H, *J* = 8), 7.54-7.51 (d, 2H, *J* = 8), 7.40-7.29 (m, 3H), 6.93-6.91 (d, 2H, *J* = 8), 3.05 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 160.12, 133.55, 131.97, 128.83, 128.46, 124.10, 115.88, 114.51, 89.89, 88.59, 55.81; FT-IR (KBr): 3472, 3414, 2925, 1895, 1647, 1597, 1502, 1540, 1245, 1023, 821, 751, 685.

4-(phenylethynyl)benzonitrile (1e)^{16c}: Pale yellow solid, m.p: 110-112 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.67-7.62 (m, 4H), 7.59-7.57 (m, 2H), 7.42-7.39 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 132.58, 132.57, 132.51, 129.66, 129.04, 128.74, 122.72, 119.07, 111.96, 94.30, 88.26; FT-IR (KBr): 3413, 2929, 2822, 1634, 1440, 1390, 1375, 1098, 1050, 706, 510.

1-chloro-4-(phenylethynyl)benzene (1f)²⁸: White solid, m.p: 78-80 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.58-7.56 (d, 2H, *J* = 8), 7.51-7.49 (d, 2H, *J* = 8), 7.42-7.39 (m, 2H), 7.39-7.35 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 134.77, 133.33, 132.12, 129.22, 129.01, 128.93, 123.43, 122.29, 90.84, 88.77; FT-IR (KBr): 3413, 1949, 1634, 1440, 1271, 1218, 908, 748, 680.

4-(phenylethynyl)benzaldehyde (1h): Yellow solid, ¹H NMR (400 MHz, CDCl₃) δ(ppm): 10.05 (s, 1H), 7.91-7.89 (d, 2H, *J* = 8), 7.72-7.70 (d, 2H, *J* = 8), 7.60-7.58 (m, 2H), 7.43-7.40 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 191.97, 135.90, 132.62, 130.12, 130.10, 129.49, 128.99, 122.99, 93.95, 89.01. FT-IR (KBr): 3416, 3047, 2922, 2850, 2739, 1939, 1603, 1474, 1374, 1268, 1197, 1164, 1096, 1029, 907, 813, 747, 684, 509.

5-(phenylethynyl)pyrimidine (1i): White solid, ¹H NMR (400 MHz, CDCl₃) δ(ppm): 9.18 (s, 1H), 8.90 (s, 2H), 7.60-7.58 (m, 2H), 7.44-7.42 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 159.13, 157.12, 132.30, 129.92, 129.08, 122.40, 120.95, 96.94, 82.98. FT-IR (KBr): 3471, 3414, 2922, 2856, 2218, 2038, 1627, 1456, 1412, 1261, 1091, 802, 619, 476.

2-(phenylethynyl)thiophene (1j)²⁹: Light yellow solid, m.p: 48-49 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.57-7.53 (m, 2H), 7.41-7.36 (m, 3H), 7.33-7.31 (m, 2H), 7.06-7.04 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 132.42, 131.92, 128.94, 128.89, 127.78, 127.62, 123.81, 123.42, 93.53, 83.11; FT-IR (KBr): 3414, 3085, 2960, 2922, 1955, 1926, 1425, 1261, 1096, 1024, 911, 751, 536.

1-methyl-4-(phenylethynyl)benzene (1k)²⁶: White solid, m.p: 70-72 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.57-7.54 (m, 2H), 7.47-7.45 (d, 2H, *J* = 8), 7.40-7.35 (m, 3H), 7.20-7.18 (d, 2H, *J* = 8), 2.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 138.91, 132.06, 132.01, 129.63, 128.83, 128.59, 123.96, 120.66, 90.05, 89.22, 22.05; FT-IR (KBr): 3552, 3474, 3414, 2958, 1626, 1500, 1261, 1098, 867, 751, 626.

3-phenylprop-2-yn-1-ol (1l)²⁷: ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.48-7.46 (m, 2H), 7.36-7.33 (m, 3H), 4.53 (s, 2H), 1.73 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 132.19, 129.02, 128.83, 123.02, 52.20, 87.66, 86.24. FT-IR (KBr): 3300, 3065, 2922, 2859, 2237, 1959, 1888, 1745, 1597, 1488, 1441, 1363, 1259, 1027, 955, 800, 756, 690, 571, 520.

3-(4-chlorophenyl)prop-2-yn-1-ol (1n): ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.39-7.37 (m, 2H), 7.31-7.29 (m, 2H), 4.51 (s, 2H), 2.09 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 135.08, 133.42, 129.19, 121.50, 88.65, 85.09, 51.98. FT-IR (KBr): 3550, 3365, 2903, 2438, 2233, 1907, 1627, 1481, 1433, 1366, 1260, 1089, 1023, 950, 893, 823, 744, 638, 520, 477.

1-methyl-4-((4-nitrophenyl)ethynyl)benzene (1o): Yellow solid, m.p: 145-147 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 8.25-8.22 (d, 2H, *J* = 12), 7.69-7.66 (d, 2H, *J* = 12), 7.49-7.47 (d, 2H, *J* = 8), 7.23-7.21 (d, 2H, *J* = 8), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 147.33, 140.17, 132.67, 132.27, 131.03, 129.83, 124.14, 119.52, 95.61, 87.58, 22.12; FT-IR (KBr): 3414, 2958, 2921, 2854, 2359, 2203, 1920, 1647, 1585, 1513, 1337, 1265, 1097, 850, 806.

2-methyl-4-nitro-1-(p-tolylethynyl)benzene (1p): Yellow solid, m.p: 130-132 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 8.14-8.13 (d, 1H), 8.07-8.04 (dd, 1H), 7.64-7.62 (d, 1H, *J* = 8), 7.49-7.47 (d, 2H, *J* = 8), 7.24-7.22 (d, 2H, *J* = 8), 2.63 (s, 3H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 147.24, 142.05, 140.09, 132.77, 130.80, 129.83, 124.76, 121.35, 119.79, 99.41, 86.67, 22.11, 21.38; FT-IR (KBr): 3413, 2921, 2852, 2199, 1915, 1646, 1507, 1336, 1086, 1031, 807, 702, 522.

1-methoxy-4-(p-tolylethynyl)benzene (1q)²⁹: White solid, m.p: 126-129 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.50-7.48 (d, 2H, *J* = 8), 7.45-7.43 (d, 2H, *J* = 8), 7.18-7.16 (d, 2H, *J* = 8), 6.91-6.89 (d, 2H, *J* = 8), 3.86 (s, 3H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 159.97, 138.53, 133.48, 131.84, 129.59, 120.97, 116.07, 114.46, 89.14, 88.69, 55.81, 22.01; FT-IR (KBr): 3550, 3474, 3414, 2961, 2924, 1730, 1607, 1507, 1452, 1251, 1098, 1024, 610, 519.

2-(p-tolylethynyl)thiophene (1r): Light yellow solid, m.p: 64-66 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.45-7.43 (d, 2H, *J* = 8), 7.31-7.29 (d, 2H, *J* = 8), 7.20-7.18 (d, 2H, *J* = 8), 7.05-7.03 (d, 1H, *J* = 8), 2.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 139.13, 132.16, 131.83, 129.66, 127.57, 124.05, 120.32, 93.72, 82.43, 22.06; FT-IR (KBr): 3475, 3414, 3050, 2922, 1628, 1485, 1434, 1097, 1024, 806, 510.

1-chloro-4-(p-tolylethynyl)benzene (1s): White solid, m.p: 140-142 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.49-7.45 (m, 4H), 7.36-7.34 (d, 2H, *J* = 8), 7.21-7.19 (d, 2H, *J* = 8), 2.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 139.18, 134.55, 133.26, 132.01, 129.69, 129.17, 122.50, 120.35, 91.04, 88.13, 22.06; FT-IR (KBr): 3552, 3474, 3413, 2958, 2855, 1625, 1475, 1259, 1176, 1082, 692, 504.

1-fluoro-4-(p-tolylethynyl)benzene (1t)²⁶: White solid, m.p: 97-98 °C; ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.55-7.51 (m, 2H), 7.46-7.44 (d, 2H, *J* = 8), 7.20-7.18 (d, 2H, *J* = 8), 7.09-7.05 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 164.13, 161.65, 139.00, 133.94, 133.85, 131.95, 129.66, 120.48, 120.08, 120.05, 116.22, 116.00, 89.70, 88.13, 22.03; FT-IR (KBr): 3414, 3025, 2901, 1628, 1545, 1434, 1097, 1025, 906, 730, 516.

5-(p-tolylethynyl)pyrimidine (1u): White solid, ¹H NMR (400 MHz, CDCl₃) δ(ppm): 9.17 (s, 1H), 8.89 (s, 2H), 7.49-7.47 (d, 2H, *J* = 8), 7.24-7.22 (d, 2H, *J* = 8), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ(ppm): 159.04, 156.94, 140.28, 132.20, 129.84, 119.17, 97.20, 82.22, 22.13. FT-IR (KBr): 3471, 3415, 2957, 2921, 2855, 2210, 1930, 1612, 1540, 1502, 1260, 1173, 1153, 1096, 1027, 903, 709, 626, 532, 464.

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