FULL PAPER



Magnetic copper ferrite catalyzed homo- and cross-coupling reaction of terminal alkynes under ambient atmosphere

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1 | INTRODUCTION

1,3-Diynes are structurally important compounds that are present in numerous natural products, pharmaceuticals, agrochemicals and medicinally molecules. Conjugated 1,3diynes as a versatile ingredient play an important role in the preparation of various functional organic molecules, such as macrocyclic annulenes, organic conductors, acetylenic oligomers, liquid crystals and supramolecular materials.^[1] The oxidative homocoupling reaction of terminal alkynes (Glaser-Hay reaction) was one of the classical protocols for the synthesis of symmetrical conjugated 1,3-diynes.^[2] Various catalytic systems have been developed for this reaction using O_2 or air as the oxidant, including the use of Cu,^[3–9] Pd,^[10] Ag,^[11] Au^[12] and bimetallic Pd/Cu,^[13,14] Pd/Ag^[15] and Fe/Cu.^[16] Some heterogeneous catalysts,^[17] like silica/ chitosan core-shell hybrid-microsphere-supported CuI,^[18] copper nanoparticles supported on silica coated maghemite,^[19] copper immobilized on functionalized

The application of non-toxic and magnetically separable nano-CuFe₂O₄ as an efficient catalyst for oxidative homo- and cross-coupling reaction of terminal alkynes is described. A wide range of symmetrical and unsymmetrical 1,3-diynes have been synthesized in moderate to good yields under ambient atmosphere. The nano CuFe₂O₄ can be recovered with a magnet and reused at least five consecutive cycles with no appreciable loss of its catalytic activity.

KEYWORDS

cross-coupling, Glaser reaction, homo-coupling, magnetic nano CuFe2O4, terminal alkynes

silica.^[20] copper,^[21–23] polymer-supported Cu(I) immobilized on functionalized SBA-15,^[24] immobilized copper in MCM-41,^[25] mesoporous silica-supported copper,^[26] copper immobilized on nano-silica triazine dendrimer,^[27] copper-impregnated magnetite^[28] have also been successfully employed to promote this reaction. In 2016, Sheng et al. reported that copper porphyrin acted as an efficient catalyst with high TON.^[29] Diaziridinone^[30] and 3,4-dihalo-2(5H)furanones^[31] have been investigated as oxidants for this transformation. For unsymmetrical conjugated diynes, Cucatalyzed Cadiot-Chodkiewicz coupling between а haloalkyne and a terminal alkyne is the most commonly used procedure, in which the terminal alkyne acts as the nucleophile and the haloalkyne acts as the electrophile in the presence of an amine base.^[32] In this reaction, prefunctionalized haloalkynes from terminal alkynes by halogenation were required. From an environmental and economic viewpoint, the direct heterocoupling of two different terminal alkynes is greener and more cost-effective. In 2014, Peng et al. reported Au-catalyzed heterocoupling of substituted aromatic alkynes with aliphatic alkynes for the synthesis of unsymmetrical conjugated divnes in the presence of a N,N-ligand (1,10-Phen) and using PhI(OAc)₂ as an oxidant.^[33] Bimetallic Pd/Cu,^[14] and Ni/Cu^[34] have been developed for the selective heterocoupling of terminal alkynes in the presence of ligands and oxidants. Recently, Su and co-workers reported a facile copper-catalyzed selective heterocoupling between two different aromatic alkynes and between two different aliphatical alkynes in the pres- N^1, N^1, N^2, N^2 -tetramethylethylenediamine ence of (TMEDA).^[35] Significant progress was recently made by Hwang et al., in which visible light-promoted copper-catalyzed process without the need of bases/ligands, additives and expensive Pd and Au catalysts has been disclosed.^[36] Despite these significant achievements, some reported catalytic systems suffer from the disadvantages such as requirement of expensive transition metal and complex ligands, high temperature, long reaction time, usage of a large excess of one terminal alkyne, low selectivity, or employment of an increased light source. Therefore, the further development of an economic and effective approach for the construction of symmetrical and unsymmetrical 1,3-diynes is still highly desired.

With the advancement of nanoscience, magnetic nanoparticles (MNPs) as new types of heterogeneous catalyst have attracted considerable interest because of their great advantages such as high surface areas, improved the dispersion in the reaction medium, high chemical stability, low toxicity, easy separation (using an external magnet). reusability and environmental friendliness.^[37] Among various MNPs, copper ferrite (CuFe₂ O_4) is one of the most versatile magnetic materials and show remarkable catalytic performance in many organic transformations^[38] such as hydroboration of alkynes,^[39] S-arylation of thiourea,^[40] transesterification of β -ketoesters,^[41] Ullmann coupling,^[42] oxidative hydroxylation of arylboronic acids,^[43] oxidative amidation of aldehydes,^[44] synthesis of N-2-aryl-substituted 1,2,3-triazoles,^[45] sulfides,^[46] 2-substituted benzoxazole^[47] and propynyl-1*H*-imidazoles derivatives.^[48] With our continuous interest in application of magnetic nano catalyst to develop environmentally friendly methodology,^[49] we discovered that magnetic nano-CuFe₂O₄ is an active catalyst for the synthesis of symmetrical and unsymmetrical 1,3-diynes by oxidative homo- and cross-coupling reaction of terminal alkynes (Scheme 1).



2 | EXPERIMENTAL

All the chemical and reagents were obtained from commercial suppliers and used as received without further purification. Melting points were taken with an X-5 apparatus and were uncorrected. XRD patterns were obtained on a PANalytical X'Pert Pro X-ray diffractormeter using Cu-Kα radiation as the X-ray source with a scanning rate of 0.05 °/s from 20 to 80°. Transmission electron microscope (TEM) were carried out on a Hitachi H-7650 instrument operating at 80 KV. Scanning electron microscope (SEM) images of samples were obtained using a Hitachi S-4800 instrument. Magnetic properties were measured using a Physical Property Measurement System (PPMS-6700). ¹H NMR and ¹³C NMR spectra were recorded at 500 and 125 MHz (Bruker Avance III 500, Rheinstetten, Germany) instrument, respectively, using TMS as internal standard.

2.1 | Preparation of magnetic CuFe₂O₄ nanoparticles

Magnetic CuFe₂O₄ nanoparticles were prepared according to reported chemical co-precipitation method.^[41] Briefly, to a solution of Cu(OAc)₂ (0.91 g, 5 mmol) and Fe(NO₃)₃·9H₂O (4.04 g, 10 mmol) in 50 ml of distilled water, 4 M NaOH was added at room temperature over a period of 10 min to form a reddish black precipitate. Then the reaction mixture was heated at 90 °C with stirring for 2 hours. After 2 h, it was cooled to room temperature and the resulting precipitate was separated by a powerful magnet and the precipitate was washed with absolute EtOH and hot water to remove impurities. Finally, the product was dried at 120 °C in an air oven and calcined at 700 °C for 2 h to obtain nano-CuFe₂O₄.

2.2 | General procedure for homo- and crosscoupling reaction of terminal alkynes:

A mixture of a terminal alkyne (2.0 mmol for homocoupling) or two different terminal alkynes (1.0: 1.0 mmol, for cross-coupling), pyrrolidine (0.25 mmol), CuFe₂O₄ (0.06 mmol, 0.06 equiv.) in CH₃CN (2 ml) was stirred for 24 h under ambient atmosphere at room temperature (monitored by TLC). After completion of the reaction, the catalyst was removed with a permanent magnet. Then water (5 ml) was added and extracted with ethyl acetate (3 × 10 ml). The combined solvent was evaporated under reduced pressure and the resulting residue was purified by chromatography on silica gel (hexane/ethyl acetate) to afford the corresponding pure product. The structures of the products were identified by their FTIR, 1H NMR, ¹³C NMR and MS spectra (see Supporting Information).

2.3 | Spectral and analytical data for new compounds

2.3.1 | 6-(4-Bromophenyl)hexa-3,5-diyn-1-ol (3i)

Yellow solid, 114–115 °C; IR (KBr): 3343, 1550, 1484, 1390, 1068, 1042, 1009, 820, 522 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 2.64 (t, J = 6.5 Hz, 2H), 3.74 (t, J = 6.0 Hz, 1H), 3.80 (t, J = 6.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 24.0, 60.7, 66.7, 74.2, 75.1, 81.8, 120.7, 123.5, 131.7, 133.9 ppm; HRMS (EI, m/z): calcd. For C₁₂H₉BrO (M⁺): 247.9837; found: 247.9841.

2.3.2 | Methyl 5-(4-chlorophenyl)penta-2,4diynoate (3 k)

Yellow solid, 105–106 °C; IR (KBr): 3448, 1734, 1718, 1685, 1653, 1617, 1560, 1420, 1309, 1152, 1033, 728 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 3.82 (s, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 53.1, 71.0, 72.0, 73.1, 82.4, 118.9, 125.3, 132.0, 134.4, 153.2 ppm; HRMS (EI, m/z): calcd. For C₁₂H₇BrO₂ (M⁺): 261.9629; found: 261.9631.

2.3.3 | **1-butyl-4-((4-methoxyphenyl)buta-1,3-diyn-1-yl)benzene** (3n)

White solid, 79–80 °C; IR (KBr): 3239, 2452, 2247, 1617, 1498, 1418, 1298, 1213, 673, 513 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 0.92 (t, J = 7.5 Hz, 3H), 1.36–1.33 (m, 2H), 1.61–1.57 (m, 2H), 2.61 (t, J = 7.5 Hz, 2H), 3.82 (s, 3H), 6.85 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 10 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 13.9, 22.3, 33.3, 35.6, 55.3, 73.5, 81.3, 113.8, 114.1, 119.0, 128.5, 132.3, 134.0, 144.4, 160.3 ppm; HRMS



FIGURE 1 SEM images of CuFe₂O₄ nanoparticles

(EI, m/z): calcd. For $C_{21}H_{20}O$ (M⁺): 288.1514; found: 288.1510.

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3 | RESULTS AND DISCUSSION

Magnetic $CuFe_2O_4$ nanoparticles were prepared by the chemical co-precipitation and the thermal decomposition method. The morphology of copper ferrite NPs was ascertained by scanning electron microscopy (SEM). The SEM image in Figure 1 showed that $CuFe_2O_4NPs$ have a mean diameter of about 30–35 nm and a nearly spherical shape. The TEM image revealed that the nanoparticles are



FIGURE 2 TEM images of CuFe₂O₄ nanoparticles



FIGURE 3 XRD pattern of CuFe₂O₄ nanoparticles

almost uniform in size with a narrow distribution (Figure 2). The X-ray diffraction (XRD) patterns indicated that $CuFe_2O_4$ NPs presented the tetragonal structure with good crystallinity, in which all diffraction peaks (18.3, 30.3, 35.6, 42.8, 57.1, and 62.98) are basically consistent with



FIGURE 4 Magnetization curve of CuFe₂O₄ nanoparticles

 TABLE 1
 Optimization of reaction conditionsa

the standard data for $CuFe_2O_4$ structure (JCPDS card No. 00–034-0425),^[45] and no other unexpected peaks are found (Figure 3). Magnetic property of $CuFe_2O_4$ was investigated with a vibrating sample magnetometer (VSM) at room temperature. The magnetic hysteresis curve of $CuFe_2O_4$ nanoparticles revealed that its saturation magnetization value was 41.0 emu g-1, indicating that it is suitable for magnetic separation (Figure 4). Elemental analysis of $CuFe_2O_4$ by using atomic absorption spectroscopy (AAS) gave 26.60% Cu and 46.70% Fe, which corresponds to a Cu/Fe molar ratio of approximately 1:2.

To test the activity of the prepared $CuFe_2O_4$, homocoupling of phenylacetylene was selected as a model reaction to optimize the reaction conditions. As shown in Table 1, it was found that product could not be detected when the reaction was carried out at room temperature in CH₃CN in the presence of pyrrolidine for 24 h in the absence of any catalyst under open air (Table 1, entry 1), which indicated that the catalyst should be absolutely necessary for this transformation. A concentration of 6 mol% was sufficient to complete the reaction with maximum yield (Table 1, entry 5). To identify the best medium for the reaction, we performed the model reaction

EntryCatalyst loading (mmol%)BaseSolventYield (%) ^b 10PyrrolidineCH3CN023PyrrolidineCH3CN3134PyrrolidineCH3CN5645PyrrolidineCH3CN6956PyrrolidineCH3CN9566PyrrolidineH2OTrace76PyrrolidinePge 400Trace86PyrrolidineTHF5896PyrrolidineTHF58106Pyrrolidine (0)CH3CNTrace126Pyrrolidine (10)CH3CN12136Pyrrolidine (10)CH3CN21146Pyrrolidine (20)CH3CN95156Pyrrolidine (20)CH3CN95166Pyrrolidine (20)CH3CN95176Fi3NCH3CN12186Pyrolidine (26)CH3CN12196MorpholineCH3CN12196MorpholineCH3CN69206MorpholineCH3CN69216MorpholineCH3CN692286Pyrolidine (26)CH3CN69196MorpholineCH3CN69206MorpholineCH3CN69216MorpholineCH3CN69236Morpholin		2	CuFe ₂ O ₄		
1 0 Pyrrolidine CH3CN 0 2 3 Pyrrolidine CH3CN 31 3 4 Pyrrolidine CH3CN 56 4 5 Pyrrolidine CH3CN 69 5 6 Pyrrolidine CH3CN 95 6 6 Pyrrolidine CH3CN 95 6 6 Pyrrolidine H2O Trace 7 6 Pyrrolidine Peg 400 Trace 8 6 Pyrrolidine THF 58 9 6 Pyrrolidine The 85 10 6 Pyrrolidine (0) CH3CN Trace 11 6 Pyrrolidine (0) CH3CN Trace 12 6 Pyrrolidine (0) CH3CN 12 13 6 Pyrrolidine (0) CH3CN 21 14 6 Pyrrolidine (20) CH3CN 95 15 6 Pyrrolidine (26)	Entry	Catalyst loading (mmol%)	Base	Solvent	Yield (%) ^b
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3 4 Pyrolidine CH ₃ CN 56 4 5 Pyrolidine CH ₃ CN 69 5 6 Pyrolidine CH ₃ CN 95 6 6 Pyrolidine CH ₃ CN 95 6 6 Pyrolidine H ₂ O Trace 7 6 Pyrolidine Peg 400 Trace 8 6 Pyrolidine THF 58 9 6 Pyrolidine Toluene 85 10 6 Pyrolidine (0) CH ₃ CN 12 12 6 Pyrolidine (0) CH ₃ CN 12 13 6 Pyrolidine (10) CH ₃ CN 12 14 6 Pyrolidine (20) CH ₃ CN 95 15 6 Pyrolidine (26) CH ₃ CN 12 14 6 Pyrolidine (26) CH ₃ CN 12 15 6 Pyrolidine (26) CH ₃ CN 12 16 Pyrolidine (2	2	3	Pyrrolidine	CH ₃ CN	31
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146Pyrrolidine (20) CH_3CN 75156Pyrrolidine (26) CH_3CN 95166 K_2CO_3 CH_3CN Trace176 Et_3N CH_3CN 12186Pyridine CH_3CN 31196Morpholine CH_3CN 69206Benzylamine CH_3CN 81216Piperidine CH_3CN 85	13	6	Pyrrolidine (15)	CH ₃ CN	21
156Pyrolidine (26) CH_3CN 95166 K_2CO_3 CH_3CN Trace176 Et_3N CH_3CN 12186Pyridine CH_3CN 31196Morpholine CH_3CN 69206Benzylamine CH_3CN 81216Piperidine CH_3CN 85	14	6	Pyrrolidine (20)	CH ₃ CN	75
16 6 K_2CO_3 CH_3CN $Trace$ 17 6 Et_3N CH_3CN 12 18 6 Pyridine CH_3CN 31 19 6 Morpholine CH_3CN 69 20 6 Benzylamine CH_3CN 81 21 6 Piperidine CH_3CN 85	15	6	Pyrrolidine (26)	CH ₃ CN	95
17 6 Et ₃ N CH ₃ CN 12 18 6 Pyridine CH ₃ CN 31 19 6 Morpholine CH ₃ CN 69 20 6 Benzylamine CH ₃ CN 81 21 6 Piperidine CH ₃ CN 85	16	6	K ₂ CO ₃	CH ₃ CN	Trace
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19 6 Morpholine CH ₃ CN 69 20 6 Benzylamine CH ₃ CN 81 21 6 Piperidine CH ₃ CN 85	18	6	Pyridine	CH ₃ CN	31
20 6 Benzylamine CH ₃ CN 81 21 6 Piperidine CH ₃ CN 85	19	6	Morpholine	CH ₃ CN	69
21 6 Piperidine CH ₃ CN 85	20	6	Benzylamine	CH ₃ CN	81
	21	6	Piperidine	CH ₃ CN	85

^aReaction condition: phenylacetylene (2.0 mmol), CuFe₂O₄ (0.06 mmol) and base (0.25 mmol) in solvent (2 ml) under open air, stirred at room temperature for 24 h otherwise specified in the table.

^bIsolated yields.

TABLE 2 Synthesis of symmetrical 1,3-diynes catalyzed by CuFe2O4a

$2R \xrightarrow{\qquad} \frac{CuFe_2O_4, Pyrrolidine}{CH_3CN, r.t.} R \xrightarrow{\qquad} R$					
Entry	R	Product	Yield/% ^b		
1	Ph	2a	95		
2	$4-MeOC_6H_4$	2b	92		
3	$3-MeC_6H_4$	2c	90		
4	$4-\text{EtC}_6\text{H}_4$	2d	88		
5	4- n -BuC ₆ H ₄	2e	80		
6	4- t -BuC ₆ H ₄	2f	85		
7	$4\text{-me}(CH_2)_5C_6H_4$	2g	79		
8	$3-FC_6H_4$	2h	90		
9	4-FC ₆ H ₄	2i	87		
10	2-thiophenyl	2j	75		
11	3-pyridyl	2k	71		
12	$n-C_5H_{11}$	21	86		
13	<i>n</i> -C ₆ H ₁₃	2m	88		
14	$C_6H_5CH_2CH_2CH_2$	2n	90		

^aReaction condition: alkyne (2.0 mmol), CuFe₂O₄ (0.06 mmol) and pyrrolidine (0.25 mmol) in CH₃CN (2 ml) stirred at room temperature for 24 h under open air. ^bIsolated yields.

with different solvents such as H_2O , PEG 400, THF, toluene, CH_2Cl_2 and MeCN. MeCN was found to be the best reaction medium. Further examination of the reaction condition indicated that pyrrolidine was the most suitable base for the formation of the expected product. Other organic and



SCHEME 2 Synthesis of unsymmetrical 1,3-diynes catalyzed by $CuFe_2O_4Reaction condition: two different alkynes (1.0 mmol +1.0 mmol), <math>CuFe_2O_4$ (0.06 mmol) and pyrrolidine (0.24 mmol) in CH_3CN (2 ml) stirred at room temperature for 24 h under open air

inorganic bases were poorer for promoting this model reaction. It was also found that the use of 25 mmol% pyrrolidine is sufficient to promote the reaction.

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Under the optimized conditions, the homocoupling reaction of a series of terminal alkynes was evaluated and the results are summarized in Table 2. The terminal alkynes bearing aryl electron-rich or electron-deficient aryl groups proceeded homocoupling reaction smoothly and afford the corresponding aromatic 1,4-disubstituted-1,3-diyne derivatives in good to excellent yields. The heteroatom-containing 2-ethynylthiophene was proved to be a suitable substrate and converted to 1,3-diyne **2j** in 75% yield



FIGURE 5 Reusability of catalyst

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TABLE 3 The homo-coupling of phenylacetylene using different catalytic system	stem
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Entry	Reaction conditions	Yield/%	Reference
1	CuCl ₂ (10 mol%), DBU(1.2 equiv.) in THF, r. t. 24 h	92	3a
2	CuNPs/TiO ₂ (1 mol %), piperidine (30 mol %) in THF, 65°C, 6 h	96	3b
3	CuCl (5 mol%), 2,2'-dipyridyl (10 mol%) in DMF, r. t. 2 h	99	4
4	CuSO ₄ ·5H ₂ O/(5 mol%), KOAc (1 equiv.), I ₂ (0.25 equiv.), in H ₂ O, 120 °C, 24 h	95	5
5	CuI (5 mol%), TMEDA (10 mol%), Et ₃ N (3.0 equiv.) in acetone, r.t. 20 h	91	6
6	CuI (5 mol%), DMAP(10 mol%) in MeCN, r.t. 1 h	97	7
7	CuI (10 mol%), pyrrolidine (10 mol%) in EL, 50 °C, 16 h	90	9
8	Ph ₃ PAuCl (5 mol%), PhI(OAc) ₂ (1.2 equiv), K ₂ CO ₃ (1.5 equiv) in 1,2-DCE, 60 °C, 6 h	91	12
9	Pd(II) complex (5 mol%), AgNO ₃ (0.5 equiv.), and NEt ₃ (1 equiv.) in THF/H ₂ O, 60 °C, 10 h	93	15
10	CuBr (5 mol%), FeCl ₃ (10 mol%), CH ₃ ONa (3.0 equiv.) in THF, r. t., 20 h	90	16
11	Cu/SiO ₂ (2 mol%), piperidine (1.0 equiv.) in toluene, 100 °C, 2.5 h	96	20
12	Porous polymer-supported cu (2.5 mol%) in DMF, 120 °C, O2, 40 min	99	21
13	Polystyrene-supported cu (10 mol%), piperidine (1.0 equiv) in toluene, 60 °C, 24 h	96	23
14	Cu(I) immobilized on functionalized SBA-15 (3 mol%) in DMSO, O2, 50 °C, 6 h	99	24
15	MCM-41-immobilized cu(I) complex (1 mol%), piperidine (0.1 equiv.) in CH ₂ Cl ₂ , r. t., 2 h	94	25
16	CuFe ₂ O ₄ (6 mmol%), pyrrolidine (0.24 equiv.) in CH ₃ CN, r. t., 24 h	95	This work

(Table 2, entry 10). Interestingly, we also successfully expanded the scope of substrates to heteroaromatic alkyne. For example, 3-ethynylpyridine underwent this Glaser-type dimerization and provided 1,4-di(pyridin-3-yl)buta-1,3-diyne (2 k) in 71% yield. Furthermore, aliphatic alkynes such as 1-heptyne, 1-octyne as well as 5-phenyl-1-pentyne were proved to be suitable substrates under these conditions, furnishing the corresponding conjugated dines in high yields (entries 12–14).

Following successful examining homo-coupling reactions with this catalytic system, the scope of the reaction was extended to the cross-coupling reactions between two different terminal alkynes. As shown in Scheme 2, various aromatic terminal alkynes substituted with alkyl, F, Cl and Br was subjected to cross-coupling with but-3-yn-1-ol under above conditions. The reaction went on well and afforded unsymmetrical 1,3-diynes 3a-3i in moderate to good yields. Similarly, 1-chloro-4-ethynylbenzene and 1-bromo-4ethynylbenzene also reacted with methyl propiolate to provide the cross coupled products in 65% (3j) and 66%(3k) yields, respectively. In addition, this catalytic system was applied to two different aromatic terminal alkynes. For example, 1-ethynyl-4-methoxybenzene reacted with ethynylbenzene containing different functional groups to give the heterocoupling products (31-3n) in moderate yields with good selectivity. In the course of this reaction, due to the presence of homo-couplings as side reactions unavoidably, the cross coupled products were obtained in low yields.

The ability to easily recover and recycle copper ferrite was also investigated by homo-coupling of phenylacetylene as a test model. After the completion of reaction, the catalyst was separated magnetically from the reaction mixtures and then washed with ethyl acetate and water, dried at 110 °C, and reused for the next round without further purification under similar reaction conditions. The catalyst can be used up to fifth cycle with slight decrease in product yield (Figure 5). The ICP-MS analysis of the filtrate of reaction was carried out after the completion of reaction. ICP-MS study indicated that the Cu and Fe contents were 0.12 and 0.20 ppm, respectively. Furthermore, the filtered solution did not exhibit any further reactivity. The results confirm that copper ferrite has good stability and recyclable applicability for Glaser-Hay reaction.

In order to show the merits and limitations of the present work in comparison with other reported catalytic systems in the literatures, we summarized some of results for the synthesis of 1,2-diphenylethyne via homo-coupling of phenylacetylene in Table 3. As can be seen in this table, the present catalytic system is an equally or more efficient to those previously reported in this reaction, since the use of precious metal catalyst,^[12, 15,] high reaction temperature,^[5,9,12,15,20,21,23,24,3] or the employment of unrecyclable catalysts^[4–7,9,16,3] can be avoided.

4 | CONCLUSION

In conclusion, magnetic nano-CuFe₂O₄ has been proven to be an effective heterogeneous catalyst for the homoand cross-coupling reaction of terminal alkynes. The corresponding symmetrical and unsymmetrical 1,3-diynes are obtained in moderate to good yields. The catalyst can be readily recovered with a permanent magnet and reused for five runs without significant loss of its catalytic activity.

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