Copper-Impregnated Magnetite as a Heterogeneous Catalyst for the Homocoupling of Terminal Alkynes

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Abstract: Copper-impregnated magnetite is a versatile heterogeneous catalytic system for the synthesis of 1,3-diynes by the homocoupling of terminal alkynes. This catalyst does not require the use of pressurized oxygen as the oxidant and it does not need a solvent or harsh conditions to give the expected products. Moreover, the catalyst can be removed from the reaction medium simply by using a magnet. The reaction occurs at the lowest copper loading reported for any heterogeneous catalyst.

Key words: alkynes, copper, heterogeneous catalysis, iron, supported catalysis, coupling, furans

The homocoupling of terminal alkynes[1] to give 1,3-diynes has attracted a great deal of attention in organic chemistry because of the role of diynes as building blocks for many natural products[2] or for pharmaceuticals with antiinflammatory, antibacterial, antitumor, or antifungal activities. Furthermore, 1,3-diynes have attracted the attention of chemists as interesting materials that are useful as precursors of polymers,[3] macrocycles,[4] or supramolecular structures.[5]

The symmetric coupling of simple terminal acetylenes,[6] known as the Glaser–Hay reaction, was discovered over a century ago, and the methodology for this reaction was improved shortly afterwards.[7] Among the various metallic salts that were used, copper emerged as the best metal for catalyzing the transformation. In fact, the number of copper complexes that have been identified as being capable of successfully inducing this transformation continues to increase.[8] However, homogeneous catalysts have some important drawbacks, such the need for high metal loadings and the inability to recycle the catalyst. A homogeneous copper acetate–poly(ethylene glycol) catalyst system[8b] has been recycled up to five times, although this was accompanied by a decrease in activity after each reactivation step of treatment with acetic acid.

Heterogeneous catalysts have been designed for performing this transformation and to facilitate the removal, recovery, and recycling of the catalysts. Although, there are several examples of insoluble copper derivatives that are able to induce the Glaser–Hay reaction,[9] the most widely used strategy has involved the use of copper salts supported on various inert oxides, such as hydrotalcite,[10] alumina,[11] zeolites,[12] titania,[13] silicotungstate complexes,[14] molecular sieves,[15] or mesoporous silica.[16] However, the use of such catalysts entails some drawbacks that require elimination, such as the need for a high metal loading,[9–16] the need to use high temperatures,[12,13a,14,15] the need for non-environmentally benign solvents,[9b,10b,c,12,13a,14–16] the need to use pressurized oxygen,[10a,b,13a,14,15] and, in some cases, the lack of recyclability of the catalyst.[9a,b,10b,11,12,13a]

An interesting cooperative effect was observed when the reaction was carried out in the presence of homogeneous mixtures containing a copper and an iron salt.[17] In this case, the loading of the copper salt could be reduced to 0.1 mol% in the presence of 10 mol% of iron(III) acetylacetonate. We recently developed a new, simple, and robust method for immobilizing various metal oxides[18] on magnetite.[19] With the cooperative effect of copper and iron in mind, we decided to test a copper-impregnated magnetite catalyst[20] in the Glaser–Hay reaction. Here, we report the first catalyst for this reaction that is derived from copper, a cheap and safe first-row transition metal, impregnated on magnetite and we report its use in the coupling of several terminal alkynes.

We selected the homocoupling of ethynylbenzene (**1a**) in the presence of piperidine as a base as a model reaction for optimizing the conditions (Table 1). Initially, we examined the reaction in various solvents (Table 1, entries 1–9), and we found that the best results were, in fact, obtained in the absence of any solvent. Increasing the temperature for the reaction did not improve the results (entry 10), whereas the reaction at room temperature only gave traces of product **2a** (entry 11). The reaction failed in the absence of the base (entry 12). We also examined the effects of changing the base by using various amines (entries 13–15), and we obtained similar yields in only four hours with various primary amines; however, the corresponding amides were also obtained as byproducts. When we used other organic or inorganic bases (entries 16–20), we obtained lower yields. The product **2a** was obtained in quantitative yield only when we used potassium *tert*-butoxide as the base, (entry 21). When the reaction was carried out in the presence of 50 mol% of the base, the yield decreased (entry 22); we therefore concluded that a stoichiometric amount of the base is needed for the homocoupling (entries 21–22). Increasing the amount of base further did not reduce the reaction time (entry 23). When the reaction was performed under an argon atmosphere, the yield decreased to 38% (entry 24). This confirmed that the oxygen present in the air plays an important role in the process and that it acts as the ultimate source of oxygen.

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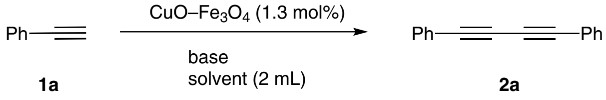
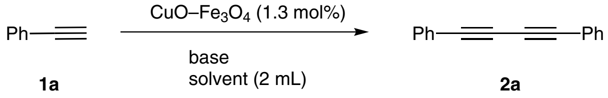
We then examined the effects of the amount of catalyst used (entries 25–27). Decreasing the amount of catalyst to 0.26 mol% produced a 99% yield of **2a**, although a longer reaction time (48 hours) was needed (entry 25). Reactions with a higher or lower loading of the metal did not improve the results (entries 26 and 27). Finally, when we repeated the reaction under the optimized conditions but in the absence of the catalyst, we recovered the starting material after one week (entry 28). Note that performing the reaction under an atmosphere of pure oxygen did not change the results (entries 21 and 29).

Table 1 Optimization of the Reaction Conditions



Entry[a]	Base (mol%)	Solvent	Temp (°C)	Time (h)	Yield[b] of **2a** (%)
1	piperidine (100)	THF	60	24	84
2	piperidine (100)	toluene	60	24	85
3	piperidine (100)	MeCN	60	24	57
4	piperidine (100)	1,4-dioxane	60	24	87
5	piperidine (100)	DMF	60	24	54
6	piperidine (100)	H_2O	60	24	6
7	piperidine (100)	DMSO	60	24	14
8	piperidine (100)	EtOH	60	24	0
9	piperidine (100)	–	60	24	90
10	piperidine (100)	–	90	24	73
11	piperidine (100)	–	25	24	2
12	–	–	60	24	0
13[c]	$BuNH_2$ (100)	–	60	4	87
14	Et_3N (100)	–	60	24	5
15	DABCO (100)	–	60	24	79
16	KOAc (100)	–	60	24	0
17	*t*-BuONa (100)	–	60	24	16
18	MeONa (100)	–	60	24	2
19	$CsOH\cdot H_2O$ (100)	–	60	24	60
20	KOH (100)	–	60	24	88
21	*t*-BuOK (100)	–	60	24	99
22	*t*-BuOK (50)	–	60	24	75
23	*t*-BuOK (200)	–	60	24	99
24[d]	*t*-BuOK (100)	–	60	24	38
25[e]	*t*-BuOK (100)	–	60	48	99
26[f]	*t*-BuOK (100)	–	60	48	26
27[g]	*t*-BuOK (100)	–	60	24	99
28[h]	*t*-BuOK (100)	–	60	168	0
29[i]	*t*-BuOK (100)	–	60	24	99

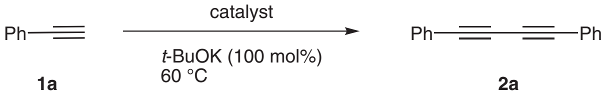
Table 1 Optimization of the Reaction Conditions (continued)



[a] Reaction carried out using **1a** (2 mmol) under air.
[b] Isolated yields after column chromatography.
[c] *N*-Butyl-2-phenylacetamide was isolated in 13% yield.
[d] Reaction carried out under argon.
[e] Reaction carried out with 0.26 mol% of catalyst.
[f] Reaction carried out with 0.13 mol% of catalyst.
[g] Reaction carried out with 2.6 mol% of catalyst.
[h] Reaction carried out in the absence of the catalyst.
[i] Reaction carried out under O_2.

Having determined the optimal conditions, we examined the reactions with a variety of catalysts, prepared by a simple impregnation protocol (Table 2). First, we evaluated the activity of the support by using magnetite as the sole catalyst. Nanoparticles or microparticles of magnetite were used, and the results showed that bare magnetite had

Table 2 Optimization of the Catalyst



Entry[a]	Catalyst (mol%)	Time (d)	Yield[b] (%) of **2a**
1	CuO/Fe_3O_4 (0.26)	2	99
2	Fe_3O_4 (0.13)	7	68
3	Fe_3O_4 (0.13)[c]	7	78
4	Ru_2O_3/Fe_3O_4 (0.28)	2	0
5	CoO/Fe_3O_4 (0.35)	2	0
6	IrO_2/Fe_3O_4 (0.03)	2	0
7	NiO/Fe_3O_4 (0.2)	2	41
8	PdO/Fe_3O_4 (0.24)	2	1
9	$PtO–PtO_2/Fe_3O_4$ (0.12)	2	1
10	Pd(II,0)–Cu(II)/Fe_3O_4 (0.3:0.16)	2	89
11	Cu(II,0)–Ni(II)/Fe_3O_4 (0.22:0.18)	2	99
12	CuO (0.26)	2	89
13	CuO (0.26) + Fe_3O_4 (0.13)	2	88

[a] Reactions were carried out by using **1a** (2 mmol) under air.
[b] Isolated yields after column chromatography.
[c] Reaction performed with nanoparticulate magnetite (< 50 nm).

a lower activity than the copper-impregnated form, needing longer reaction times and giving lower yields (Table 2, entries 1, 2, and 3). Ruthenium,[18b] cobalt,[18b] iridium,[18e] palladium,[18c] and platinum[18d] did not show any activity in this transformation. The nickel catalyst[18b] showed a moderate activity, giving the expected product in 41% yield (entry 7). Reactions using bimetallic catalysts gave the expected product in high yields (entries 10–11), with the copper–nickel[18c] catalyst attaining a quantitative yield. Reactions using copper oxide alone or together with magnetite gave slightly lower yields than that obtained with the impregnated catalyst (compare entries 1, 12, and 13), but we do not have any clear explanation for this cooperative effect.

Having established the optimal reaction conditions, we examined the problem of recycling (Figure 1). When the catalyst was recovered from the reaction mixture by using a magnet, washed with methanol, and reused under the same conditions, we obtained the expected product **2a** in 99% yield. However, in the fourth cycle of use and recovery, the yield was only 75%, indicating that there is a small decrease in the activity of the catalyst. In the fifth cycle, the yield fell sharply to 20%.

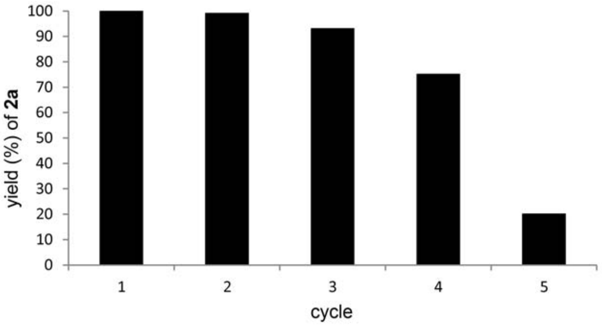
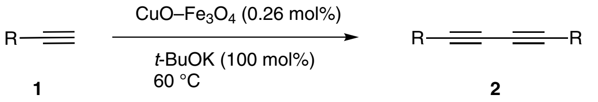


Figure 1 Yields obtained with recycled CuO/Fe_3O_4 catalyst

The nanosize distribution of the catalyst, as measured from transmission electron microscopy, remained about the same before and after the reaction. Before the reaction, 73% of the copper oxide particles on the surface of the catalyst measured between 2 and 6 nm, whereas the corresponding figure after the reaction was 68%. X-ray photoelectron spectroscopy studies on the used catalyst showed that the copper was partially reduced from an initial 4:1 mixture of Cu(II) and Cu(0) to a 1:1 mixture of these oxidation states. The inductively coupled plasma–mass spectroscopy analysis of the reaction solution showed the presence of copper (6.2% of the initial amount) and iron (0.22% of the initial amount). A similar result was obtained when the catalyst was removed before the mixture was cooled. These results appear to show that not all copper on the surface of magnetite has the same activity, and that the most-active species appear to leach fastest.

We also applied our optimized conditions to other substrates. Reaction using various substituted arylalkynes **1** gave the expected products **2** (Table 3). The reactions seems to be more affected by the presence of chelating groups than by the electronic nature of the substrates, and reactants with the strongest chelating ability gave the lowest yields (entries 1–5). The presence of steric hindrance in the aryl moiety decreased the yield (entry 6). Finally, the reaction could also be performed by using less-reactive aliphatic alkynes, and the expected products **2** were obtained in all the cases, albeit in slightly lower yields (entries 10–14).

Table 3 Preparation of Various 1,3-Diynes

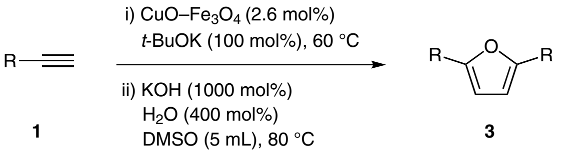


Entry[a]	R	Product	Time (d)	Yield[b] (%)
1	Ph	**2a**	2	99 (99[c])
2	4-$Me_2NC_6H_4$	**2b**	6	20
3	4-$MeOC_6H_4$	**2c**	7	57
4	4-MeC_6H_4	**2d**	2 (1)[c]	91 (99)[c]
5	4-ClC_6H_4	**2e**	4	99
6	2-ClC_6H_4	**2f**	2	32
7	4-$F_3CC_6H_4$	**2g**	2	99
8	4-BrC_6H_4	**2h**	7	26 (17)[c]
9	3-MeC_6H_4	**2i**	3	99
10	*c*-Hex	**2j**	3	70 (88)[c]
11	$(CH_2)_5Me$	**2k**	3	92
12	$(CH_2)_7Me$	**2l**	7 (3)[c]	50 (74)[c]
13	$(CH_2)_9Me$	**2m**	7	31
14	$(CH_2)_3Cl$	**2n**	2	99

[a] Reactions were carried out by using **1a** (2 mmol) under air.
[b] Isolated yields after column chromatography.
[c] With Cu(II,0)–Ni(II)/Fe_3O_4 (0.22/0.18 mol%) catalyst.

Encouraged by the success that we achieved in homocoupling of terminal alkynes, we examined the hydration reaction of 1,3-diynes to afford the corresponding 2,5-disubstituted furans, a reaction that is catalyzed by various copper salts.[21] We performed the reaction with compound **2a** in dimethyl sulfoxide in the presence of potassium hydroxide and copper oxide/magnetite at 80 °C. To our delight, we obtained the desired furan **3a** in quantitative yield. However, it should be pointed out that the hydration reaction performed in the absence of the catalyst also, surprisingly, gave furan **3a** in the same yield. We then attempted a direct, two-step, one-pot transformation of various alkynes into the corresponding 2,5-disubstituted furans **3** (Table 4). Having obtained the diyne in the first reaction step, we removed the catalyst with a magnet and, without purification of the reagents, we added dimethyl sulfoxide and aqueous potassium hydroxide. Excellent results were obtained for various types of 4-substituted aryl diynes (entries 2–5). Unfortunately, when we used a cycloaliphatic diyne, the reaction failed (entry 5) and the substrate was recovered.

Table 4 One-Pot Preparation of 2,5-Furans

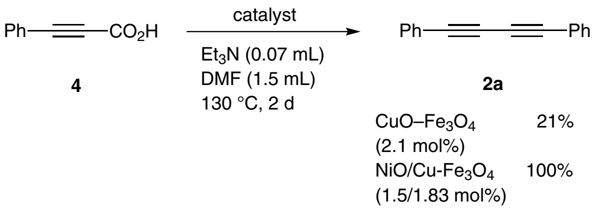


Entry[a]	R	Product	Time (d)	Yield[b] (%)
1	Ph	**3a**	3	99
2	4-$MeOC_6H_4$	**3b**	8	59
3	4-MeC_6H_4	**3c**	3	90
4	4-$F_3CC_6H_4$	**3d**	3	99
5	*c*-Hex	**3e**	5	0

[a] Reaction carried out by using **1** (2 mmol) and H_2O (4 mmol) under air.

[b] Isolated yield after column chromatography.

Finally, we examined the decarboxylative coupling reaction[22] of 3-phenylprop-2-ynoic acid (**4**). The copper catalyst gave only a 21% yield of the expected diyne **2a**. However, this product was obtained quantitatively when we used NiO–Cu/Fe_3O_4 as the catalyst (Scheme 1).



Scheme 1 Decarboxylative coupling reaction of 3-phenylprop-2-ynoic acid

In conclusion, we have demonstrated that copper-impregnated magnetite is a good catalyst for homocoupling of terminal alkynes under solvent-free conditions and in the absence of oxygen pressure. Furthermore, this reaction requires the lowest reported loading of copper for any heterogeneous catalysis. Moreover, the catalyst can be easily removed from the reaction medium merely by using a magnet, and it can be reused up to three times without any reduction in yield.

Melting points were determined by using a Reichert Thermovar apparatus. NMR spectra were recorded on a Bruker AC–300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) with $CDCl_3$ as the solvent and TMS as internal standard. FTIR spectra were recorded on a JASCO 4100LE (Pike Miracle ATR) spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Himazdu QP–5000 spectrometer. TLC was performed on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2-mm layer of silica gel. Detection was performed by irradiation with UV_{254} after staining with phosphomolybdic acid [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot 4\ H_2O$ (10 g), concd H_2SO_4 (60 mL), and H_2O (940 mL)]. Chromatographic analyses were performed by using an instrument equipped with a flame-ionization detector and a 30-m capillary column (0.32 mm diameter, 0.25 μm film thickness, HP–5 stationary phase) and with N_2 (2 mL/min) as the carrier gas; the chromatograph was operated at a pressure of 10 psi with an injector temperature of 270 °C and a detector temperature of 300 °C. Retention times (t_R) for all samples are reported for the same gradient: 60 °C for 3 min, increasing by 15 °C/min to 270 °C, then 270 °C for 15 min. Column chromatography was performed by using 35–70 mesh silica gel 60. All reagents were commercially available (Acros, Aldrich, Fluorochem) and were used as received. Inductively coupled plasma–mass spectral analyses were carried out on a Thermo Elemental VGPO-ExCell spectrometer. X-ray fluorescence analyses were carried out on a Philips Magix Pro (PW2400) X-ray spectrometer equipped with a Rh X-ray tube and a Be window. The reactions were performed in a twelve-vessel carousel reaction station (Radleys). The NiO–Cu/Fe_3O_4 and CuO/Fe_3O_4 catalyst were prepared according to the procedures described in the literature.[18c,20c]

Catalyst Preparation; General Procedure

Commercially available Fe_3O_4 (< 5 μm, BET area: 9.86 m^2/g; 4 g, 17 mmol) was added to a stirred soln of the appropriate metal chloride MCl_n (1 mmol) [or a mixture of M^1Cl_n (1 mmol) and $M^2Cl_{n'}$ (1 mmol) for bimetallic species] in deionized H_2O (120 mL). In the cases of the Pd and Cu–Pd catalysts, a large excess of KCl (1 g, 13 mmol) was also added to the initial soln to increase the solubility of the $PdCl_2$. After 10 min at r.t., the mixture was slowly basified with 1 M aq NaOH to a pH of about 13. The mixture was then stirred for 1 d at r.t. under air. The catalyst was collected by filtration, washed with deionized H_2O (3 × 10 mL), and dried for 24 h at 100 °C in a standard glassware oven.

1,3-Diynes 2a–n; General Procedure

t-BuOK (224 mg, 2 mmol) and CuO/Fe_3O_4 (10 mg, 0.26 mol%) or NiO–Cu/Fe_3O_4 (10 mg, 0.18/0.22 mol%) were added to a stirred soln of the appropriate alkyne **1** (2 mmol) under air, and the mixture was vigorously stirred at 60 °C until the reaction was complete. The catalyst was collected by using a magnet and washed successively with EtOAc (2 × 5 mL) and H_2O (2 × 5 mL). The collected organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by column chromatography.

1,1′-Buta-1,3-diyne-1,4-diyldibenzene (2a)[13b]

White solid; yield: 200 mg (99%); t_R = 15.8 min; mp 83–85 °C (hexane); R_f = 0.67 (hexane–EtOAc, 4:1).

IR (ATR): 3050, 1593, 1485 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.30 (m, 6 H, ArH), 7.45–7.50 (m, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 73.9 (2 C), 81.5 (2 C), 121.8 (2 C), 128.4 (4 C), 129.2 (2 C), 132.5 (4 C).

MS (EI, 70 eV): *m/z* (%) = 101 (8), 200 (22), 201 (11), 202 (100) [M^+], 203 (17) $[M + H]^+$.

4,4′-Buta-1,3-diyne-1,4-diylbis(*N*,*N*-dimethylaniline) (2b)[9a]

Pale-brown solid; yield: 58 mg (20%); t_R = 13.4 min; mp 215–217 °C (hexane); R_f = 0.43 (hexane–EtOAc, 4:1).

IR (ATR): 1598, 1358, 1225 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.00 (s, 12 H, CH_3 × 4), 6.65–6.70 (d, *J* = 8.8 Hz, 4 H, ArH), 7.35–7.40 (d, *J* = 8.8 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.2 (4 C), 74.7 (2 C), 84.8 (2 C), 108.8 (2 C), 111.7 (4 C), 133.2 (4 C), 150.4 (2 C).

MS (EI, 70 eV): *m/z* (%) = 51 (15), 77 (40), 78 (11), 155 (19), 183 (12), 201 (70), 202 (100), 203 (22), 207 (60), 208 (14), 229 (19), 269 (10), 288 (10) [M$^+$].

1,1′-Buta-1,3-diyne-1,4-diylbis(4-methoxybenzene) (2c)[23]

Pale-yellow solid; yield: 150 mg (57%); t_R = 20.7 min; mp 131–133 °C (hexane); R_f = 0.37 (hexane–EtOAc, 4:1).

IR (ATR): 3004, 2939, 2837, 1598, 1502 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 6 H, CH_3 × 2), 6.80–6.85 (d, *J* = 8.8 Hz, 4 H, ArH), 7.45–7.50 (d, *J* = 8.8 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3 (2 C), 72.9 (2 C), 81.2 (2 C), 113.9 (2 C), 114.1 (4 C), 134.0 (4 C), 160.2 (2 C).

MS (EI, 70 eV): *m/z* (%) = 131 (13), 176 (15), 219 (14), 247 (58), 248 (11), 262 (100) [M$^+$], 263 (19) [M + H]$^+$.

1,1′-Buta-1,3-diyne-1,4-diylbis(4-methylbenzene)(2d)[15]

Pale-yellow solid; yield: 209 mg (91%); t_R = 17.5 min; mp 118–120 °C (hexane); R_f = 0.8 (hexane–EtOAc, 4:1).

IR (ATR): 3032, 1501 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 6 H, CH_3 × 2), 7.10–7.15 (d, *J* = 8.0 Hz, 4 H, ArH), 7.35–7.40 (d, *J* = 8.0 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (2 C), 73.4 (2 C), 81.5 (2 C), 118.8 (2 C), 129.2 (4 C), 132.4 (4 C), 139.5 (2 C).

MS (EI, 70 eV): *m/z* (%) = 215 (17), 226 (13), 228 (12), 229 (22), 230 (100) [M$^+$], 231 (19) [M + H]$^+$.

1,1′-Buta-1,3-diyne-1,4-diylbis(4-chlorobenzene) (2e)[15]

Pale-yellow solid; yield: 268 mg (99%); t_R = 18.0 min; mp 165–167 °C (hexane); R_f = 0.77 (hexane–EtOAc, 4:1).

IR (ATR): 1483, 1395, 1092 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.35 (d, *J* = 8.7 Hz, 4 H, ArH), 7.45–7.50 (d, *J* = 8.7 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 76.6 (2 C), 80.8 (2 C), 119.3 (2 C), 128.9 (4 C), 133.7 (4 C), 134.0 (2 C).

MS (EI, 70 eV): *m/z* (%) = 200 (28), 270 (100) [M$^+$], 271 (18) [M + H]$^+$, 272 (65) [M + 2]$^+$, 273 (11), [M + 3]$^+$, 274 (11), [M + 4]$^+$.

1,1′-Buta-1,3-diyne-1,4-diylbis(2-chlorobenzene) (2f)[9c]

White solid; yield: 87 mg (32%); t_R = 18.4 min; mp 135–138 °C (hexane); R_f = 0.5 (hexane–EtOAc, 4:1).

IR (ATR): 3068, 1463, 1433, 1053 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.25 (td, *J* = 7.5 Hz, ^4J = 1.2 Hz, 2 H, ArH), 7.30–7.35 (td, *J* = 7.5 Hz, ^4J = 1.7 Hz, 2 H, ArH), 7.40–7.45 (dd, *J* = 8.0 Hz, ^4J = 1.2 Hz, 2 H, ArH), 7.55–7.60 (dd, *J* = 7.6 Hz, ^4J = 1.7 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 78.3 (2 C), 79.4 (2 C), 121.8 (2 C), 126.5 (2 C), 129.4 (2 C), 130.3 (2 C), 134.4 (2 C), 136.9 (2 C).

MS (EI, 70 eV): *m/z* (%) = 200 (34), 270 (100) [M$^+$], 271 (18) [M + H]$^+$, 272 (64) [M + 2]$^+$, 273 (12), [M + 3]$^+$, 274 (12), [M + 4]$^+$.

1,1′-Buta-1,3-diyne-1,4-diylbis[4-(trifluoromethyl)benzene] (2g)[24]

Pale-yellow solid; yield: 335 mg (99%); t_R = 15.0 min; mp 165–168 °C (hexane); R_f = 0.7 (hexane–EtOAc, 4:1).

IR (ATR): 1610, 1407 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.65 (m, 8 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 75.6 (2 C), 80.9 (2 C), 123.7 (q, $^1J_{C–F}$ = 272.4 Hz, 2 C), 125.3 (2 C), 125.4 (q, $^3J_{C–F}$ = 3.8 Hz, 4 C), 131.1 (q, $^2J_{C–F}$ = 33 Hz, 2 C), 132.8 (4 C).

MS (EI, 70 eV): *m/z* (%) = 319 (17), 338 (100) [M$^+$], 339 (22) [M + H]$^+$.

1,1′-Buta-1,3-diyne-1,4-diylbis(4-bromobenzene) (2h)[25]

Pale-yellow solid; yield: 94 mg (26%); t_R = 20.7 min; mp 140–141 °C (hexane); R_f = 0.73 (hexane–EtOAc, 4:1).

IR (ATR): 1480, 1066 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.40 (d, *J* = 8.5 Hz, 4 H, ArH), 7.45–7.50 (d, *J* = 8.5 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 77.2 (2 C), 81.0 (2 C), 120.6 (2 C), 131.7 (2 C), 131.8 (4 C), 133.8 (4 C).

MS (EI, 70 eV): *m/z* (%) = 174 (10), 199 (11), 200 (34), 207 (19), 281 (12), 358 (52), 360 (100) [M$^+$], 361 (18) [M + H]$^+$, 362 (45) [M + 2]$^+$.

1,1′-Buta-1,3-diyne-1,4-diylbis(3-methylbenzene) (2i)[15]

Pale-yellow solid; yield: 228 mg (99%); t_R = 17.3 min; mp 65–67 °C (hexane); R_f = 0.67 (hexane–EtOAc, 4:1).

IR (film): 3035, 1479 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 6 H, CH_3 × 2), 7.15–7.25 (m, 4 H, ArH), 7.30–7.35 (m, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (2 C), 73.6 (2 C), 81.6 (2 C), 121.6 (2 C), 128.3 (2 C), 129.6 (2 C), 130.1 (2 C), 132.9 (2 C), 138.1 (2 C).

MS (EI, 70 eV): *m/z* (%) = 228 (10), 229 (10), 230 (100) [M$^+$], 231 (19) [M + H]$^+$.

1,1′-Buta-1,3-diyne-1,4-diyldicyclohexane (2j)[13b]

Pale-yellow solid; yield: 150 mg (70%); t_R = 15.1 min; mp 77–82 °C (hexane); R_f = 0.97 (hexane–EtOAc, 4:1).

IR (film): 2925, 2852, 1447 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.25 (m, 6 H, CH_2 × 3), 1.35–1.45 (m, 6 H, CH_2 × 3), 1.60–1.75 (m, 8 H, CH_2 × 4), 2.35–2.40 (m, 2 H, CH × 2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.8 (4 C), 25.7 (2 C), 29.5 (2 C), 32.3 (4 C), 65.1 (2 C), 81.9 (2 C).

MS (EI, 70 eV): *m/z* (%) = 51 (13), 53 (13), 55 (23), 63 (18), 65 (17), 67 (39), 75 (10), 76 (14), 77 (33), 78 (17), 79 (43), 80 (26), 89 (15), 91 (100), 92 (23), 93 (15), 95 (17), 102 (11), 103 (16), 104 (32), 105 (33), 115 (55), 116 (16), 117 (82), 118 (28), 119 (17), 127 (14), 128 (47), 129 (63), 130 (20), 131 (62), 132 (15), 133 (11), 141 (14), 143 (39), 144 (14), 145 (27), 157 (21), 158 (11), 171 (35), 185 (16), 207 (18), 214 (84) [M$^+$], 215 (15) [M + H]$^+$.

Hexadeca-7,9-diyne (2k)[23]

Colorless oil; yield: 201 mg (92%); t_R = 14.1 min; R_f = 0.87 (hexane–EtOAc, 4:1).

IR (ATR): 1465, 1459, 1378, 724 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.95 (m, 6 H, CH_3 × 2), 1.25–1.45 (m, 12 H, CH_2 × 6), 1.45–1.55 (m, 4 H, CH_2 × 2), 2.20–2.25 (t, *J* = 6.8 Hz, 4 H, CH_2 × 2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (2 C), 19.2 (2 C), 22.5 (2 C), 28.3 (2 C), 28.5 (2 C), 31.3 (2 C), 65.2 (2 C), 77.5 (2 C).

MS (EI, 70 eV): *m/z* (%) = 51 (13), 55 (37), 63 (11), 65 (17), 67 (46), 69 (14), 76 (10), 77 (37), 78 (31), 79 (56), 80 (12), 81 (41), 91 (100), 92 (20), 93 (43), 95 (26), 105 (63), 106 (12), 107 (26), 117 (15), 119 (43), 121 (12), 133 (25), 147 (16), 161 (10), 218 (0.3) [M$^+$].

Icosa-9,11-diyne (2l)[23]

Colorless oil; yield: 137 mg (50%); t_R = 16.6 min; R_f = 0.8 (hexane–EtOAc, 4:1).

IR (ATR): 2924, 2854, 1464, 722 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.90 (t, *J* = 6.5 Hz, 6 H, CH_3 × 2), 1.25–1.40 (m, 20 H, CH_2 × 10), 1.45–1.55 (m, 4 H, CH_2 × 2), 2.20–2.25 (t, *J* = 6.9 Hz, 4 H, CH_2 × 2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (2 C), 19.2 (2 C), 22.6 (2 C), 28.4 (2 C), 28.8 (2 C), 29.0 (2 C), 29.1 (2 C), 31.8 (2 C), 65.2 (2 C), 77.5 (2 C).

MS (EI, 70 eV): *m/z* (%) = 55 (38), 57 (14), 65 (13), 67 (50), 69 (19), 77 (32), 78 (25), 79 (61), 80 (15), 81 (57), 82 (12), 91 (100), 92 (22), 93 (52), 94 (17), 95 (38), 103 (12), 105 (60), 106 (14), 107 (41), 108 (10), 109 (15), 115 (13), 117 (21), 119 (55), 120 (15), 121 (41), 131 (10), 133 (45), 134 (12), 135 (20), 147 (32), 148 (10), 149 (12), 161 (25), 175 (14), 274 (0) [M^+].

Tetracosa-11,13-diyne (2m)[26]

Pale-yellow oil; yield: 102 mg (31%); t_R = 19.5 min; R_f = 0.8 (hexane–EtOAc, 4:1).

IR (ATR): 2953, 2923, 2853, 1464, 721 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 6 H, CH_3 × 2), 1.25–1.30 (m, 28 H, CH_2 × 14), 1.45–1.55 (m, 4 H, CH_2 × 2), 2.20–2.25 (t, *J* = 7.1 Hz, 4 H, CH_2 × 2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (2 C), 19.2 (2 C), 22.7 (2 C), 28.3 (2 C), 28.8 (2 C), 29.1 (2 C), 29.3 (2 C), 29.5 (2 C), 29.6 (2 C), 31.9 (2 C), 65.2 (2 C), 77.5 (2 C).

MS (EI, 70 eV): *m/z* (%) = 55 (50), 57 (27), 65 (11), 67 (65), 69 (33), 77 (27), 78 (24), 79 (66), 80 (21), 81 (71), 82 (20), 83 (20), 91 (100), 92 (25), 93 (55), 94 (24), 95 (57), 96 (12), 103 (11), 105 (59), 106 (17), 107 (48), 108 (15), 109 (25), 115 (12), 117 (25), 119 (60), 120 (19), 121 (67), 122 (16), 123 (11), 131 (14), 133 (54), 134 (21), 135 (30), 147 (38), 148 (17), 149 (15), 161 (35), 162 (11), 163 (11), 175 (21), 189 (15), 330 (0) [M^+].

1,10-Dichlorodeca-4,6-diyne (2n)[23]

Pale-yellow oil; yield: 200 mg (99%); t_R = 13.5 min; R_f = 0.67 (hexane–EtOAc, 4:1).

IR (ATR): 2960, 2927, 1288 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95–2.00 (p, *J* = 6.5 Hz, 4 H, $ClCH_2CH_2$), 2.45–2.50 (t, *J* = 6.8 Hz, 4 H, $ClCH_2CH_2CH_2$), 3.60–3.65 (t, *J* = 6.3 Hz, 4 H, $ClCH_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6 (2 C), 31.0 (2 C), 43.4 (2 C), 66.0 (2 C), 75.8 (2 C).

MS (EI, 70 eV): *m/z* (%) = 51 (29), 53 (11), 62 (10), 63 (36), 64 (12), 65 (22), 74 (16), 76 (25), 77 (86), 78 (25), 79 (12), 89 (29), 91 (100), 102 (14), 103 (93), 104 (33), 105 (33), 111 (11), 112 (26), 114 (61), 116 (38), 117 (45), 125 (47), 127 (20), 128 (10), 129 (20), 130 (10), 131 (39), 139 (42), 141 (15), 167 (20), 174 (20), 176 (16), 202 (88) [M^+], 204 (61) $[M + 2]^+$, 206 (10) $[M + 4]^+$.

2,5-Furans 3a–d; General Procedure

CuO/Fe_3O_4 (10 mg, 0.26 mol%) and *t*-BuOK (112 mg, 1 mmol) were added to a stirred soln of the appropriate alkyne **1** (2 mmol), and the resulting mixture was stirred at 60 °C until the reaction was complete (2–7 days; see Table 3). The catalyst was then removed by using a magnet and washed with DMSO (5 mL). The DMSO washings were combined with the original reaction soln, and KOH (280 mg, 5 mmol, 250 mol%) and H_2O (4 mmol, 400 mol%) were added under air. The resulting soln was stirred at 80 °C for 1 day, then the reaction was quenched by addition of H_2O (5 mL). The resulting mixture was extracted with EtOAc (2 × 5 mL) and the combined organic phases were dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography.

2,5-Diphenylfuran (3a)[21]

Pale-yellow solid; yield: 109 mg (99%); t_R = 15.8 min; mp 47–52 °C (hexane); R_f = 0.73 (hexane–EtOAc, 4:1).

IR (ATR): 3022, 1259, 1023, 927 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.75 (s, 2 H, CH × 2), 7.25–7.30 (m, 2 H, ArH), 7.40–7.45 (m, 4 H, ArH), 7.70–7.75 (m, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.2 (2 C), 123.7 (4 C), 127.3 (2 C), 128.7 (4 C), 130.7 (2 C), 153.3 (2 C).

MS (EI, 70 eV): *m/z* (%) = 51 (10), 77 (29), 105 (16), 115 (32), 191 (20), 220 (100) [M^+], 221 (18) $[M + H]^+$.

2,5-Bis(4-methoxyphenyl)furan (3b)[27]

White solid; yield: 83 mg (59%); t_R = 17.5 min; mp 189–192 °C (hexane); R_f = 0.20 (hexane–EtOAc, 4:1).

IR (ATR): 2839, 1600, 1509, 1018 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 6 H, CH_3 × 2), 6.58 (s, 2 H, CH × 2), 6.90–6.95 (d, *J* = 9.0 Hz, 4 H, ArH), 7.65–7.70 (d, *J* = 9.0 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3 (2 C), 105.5 (2 C), 114.1 (4 C), 124.0 (2 C), 125.0 (4 C), 152.8 (2 C), 158.8 (2 C).

MS (EI, 70 eV): *m/z* (%) = 140 (14), 265 (87), 266 (16), 280 (100) [M^+], 281 (20) $[M + H]^+$.

2,5-Bis(4-tolyl)furan (3c)[27]

White solid; yield: 112 mg (90%); t_R = 17.9 min; mp 114–117 °C (hexane); R_f = 0.73 (hexane–EtOAc, 4:1).

IR (ATR): 3020, 2914, 2856, 1605, 1503, 1021 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 6 H, CH_3 × 2), 6.70 (s, 2 H, CH × 2), 7.20–7.25 (d, *J* = 8.1 Hz, 4 H, ArH), 7.60–7.65 (d, *J* = 8.1 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (2 C), 106.3 (2 C), 123.4 (4 C), 128.0 (2 C), 129.2 (4 C), 136.9 (2 C), 153.0 (2 C).

MS (EI, 70 eV): *m/z* (%) = 129 (9), 248 (10) [M^+], 249 (20) $[M + H]^+$.

2,5-Bis[4-(trifluoromethyl)phenyl]furan (3d)[21]

Pale-yellow solid; yield: 176 mg (99%); t_R = 15.5 min; mp 139–141 °C (hexane); R_f = 0.57 (hexane–EtOAc, 4:1).

IR (film): 1617 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90 (s, 2 H, CH × 2), 7.65–7.70 (d, *J* = 8.1 Hz, 4 H, ArH), 7.85–7.90 (d, *J* = 8.1 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.4 (2 C), 123.9 (4 C), 124.1 (q, $J_{C–F}$ = 271.8 Hz, 2 C), 125.8 (q, $J_{C–F}$ = 3.7 Hz, 4 C), 129.4 (q, $^2J_{C–F}$ = 33.2 Hz, 2 C), 133.4 (2 C), 152.8 (2 C).

MS (EI, 70 eV): *m/z* (%) = 145 (17), 173 (11), 183 (21), 337 (10), 356 (100) [M^+], 357 (20) $[M + H]^+$.

1,1′-Buta-1,3-diyne-1,4-diyldibenzene (2a) by Decarboxylative Coupling of 3-Phenylprop-2-ynoic Acid (4)

Et_3N (0.07 mL, 138 mol%), DMF (1.5 mL), and $CuO–Fe_3O_4$ (50 mg, 2.1 mol%) or $NiO–Cu/Fe_3O_4$ (50 mg, 1.5 + 1.83 mol%) were added to a stirred soln of alkynoic acid **4** (0.6 mmol) under air, and the resulting mixture was stirred at 130 °C for 2 days. The catalyst was removed by using a magnet and washed with EtOAc (2 × 5 mL) and H_2O (2 × 5 mL). The collected organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography; yield: 21% ($CuO–Fe_3O_4$) or quant ($NiO–Cu/Fe_3O_4$).

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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