Copper(I) Iodide Catalyzed Cross-Coupling Reaction of Terminal Alkynes with 1-Bromoalkynes: A Simple Synthesis of Unsymmetrical Buta-1,3-diynes

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Abstract: A simple synthesis of unsymmetrical buta-1,3-diynes by cross-coupling of terminal alkynes with 1-bromoalkynes in the presence of copper(I) iodide and tris(*o*-tolyl)phosphine was developed that gives good yields under simple and mild reaction conditions. The scope and limitations of the cross-coupling reaction were investigated.

Key words: alkynes, catalysis, cross-coupling, alkadiynes

Buta-1,3-diynes are important building blocks in the organic syntheses of natural products,[1] industrial and pharmaceutical intermediates,[2] organic–inorganic composites,[3] and electronic and optical materials.[4] Numerous methods have been developed for the preparation of buta-1,3-diynes. An efficient and useful method for preparing symmetrical buta-1,3-diynes by treatment of terminal alkynes with copper(I) chloride in the presence of ammonium hydroxide was developed by Glaser in 1869.[5] Subsequently, many improved methods for preparing buta-1,3-diynes have been developed on the basis of Glaser's discovery.[6] Palladium(0)/copper(I)-catalyzed coupling is also an important method for the synthesis of buta-1,3-diynes.[7] However, most of these coupling reactions are homo-coupling reactions of terminal acetylenes to form symmetrical buta-1,3-diynes.[8] Therefore, the synthesis of unsymmetrical buta-1,3-diynes has attracted a great deal of attention over a long period.[9] Currently, the main methods used for constructing unsymmetrical buta-1,3-diynes are the Cadiot–Chodkiewicz coupling reaction and its modifications.[10] Though powerful in many cases, these coupling reactions frequently give large amounts of the symmetrical buta-1,3-diyne products. Recently, Lei described an efficient method for the synthesis of unsymmetrical buta-1,3-diynes from terminal alkynes and 1-bromoalkynes in the presence of a palladium catalyst;[11] however, such catalysts are expensive and unstable to air. To improve this cross-coupling reaction, we investigated the possibility of performing the cross-coupling of terminal alkynes with 1-bromoalkynes in the absence of a palladium catalyst. Here, we report a new route to unsymmetrical buta-1,3-diynes from terminal alkynes and 1-bromoalkynes by coupling in the presence of copper(I) iodide with tris(*o*-tolyl)phosphine as a ligand under mild and simple reaction conditions.

Initially, our investigation was directed towards optimizing the reaction conditions for the cross-coupling of 1-ethynyl-4-methoxybenzene (**1a**) with (bromoethynyl)benzene (**2a**) in the presence of copper(I) iodide as a catalyst. First, we examined the effect of the ligand on the cross-coupling reaction, and our results are shown in Table 1. Only a trace of the cross-coupling product **3a** was detected by TLC in the absence of a ligand (Table 1, entry 1). However, the cross-coupling product **3a** was obtained in 94% yield when tris(*o*-tolyl)phosphine was used as the ligand in ethanol (entry 2). The use of triphenylphosphine as the ligand also gave **3a** in a comparable yield (entry 3). Other phosphine ligands, such as diphenyl(*p*-tolyl)phosphine, tri-*tert*-butylphosphine, or ethane-1,2-diylbis(diphenylphosphine) (DPPE) gave inferior results (entries 4–6). Poor yields were also obtained with pyridine, 1,4-diazabicyclo[2,2,2]octane (DABCO), 1,10-phenanthroline, quinoline, or 2-acetylcyclohexanone (entries 7–11, respectively).When 2-aminoethanol was used as the ligand, no cross-coupling product was detected (entry 12). Further investigations in various solvents showed that ethanol is the optimal solvent for the cross-coupling reaction (entry 2). Slightly lower yields of product **3a** were obtained when acetonitrile, 1,2-dichloroethane (DCE), nitromethane, *N*,*N*-dimethylformamide (DMF), or toluene was used as the solvent instead of ethanol, whereas only moderate yields were obtained in 1,4-dioxane, tetrahydrofuran (THF), or water (entries 13–20).

Next, we examined the influence of the copper salt and the base on the cross-coupling reaction, and our results are summarized in Table 2. Various copper salts were screened as catalysts in the presence of tris(*o*-tolyl)phosphine in ethanol, and copper(I) iodide was found to be the optimal choice (Table 2, entry 1). The yield of the product **3a** decreased when copper(I) bromide or chloride was used instead of the iodide (entries 2 and 3). Other copper salts, such as copper(II) chloride, copper(II) bromide, bis(acetylacetonato)copper(II), or copper(II) triflate gave inferior results, generating **3a** in 84, 82, 56 and 77% yield, respectively (entries 4–7). With regard to the effect of bases on the reaction, potassium carbonate was found to be an excellent base, and trisodium phosphate was also effective (entries 1 and 8, respectively)). Use of cesium carbonate, sodium hydroxide, or potassium *tert*-butoxide

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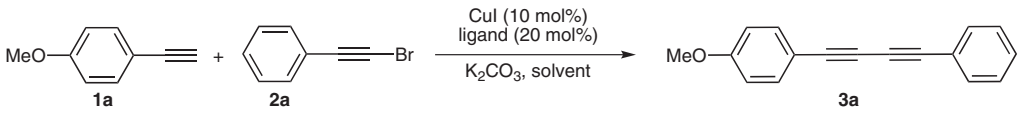
Table 1 Effect of the Ligand and Solvent on the Cross-Coupling Reaction



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

Entry[a]	Ligand	Solvent	Yield[b] (%)
1	–	EtOH	<10
2	P(*o*-Tol)$_3$	EtOH	94
3	PPh$_3$	EtOH	91
4	(*p*-Tol)PPh$_2$	EtOH	59
5	P(*t*-Bu)$_3$	EtOH	71
6	DPPE	EtOH	63
7	pyridine	EtOH	34
8	DABCO	EtOH	42
9	1,10-phenanthroline	EtOH	45
10	quinoline	EtOH	44
11	2-acetylcyclohexanone	EtOH	42
12	HO(CH$_2$)$_2$NH$_2$	EtOH	–[c]
13	P(*o*-Tol)$_3$	MeCN	82
14	P(*o*-Tol)$_3$	DCE	84
15	P(*o*-Tol)$_3$	MeNO$_2$	78
16	P(*o*-Tol)$_3$	DMF	79
17	P(*o*-Tol)$_3$	toluene	74
18	P(*o*-Tol)$_3$	1,4-dioxane	67
19	P(*o*-Tol)$_3$	THF	61
20	P(*o*-Tol)$_3$	H$_2$O	57

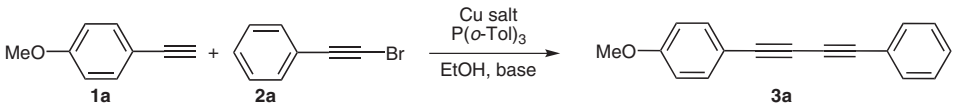
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.65 mmol), CuI (0.05 mmol), ligand (0.10 mmol), K_2CO_3 (1.0 mmol), solvent (2.0 mL), 100 °C, 12 h, under N_2.
[b] Isolated yield.
[c] Not detected.

gave moderate yields of **3a** (entries 9–11). The organic bases triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave the cross-coupling product in 71 and 59%, respectively (entries 12 and 13).

With these optimized reaction conditions in hand, we explored the scope and efficiency of the cross-coupling reaction, as shown in Table 3. Various terminal alkynes and 1-bromoalkynes were used as the reaction substrates, and the corresponding unsymmetrical buta-1,3-diynes were generally obtained in good yields. Various polar alkynes were used to overcome problems in separation. Aromatic 1-bromoalkynes **2**, containing various substituents, reacted with terminal alkynes **1** to give the corresponding products **3** in good yields (Table 3, entries 2 and 4). Aliphatic 1-bromoalkynes, such as 1-bromooct-1-yne (**2c**), also gave the desired product in 78% yield (entry 3).

To evaluate the scope of the cross-coupling reaction in more detail, several terminal alkynes were also tested in the optimized reaction conditions. Clearly, substituents on the aromatic terminal alkynes had no obvious effect on the yield of the reaction (entries 4–9). A good yield of the product was obtained when 1-ethynyl-2-nitrobenzene (**1h**) was used as reaction substrate (entry 10). The heteroaromatic terminal alkyne 3-ethynylpyridine (**1i**) gave the corresponding product **3i** in 77% yield (entry 11). Aliphatic alkynes also gave the desired cross-coupling products in good yields (entries 12–16 and 18). Note that the reaction of 5-chloropent-1-yne (**1m**) with **2a** gave the desired product **3n** in 81% yield, and the chloro group was well tolerated (entry 17). Also note that the cross-coupling reactions of terminal aromatic alkynes with 2-arylethynyl bromides were clean and gave excellent yields of the

Table 2 Effect of the Copper Source and Base on the Cross-Coupling Reaction



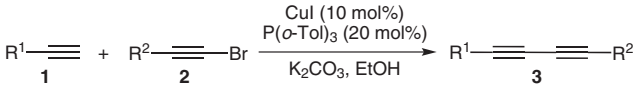
1a **2a** **3a**

Entry[a]	Cu salt	Base	Yield[b] (%)
1	CuI	K_2CO_3	94
2	CuCl	K_2CO_3	80
3	CuBr	K_2CO_3	79
4	$CuCl_2$	K_2CO_3	84
5	$CuBr_2$	K_2CO_3	82
6	$Cu(acac)_2$	K_2CO_3	56
7	$Cu(OTf)_2$	K_2CO_3	77
8	CuI	Na_3PO_4	91
9	CuI	Cs_2CO_3	69
10	CuI	NaOH	64
11	CuI	*t*-BuOK	67
12	CuI	Et_3N	71
13	CuI	DBU	59

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.65 mmol), copper salt (0.05 mmol), P(*o*-Tol)$_3$ (0.10 mmol), base (1.0 mmol), EtOH (2.0 mL), 100 °C, 12 h, under N_2.
[b] Isolated yield.

cross-coupling products. The cross-coupling reactions of terminal aromatic or aliphatic alkynes with 2-arylethynyl bromides gave the corresponding cross-coupling products in 73–90% yields, along with less than 10% of the corresponding homo-coupled byproducts. However, the reactions of terminal aliphatic alkynes with 2-alkylethynyl bromides resulted in no cross-coupling product, and about a 10% yield of the homocoupling product was detected together with unchanged starting materials, which could be recovered.

Table 3 Copper(I) Iodide Catalyzed Cross-Coupling Reaction of Terminal Alkynes with 1-Bromoalkynes



1 **2** **3**

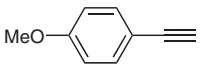
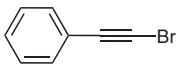
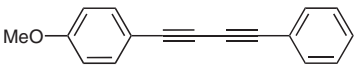
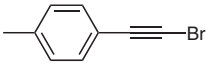
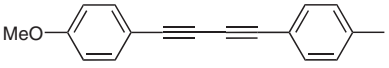
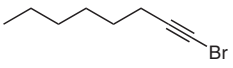
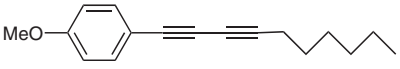
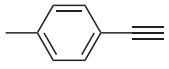
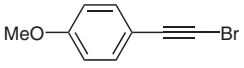
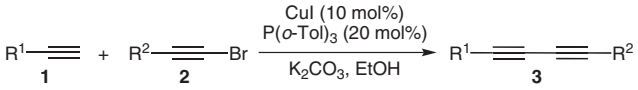
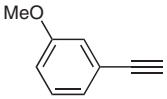
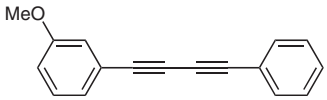
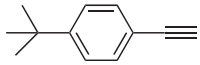
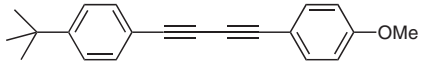
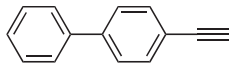
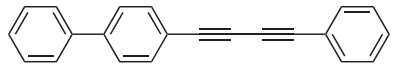
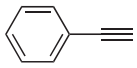
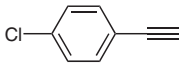
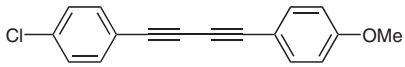
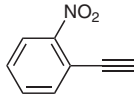
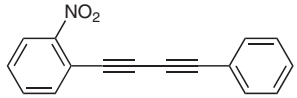
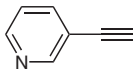
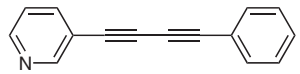
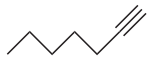
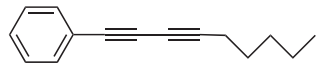
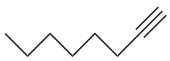
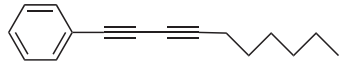
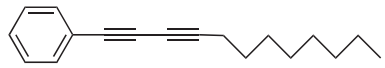
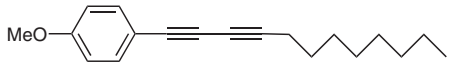
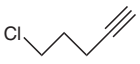
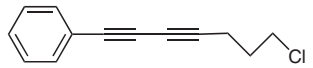
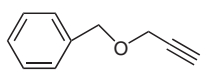
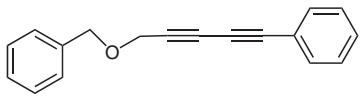
Entry[a]	1	2	3	Yield[b] (%)
1	 **1a**	 **2a**	 **3a**	94
2	**1a**	 **2b**	 **3b**	90
3	**1a**	 **2c**	 **3c**	78
4	 **1b**	 **2d**	**3b**	90

Table 3 Copper(I) Iodide Catalyzed Cross-Coupling Reaction of Terminal Alkynes with 1-Bromoalkynes (continued)



Entry[a]	1	2	3	Yield[b] (%)
5	 **1c**	**2a**	 **3d**	89
6	 **1d**	**2d**	 **3e**	92
7	 **1e**	**2a**	 **3f**	96
8	 **1f**	**2d**	**3a**	94
9	 **1g**	**2d**	 **3g**	88
10	 **1h**	**2a**	 **3h**	81
11	 **1i**	**2a**	 **3i**	77
12	 **1j**	**2a**	 **3j**	80
13	 **1k**	**2a**	 **3k**	86
14	**1k**	**2d**	**3c**	73
15	 **1l**	**2a**	 **3l**	90
16	**1l**	**2d**	 **3m**	79
17	 **1m**	**2a**	 **3n**	81
18	 **1n**	**2a**	 **3o**	92

[a] *Reaction conditions*: Terminal alkyne (0.50 mmol), 1-bromoalkyne (0.65 mmol), CuI (0.05 mmol), P(*o*-Tol)$_3$ (0.10 mmol), K_2CO_3 (1.0 mmol), EtOH (2.0 mL), 100 °C, 12 h, under N_2.
[b] Isolated yields.

In summary, we have developed a new route to unsymmetrical buta-1,3-diynes from terminal alkynes and 1-bromoalkynes by cross-coupling in the presence of copper(I) iodide and tris(*o*-tolyl)phosphine as ligand in ethanol under mild conditions. This method provides an efficient and simple technique for the synthesis of unsymmetrical buta-1,3-diynes that compares favorably with previous methods for the syntheses of these compounds. Applications and the development of our new reaction system are now under investigation.

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-400 MHz FT-NMR spectroscope. Chemical shifts are given as δ value with reference to TMS as internal standard. High-resolution mass spectra were recorded on a Waters Micromass GCT instrument. Products were purified by flash column chromatography on 230–400 mesh silica gel.

1-Methoxy-4-(4-phenylbuta-1,3-diyn-1-yl)benzene (3a);[10b] Typical Procedure

A reaction flask was charged with CuI (9.6 mg, 0.05 mmol), P(*o*-Tol)$_3$ (30.4 mg, 0.10 mmol), K_2CO_3 (138 mg, 1.0 mmol), 1-ethynyl-4-methoxybenzene (**1a**; 76 mg, 0.50 mmol), 1-(2-bromoethynyl)benzene (**2a**; 118 mg, 0.65 mmol), and anhyd EtOH (2.0 mL). The mixture was stirred for 12 h at 100 °C then cooled to r.t. The mixture was diluted with EtOAc (3 × 5.0 mL), filtered through a pad of Celite, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, PE or cyclohexane gradient); yield: 109 mg (94%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (dd, *J* = 1.6, 7.6 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.37–7.31 (m, 3 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.31, 134.08, 132.38, 129.00, 128.38, 121.93, 114.11, 113.61, 81.78, 80.98, 74.13, 72.69, 55.29.

1-Methoxy-4-[4-(4-methylphenyl)buta-1,3-diyn-1-yl]benzene (3b)[12]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.23, 139.38, 134.05, 132.31, 129.18, 118.80, 114.09, 113.75, 81.43, 81.28, 73.49, 72.81, 55.30, 21.60.

1-Deca-1,3-diyn-1-yl-4-methoxybenzene (3c)[15]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, *J* = 8.8 Hz, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 3.80 (s, 3 H), 2.35 (t, *J* = 7.2 Hz, 2 H), 1.60–1.53 (m, 2 H), 1.46–1.38 (m, 2 H), 1.36–1.27 (m, 4 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.96, 133.99, 114.00, 113.98, 84.17, 74.77, 73.10, 65.14, 55.23, 31.28, 28.53, 28.25, 22.50, 19.55, 14.02.

1-Methoxy-3-(4-phenylbuta-1,3-diyn-1-yl)benzene (3d)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.55 (d, *J* = 7.2 Hz, 2 H), 7.40–7.34 (m, 3 H), 7.29–7.25 (m, 1 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 7.07 (s, 1 H), 6.96–6.94 (m, 1 H), 3.82 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.22, 132.47, 129.52, 129.22, 128.42, 125.03, 122.65, 121.67, 116.98, 115.99, 81.55, 81.43, 73.80, 73.65, 55.27.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{17}H_{12}O$: 232.0888; found: 232.0892.

1-*tert*-Butyl-4-[4-(4-methoxyphenyl)buta-1,3-diyn-1-yl]benzene (3e)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50–7.48 (m, 4 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H), 1.34 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.22, 152.43, 134.04, 132.17, 125.43, 118.83, 114.09, 113.74, 81.39, 81.28, 73.48, 72.88, 55.27, 34.84, 31.05.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{21}H_{20}O$: 288.1514; found: 288.1518.

4-(4-Phenylbuta-1,3-diyn-1-yl)biphenyl (3f)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.60–7.52 (m, 8 H), 7.46–7.42 (m, 2 H), 7.38–7.31 (m, 4 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.90, 140.03, 132.92, 132.48, 129.19, 128.88, 128.43, 127.83, 127.08, 127.01, 121.75, 120.55, 81.84, 81.50, 74.55, 73.98.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{22}H_{14}$: 278.1096; found: 278.1093.

1-Chloro-4-[4-(4-methoxyphenyl)buta-1,3-diyn-1-yl]benzene (3g)[10b]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50–7.44 (m, 4 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.42, 135.12, 134.15, 133.58, 128.80, 120.47, 114.15, 113.42, 82.37, 79.75, 75.11, 72.47, 55.34.

1-Nitro-2-(4-phenylbuta-1,3-diyn-1-yl)benzene (3h)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.12 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.63–7.60 (m, 1 H), 7.57–7.54 (m, 2 H), 7.53–7.49 (m, 1 H), 7.43–7.34 (m, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.80, 133.02, 132.62, 129.67, 129.33, 128.48, 124.93, 121.18, 117.70, 84.79, 81.47, 76.09, 73.60.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{16}H_9NO_2$: 247.0633; found: 247.0636.

3-(4-Phenylbuta-1,3-diyn-1-yl)pyridine (3i)[13]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.77 (s, 1 H), 8.59 (d, *J* = 2.8 Hz, 1 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.55 (d, *J* = 6.8 Hz, 2 H), 7.42–7.34 (m, 3 H), 7.30–7.28 (m, 1 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.02, 149.14, 139.24, 132.52, 129.50, 128.45, 123.00, 121.24, 119.19, 82.71, 77.90, 77.15, 73.31.

Nona-1,3-diyn-1-ylbenzene (3j)[11]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 (dd, *J* = 1.6, 7.6 Hz, 2 H), 7.34–7.28 (m, 3 H), 2.36 (t, *J* = 7.2 Hz, 2 H), 1.62–1.55 (m, 2 H), 1.45–1.32 (m, 4 H), 0.92 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.45, 128.75, 128.29, 122.08, 84.87, 74.64, 74.36, 65.00, 30.99, 27.92, 22.15, 19.52, 13.91.

Deca-1,3-diyn-1-ylbenzene (3k)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48 (d, *J* = 7.2 Hz, 2 H), 7.36–7.26 (m, 3 H), 2.37 (t, *J* = 7.2 Hz, 2 H), 1.62–1.55 (m, 2 H), 1.47–1.40 (m, 2 H), 1.36–1.31 (m, 4 H), 0.92 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.44, 128.74, 128.29, 122.08, 84.85, 74.63, 74.38, 65.00, 31.27, 28.53, 28.20, 22.50, 19.55, 14.03.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{16}H_{18}$: 210.1409; found: 210.1411.

1-Dodeca-1,3-diyn-1-ylbenzene (3l)[14]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (dd, *J* = 1.2, 7.2 Hz, 2 H), 7.35–7.29 (m, 3 H), 2.37 (t, *J* = 7.2 Hz, 2 H), 1.60–1.55 (m, 2 H), 1.45–1.42 (m, 2 H), 1.36–1.31 (m, 8 H), 0.92 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.41, 128.71, 128.26, 122.07, 84.80, 74.60, 74.40, 65.03, 31.80, 29.13, 29.04, 28.85, 28.23, 22.63, 19.53, 14.06.

1-Dodeca-1,3-diyn-1-yl-4-methoxybenzene (3m)[16]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.42 (d, *J* = 8.8 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 2.36 (t, *J* = 7.2 Hz, 2 H), 1.61–1.54 (m, 2 H), 1.44–1.42 (m, 2 H), 1.34–1.28 (m, 8 H), 0.90 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.91, 133.97, 113.94, 113.83, 84.18, 74.74, 73.05, 65.09, 55.22, 31.79, 29.13, 29.04, 28.84, 28.26, 22.63, 19.53, 14.09.

(7-Chlorohepta-1,3-diyn-1-yl)benzene (3n)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (d, *J* = 6.4 Hz, 2 H), 7.38–7.29 (m, 3 H), 3.69 (t, *J* = 6.4 Hz, 2 H), 2.58 (t, *J* = 6.8 Hz, 2 H), 2.07–2.00 (m, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.46, 128.94, 128.32, 121.72, 82.41, 75.14, 73.99, 66.00, 43.40, 30.88, 16.97.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{13}H_{11}Cl$: 202.0549; found: 202.0548.

[5-(Benzyloxy)penta-1,3-diyn-1-yl]benzene (3o)[9]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 (dd, *J* = 1.2, 8.0 Hz, 2 H), 7.42–7.33 (m, 8 H), 4.67 (s, 2 H), 4.35 (s, 2 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.04, 132.55, 129.28, 128.43, 128.37, 128.10, 127.94, 121.32, 78.68, 78.05, 73.32, 71.67, 71.10, 57.68.

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

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