

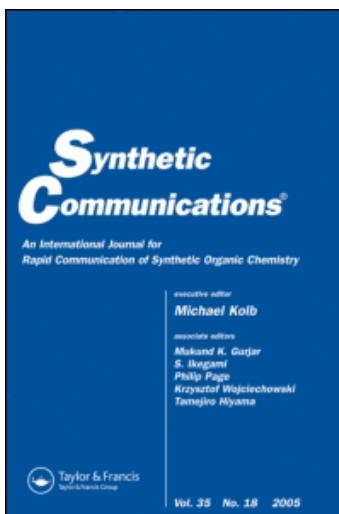
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Nanosized Iron- or Copper-Catalyzed Homocoupling of Aryl, Heteroaryl, Benzyl, and Alkenyl Grignard Reagents

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Abstract: Under very mild reaction conditions, iron or copper nanoparticles efficiently promoted the homocoupling of different Grignard reagents in tetrahydrofuran at room temperature. The nanosized iron or copper particles were generated in situ in a simple and economical way from commercially available FeCl_2 or CuCl_2 , respectively, an excess of lithium powder, and a catalytic amount (5 mol%) of 4,4'-di-*tert*-butylbiphenyl (DTBB) as electron carrier. The reaction of a series of aryl, heteroaryl, benzyl, and alkenyl Grignard reagents in the presence of a stoichiometric amount of the iron or copper nanoparticles led to the formation of the corresponding homocoupling products in good yield.

Keywords: Copper nanoparticles, Grignard reagents, homocoupling, iron nanoparticles

Transition metal-catalyzed coupling reactions of organohalogenated compounds to form carbon-carbon bonds are one of the most powerful tools in organic synthesis.^[1] In the past decade, this methodology evolved into a general and efficient route for the synthesis of many relevant chemicals, materials, and bioactive compounds.^[1,2] Among the different transition metal-based reagents utilized in these coupling reactions,

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palladium and nickel complexes are by far the most widely studied, mainly because of their selectivity, extensive applicable scope, and compatibility with many functional groups.^[3] However, most of the palladium- and nickel-based catalysts are expensive and involve the use of toxic ligands such as phosphine compounds. Therefore, the development of more convenient methodologies with respect to environmental and economic considerations is still in demand. In this sense, the use of iron- or copper-based catalysts is particularly attractive because both metals are inexpensive, readily available, and very attractive regarding environmental considerations. On the other hand, the previous or in situ transformation of the organohalogenated substrates into the corresponding Grignard reagents is a valuable alternative because it allows the use of a wide variety of metal reagents as catalysts.^[4] Since the pioneering work of Kochi et al.,^[5] iron and copper salts emerged as very attractive alternatives for the homo- and cross-coupling of Grignard reagents and halogenated compounds.^[6] In recent years, interest in the homocoupling of vinyl, aryl, and heteroaryl organomagnesium reagents^[4b,c,7,8c] has been renewed mainly because these reactions provide an easy access to the construction of a symmetrical di- or polyolefinic, aromatic or heteroaromatic backbone, with potential important applications in the field of optical materials, molecular devices, and organic conductors.^[9] Although the homocoupling of Grignard reagents has been observed as a side reaction by many authors dealing with metal-catalyzed cross-coupling reactions, few reports appear in the literature concerning the selective homocoupling of organomagnesium compounds by iron or copper catalysis. Recently, Nagano and Hayashi^[7a] and Cahiez et al.^[4b] independently reported the homocoupling of aryl Grignard reagents catalyzed by iron trichloride in the presence of noxious 1,2-dihalogenalkanes. Following that, Xu et al.^[4c] described the homocoupling of in situ generated organomagnesium compounds derived from alkyl and aryl bromides by using a combination of metallic magnesium and a catalytic amount of iron salts, although no homocoupled products were obtained using aryl chlorides as substrates. More recently, Cahiez et al.^[7f] and Liu and Lei^[7h] reported the homocoupling of aryl Grignard reagents catalyzed by iron trichloride using molecular oxygen or dry air as the oxidant. On the other hand, to the best of our knowledge, the copper-mediated homocoupling of Grignard reagents for the preparation of the corresponding symmetrical coupled products was seldom reported before.^[8]

In the past, we have been working on the reduction of different organic functional groups using new reducing systems consisting of a mixture of copper or iron hydrated salts ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, O, respectively), an excess of lithium powder, and a catalytic amount of an arene as electron carrier, in which the source of hydrogen is the salt

crystallization water.^[10,11] Our ongoing interest in exploring the synthetic scope and applicability of these active-metal-based reactive combinations prompted us to study the reactivity of the analogous copper- and iron-based systems but using the corresponding anhydrous salts to be tested in different coupling reactions. In a very recent communication,^[12] we have reported the efficiency of the $\text{FeCl}_2\text{-Li-arene}$ (cat.) system in the reductive coupling of nitro-aromatics to directly afford the corresponding azo-compounds in good yields. On the other hand, we found that the active iron and copper generated by this methodology consisted of very reactive, monodispersed spherical iron(0) or copper(0) nanoparticles. Typical transmission electron microscopy (TEM) micrographs and sizes distribution graphics for both iron and copper nanoparticles are depicted in Figs. 1 and 2, respectively.

We report herein our results on a coupling methodology of various organomagnesium compounds, including chlorides and bromides, that leads to a simple and economic preparation of biaryls, biheteroaryls, bibenzyls, and conjugated dienes, under very mild reaction conditions, using a substoichiometric amount of iron(0) or copper(0) nanoparticles, generated in situ from commercially available iron(II) chloride or copper(II) chloride respectively, lithium, and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB) as electron carrier.

Table 1 summarizes the results obtained for the reaction of a series of aryl, heteroaryl, benzyl, and vinyl Grignard reagents (1.0 mmol) with a mixture of iron(II) chloride (0.5 mmol) or copper(II) chloride (0.5 mmol), an excess of lithium powder (1:8 molar ratio, referred to the iron or copper salt), and a catalytic amount of DTBB (5.0 mol%) in tetrahydrofuran at room temperature, which led to the corresponding homocoupling

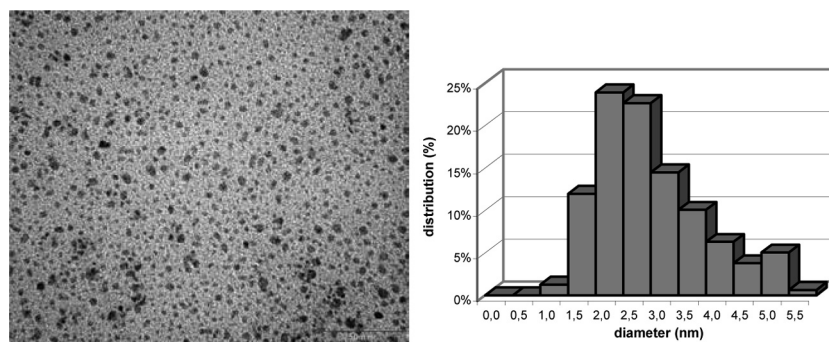


Figure 1. TEM micrograph and size distribution graphic of iron nanoparticles. The sizes were determined by measuring diameters of 200 nanoparticles randomly selected on the TEM images.

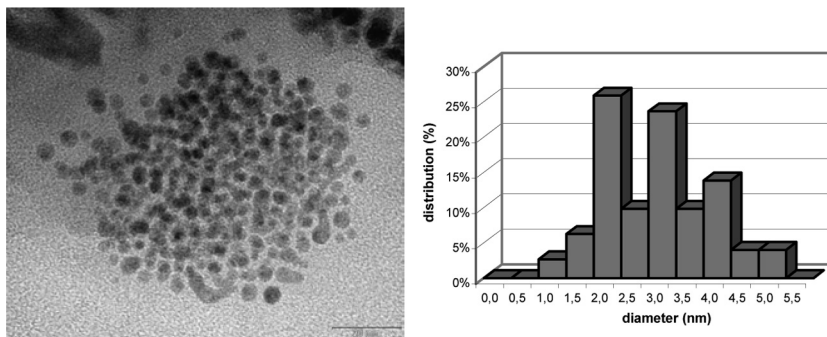
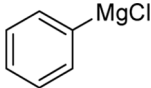
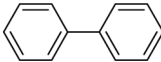
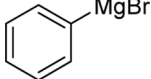
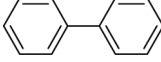
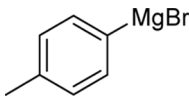
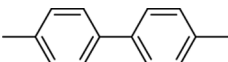
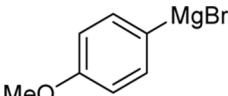
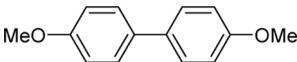
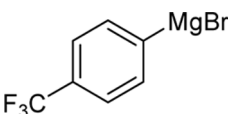
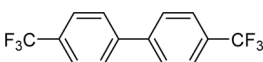
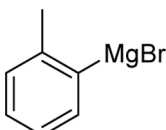
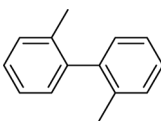
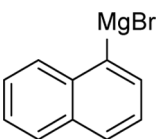
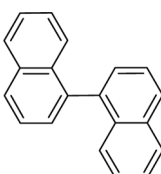
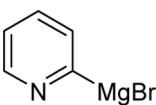
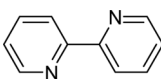


Figure 2. TEM micrograph and size distribution graphic of copper nanoparticles. The sizes were determined by measuring diameters of 200 nanoparticles randomly selected on the TEM images.

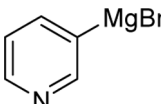
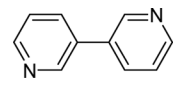
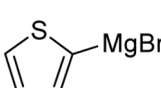
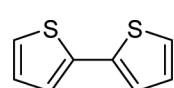
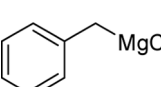
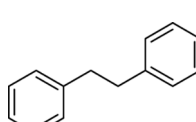
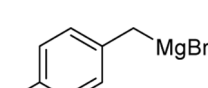
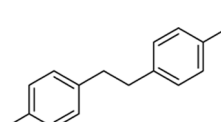
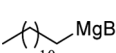

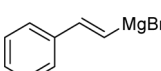
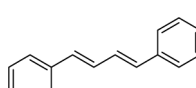
products. Both phenylmagnesium chloride and bromide gave biphenyl in excellent yield (Table 1, entries 1 and 2 respectively) either using iron(0) or copper(0) nanoparticles. Similarly, *p*-methylphenylmagnesium bromide rendered the corresponding 4,4'-dimethylbiphenyl in good yield (Table 1, entry 3). It is worth noting that for the iron-promoted homocoupling, the electronic properties of substituents attached to the aromatic ring did not affect the coupling process. Substrates bearing strong electron-releasing groups (Table 1, entry 4) or electron-withdrawing ones (Table 1, entry 5) gave the symmetrically substituted biaryls in good yield. However, the copper-based system showed a notably lower efficiency for the coupling of aryl Grignard reagents having an electron-withdrawing group on the aromatic ring (Table 1, entry 5), which is in agreement with previous results published by Lee for the copper(II) triflate-induced homocoupling of Grignard reagents.^[8c] With regard to the steric hindrance effect, substitution at the ortho positions of the aryl Grignard reagents resulted in significantly lower yields of the homocoupling products with both iron- and copper-based coupling systems (Table 1, entries 6 and 7). Interestingly, the coupling procedure was successfully applied to heteroaromatic Grignard reagents such as 2-pyridylmagnesium bromide, 3-pyridylmagnesium bromide and 2-thienylmagnesium bromide, which were efficiently converted into the corresponding biheteroaryl compounds in good yields (Table 1, entries 8, 9 and 10, respectively). Under the same conditions, benzyl Grignard reagents afforded the corresponding 1,2-diarylethanes in excellent yield (Table 1, entries 11 and 12, respectively), although other primary alkyl Grignard reagents such as dodecylmagnesium bromide (Table 1, entry 13) gave very low conversion to the desired tetracosane. Finally, it should be noted that both

Table 1. Iron- or copper-catalyzed homocoupling of Grignard reagents

Entry	Grignard reagent	Reaction time (h) ^a	Product	Yield (%) ^b	
				Fe ^c	Cu ^d
1		4		85	82
2		4		88	80
3		3		77	73
4		3		84	79
5		5		80	66
6		8		65 ^e	63 ^e
7		10		54 ^f	51 ^f
8		4		75	72

(Continued)

Table 1. Continued

Entry	Grignard reagent	Reaction time (h) ^a	Product	Yield (%) ^b	
				Fe ^c	Cu ^d
9		4		78	70
10		3		85	81
11		2		75 ^g	75 ^g
12		2		81 ^g	80 ^g
13		8		20 ^g	16 ^g
14 ^h		8		50 ⁱ	41 ⁱ

^aAll reactions were performed using RMgX (1.0 mmol), FeCl₂ or CuCl₂ (0.5 mmol), Li (8.0 mmol), DTBB (0.1 mmol), THF, 20 °C.

^bAll products were > 95% pure (GLC); isolated yield after column chromatography (hexane-ethyl acetate), based on the starting material, unless otherwise stated.

^cReaction performed with the FeCl₂-Li-DTBB(cat.) system.

^dReaction performed with the CuCl₂-Li-DTBB(cat.) system.

^eA ca. 1:1 mixture of toluene and *o*-cresol was recovered as by-products.

^fA ca. 1:1 mixture of naphthalene and 1-naphthol was recovered as by-products.

^gGLC yield based on the starting material.

^hA 1:1 mixture of *Z*- and *E*-isomers was used.

ⁱDiastereoisomeric ratio: *E/E/E/Z* = 99:1, determined by GC-MS.

iron- and copper-based coupling systems promoted the homocoupling of alkenyl Grignard reagents in a highly stereoselective way. Thus, when the previously described methodology was applied to a 1:1 mixture of (*E*)- and (*Z*)- β -styrylmagnesium bromide, the corresponding (*E,E*)-1,4-diphenylbutadiene was obtained as the main reaction product (ca. 99%), although in low to moderate yield (Table 1, entry 14).

The presence of the iron or copper nanoparticles was demonstrated to be essential by carrying out two blank experiments with *p*-methylphenylmagnesium bromide as the starting material. Thus, without using the mentioned nanoparticles, after workup of the reaction mixture, only toluene and very low yields (10–15%) of the desired homocoupling product were obtained after stirring for 12 h at room temperature.

In summary, we have developed two efficient iron- and copper-catalyzed methodologies to perform the homocoupling of aryl-, heteroaryl-, benzyl-, and alkenylmagnesium chlorides and bromides, under mild reaction conditions, based on the use of iron(0) or copper(0) nanoparticles generated in a simple and economic way from commercially available iron(II) chloride or copper(II) chloride, lithium, and a catalytic amount of DTBB as electron carrier. It should be noted that the reactions were highly stereoselective in the coupling of alkenyl Grignard reagents. We are actively exploring new applications of these coupling systems to cross-coupling reactions, and further study on the mechanistic aspects is in progress.

EXPERIMENTAL

General Procedure

All moisture-sensitive reactions were carried out under a nitrogen atmosphere. Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Other solvents used were treated prior to use by standard methods.^[13] Anhydrous iron(II) chloride and copper(II) chloride were commercially available (Aldrich). Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm , 240–400 mesh). Thin-layer chromatography (TLC) was performed on precoated silica gel plates (Merck 60, F254, 0.25 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 spectrophotometer using CDCl_3 as solvent and tetramethylsilane (TMS) as internal reference. Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 gas chromatography–mass spectrometry (GC/MS) instrument equipped with a HP-5972 selective mass detector. Infrared (FT-IR) spectra were obtained on a Nicolet-Nexus spectrophotometer. The purity of volatile

compounds and the chromatographic analyses (GC) were determined with a Shimadzu GC-9A instrument equipped with a flame-ionization detector and a 2-m column (1.5% OV17 9_A SUS Chrom 103 80/1000), using nitrogen as carrier gas. TEM images of iron and copper nanoparticles were recorded at the TEM service of the University of Alicante (Spain) using a Jeol JEM2010 microscope equipped with a lanthanum hexaboride filament and operated at an acceleration voltage of 200 kV.

Starting Grignard reagents showed in entries 1–7 and 10–14 (Table 1) were prepared in dry diethyl ether from the corresponding commercially available organic halides by the standard method.^[14] Then 2- and 3-pyridylmagnesium chlorides were prepared according to the procedure reported by Trécourt et al., by a bromine-magnesium exchange.^[15]

General Procedure for the Nanosized Iron- or Copper-Catalyzed Homocoupling of Grignard Reagents

A mixture of FeCl₂ (128 mg, 1.0 mmol) or CuCl₂ (134 mg, 1.0 mmol), lithium powder (56 mg, 8.0 mmol), and DTBB (27 mg, 0.1 mmol) in THF (5 ml) was vigorously stirred at room temperature under a nitrogen atmosphere. The reaction mixture, which was initially dark green, changed to black, thus indicating the formation of iron(0) or copper(0) nanoparticles respectively. Then, a solution of the Grignard reagent (2.0 mmol) in ether (5 ml) was added. The reaction time was monitored by gas-liquid chromatography (GLC). After total conversion of the starting material, the resulting suspension was diluted with diethyl ether (10 ml) and 10% HCl (10 ml). The organic layer was washed with water (10 ml), dried over anhydrous sodium sulfate, and evaporated (15 torr). The resulting residue was purified by column chromatography (silica gel; hexane/ethyl acetate). All the products are known compounds and were fully characterized by comparison of their physical and spectroscopic data with those of the corresponding commercially available pure samples or literature data.

Data

Biphenyl^[4c] (Entries 1 and 2)

White solid; mp 68–69 °C; IR (KBr) ν = 3031, 1941, 1880, 1573, 1481, 1342, 1173, 1081, 902, 743, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 7.34–7.46 (m, 6H), 7.59 (4H, d, J = 8.1 Hz); ¹³C NMR (300 MHz, CDCl₃) δ : 127.1, 127.2, 128.7, 141.2; MS (EI, 70 eV) m/z (%): 154 (100) [M⁺], 76 (15) [M⁺–C₆H₆].

4,4'-Dimethylbiphenyl^[16] (Entry 3)

White solid; mp 118–120 °C; IR (KBr) $\nu = 3015, 2923, 1600, 1481, 803, 723 \text{ cm}^{-1}$; ¹H NMR (300 MHz, CDCl₃) δ : 2.39 (6H, s), 7.24 (4H, d, $J = 8.1 \text{ Hz}$), 7.48 (4H, d, $J = 8.1 \text{ Hz}$); ¹³C NMR (300 MHz, CDCl₃) δ : 21.3, 127.1, 129.7, 136.9, 138.5. MS (EI, 70 eV) m/z (%): 182 (100) [M⁺], 181 (27), 167 (35), 166 (11), 165 (22).

4,4'-Dimethoxybiphenyl^[4c] (Entry 4)

White solid; mp 178–180 °C; IR (KBr) $\nu = 1614, 1506, 1276, 1250, 1178, 1040, 1015, 825, 805 \text{ cm}^{-1}$; ¹H NMR (300 MHz, CDCl₃) δ : 3.83 (6H, s), 6.95 (4H, d, $J = 9.1 \text{ Hz}$), 7.47 (4H, d, $J = 9.2 \text{ Hz}$); ¹³C NMR (300 MHz, CDCl₃) δ : 55.4, 114.3, 127.5, 133.1, 158.8; MS (EI, 70 eV) m/z (%): 214 (100) [M⁺], 199 (85), 171 (26), 156 (10), 139 (10), 128 (15).

4,4'-Bis(trifluoromethyl)biphenyl^[17] (Entry 5)

White solid; mp 92–93 °C; IR (KBr) $\nu = 1324, 1166, 1133, 1114, 1070, 829 \text{ cm}^{-1}$; ¹H NMR (300 MHz, CDCl₃) δ : 7.71 (4H, d, $J = 8.8 \text{ Hz}$), 7.78 (4H, d, $J = 8.8 \text{ Hz}$); ¹³C NMR (300 MHz, CDCl₃) δ : 124.0 (2 × CF₃, q, $J = 272 \text{ Hz}$), 125.8 (4 × CCF₃, q, $J = 3.4 \text{ Hz}$), 127.6, 130.3 (2 × CCF₃, q, $J = 34.4 \text{ Hz}$), 143.2; MS (EI, 70 eV) m/z (%): 290 (100) [M⁺], 271 (35), 240 (10), 152 (28).

2,2'-Dimethylbiphenyl^[16] (Entry 6)

Colorless oil; bp 85–90 °C/0.8 mm Hg; IR (film) $\nu = 3030, 2945, 1607, 1509, 1169, 1006, 725 \text{ cm}^{-1}$; ¹H NMR (300 MHz, CDCl₃) δ : 2.10 (6H, s), 7.24 (2H, d, $J = 7.4 \text{ Hz}$), 7.27 (2H, t, $J = 7.4 \text{ Hz}$), 7.32 (2H, t, $J = 7.3 \text{ Hz}$), 7.41 (2H, d, $J = 7.3 \text{ Hz}$); ¹³C NMR (300 MHz, CDCl₃) δ : 19.8, 125.8, 127.1, 129.4, 129.9, 135.6, 141.6; MS (EI, 70 eV) m/z (%): 182 (68) [M⁺], 167 (100), 166 (23), 165 (48), 152 (22).

1,1'-Binaphthyl^[7f] (Entry 7)

White solid; mp 156–159 °C; IR (Nujol) $\nu = 3050, 1585, 1506, 1215, 1117, 965, 805, 748, 683 \text{ cm}^{-1}$; ¹H NMR (300 MHz, CDCl₃) δ : 7.24–7.30 (1H, m), 7.42 (1H, d, $J = 8.2 \text{ Hz}$), 7.45–7.54 (2H, m), 7.60 (1H, t, $J = 7.6 \text{ Hz}$), 7.91–7.99 (2H, m); ¹³C NMR (300 MHz, CDCl₃) δ : 125.4, 125.9, 126.3,

126.8, 128.0, 128.3, 128.5, 133.1, 133.8, 138.7; MS (EI, 70 eV) m/z (%): 254 (100) [M^+], 253 (74), 252 (52), 250 (13), 126 (27).

2,2'-Bipyridyl^[18] (Entry 8)

Yellow solid, mp 70–73 °C; IR (KBr) ν = 3086, 1580, 1557, 1463, 1416, 1261, 1041, 894, 760, 656 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 7.12–7.15 (2H, m), 7.64–7.69 (2H, m), 8.47–8.50 (2H, m), 8.56–8.63 (2H, m); ^{13}C NMR (300 MHz, CDCl_3) δ : 121.2, 123.8, 136.6, 149.2, 156.3; MS (EI, 70 eV) m/z (%): 156 (100) [M^+], 155 (34), 129 (18), 128 (19), 78 (18), 51 (15).

3,3'-Bipyridyl^[4c] (Entry 9)

Orange oil; IR (neat) ν = 3029, 1592, 1592, 1468, 1427, 1401, 1333, 1200, 1025, 997, 796, 714 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 7.38–7.45 (2H, m), 7.89 (2H, ddd, J_1 = 7.8 Hz, J_2 = 2.3 Hz, J_3 = 1.8 Hz), 8.65 (2H, dd, J_1 = 4.8 Hz, J_2 = 1.8 Hz), 8.85 (2H, d, J = 2.3 Hz); ^{13}C NMR (300 MHz, CDCl_3) δ : 123.7, 133.0, 134.2, 147.9, 149.2; MS (EI, 70 eV) m/z (%): 156 (100) [M^+], 129 (11), 128 (10), 103 (09), 76 (10), 50 (08).

2,2'-Bithiophene^[19] (Entry 10)

White solid; mp 31–33 °C; IR (neat) ν = 3053, 1593, 1497, 1391, 1131, 965, 853, 815, 740 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 7.00–7.03 (2H, m), 7.17–7.22 (2H, m); ^{13}C NMR (300 MHz, CDCl_3) δ : 123.7, 124.3, 127.7, 137.4; MS (EI, 70 eV) m/z (%): 166 (100) [M^+], 124 (11), 121 (28).

Bibenzyl^[7f] (Entry 11)

White solid; mp 52–53 °C; IR (KBr) ν = 3060, 3020, 2910, 2846, 1602, 1505, 1496, 694 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 2.94 (4H, s), 7.20–7.25 (6H, m), 7.30–7.35 (4H, m); ^{13}C NMR (300 MHz, CDCl_3) δ : 37.9, 125.9, 128.3, 128.5, 141.9; MS (EI, 70 eV) m/z (%): 182 (26) [M^+], 91 (100), 65 (18).

4,4'-Dimethylbibenzyl^[20] (Entry 12)

White solid; mp 79–81 °C; IR (KBr) ν = 3010, 2959, 2941, 1520, 1465, 816, 712 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 2.26 (6H, s), 2.81 (4H, s),

6.93 (4H, s); ^{13}C NMR (300 MHz, CDCl_3) δ : 19.9, 36.6, 127.3, 128.0, 137.2, 137.8; MS (EI, 70 eV) m/z (%): 210 (21) [M^+], 195 (18), 105 (100).

E,E-1,4-Diphenylbutadiene^[7f] (Entry 14)

White solid; mp 152–153 °C; IR (KBr) ν = 3030, 3016, 1492, 1443, 1074, 998, 983, 985, 740, 691 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 6.66 (2H, dd, $J_1 = 12.0$ Hz, $J_2 = 2.9$ Hz), 7.00 (2H, dd, $J_1 = 12.0$ Hz, $J_2 = 2.9$ Hz), 7.29–7.32 (2H, m), 7.38–7.41 (4H, m), 7.48–7.52 (4H, m); ^{13}C NMR (300 MHz, CDCl_3) δ : 126.6, 127.8, 128.8, 129.4, 132.8, 137.5; MS (EI, 70 eV) m/z (%): 206 (100) [M^+], 191 (35), 178 (14), 165 (10), 128 (33), 115 (11), 91 (45).

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