Selective Semi-Hydrogenation of Terminal Alkynes Promoted by Bimetallic Cu-Pd Nanoparticles

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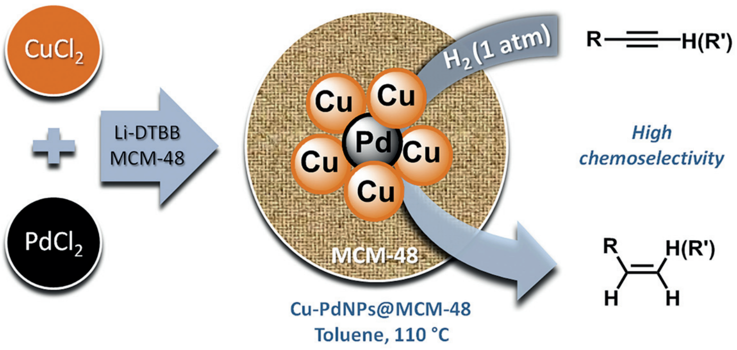


Received: 18.09.2018
Accepted after revision: 15.10.2018

DOI: 10.1055/s-0037-1610318; Art ID: ss-2018-m0630-op

Abstract The selective semi-hydrogenation of terminal alkynes was efficiently performed, under mild reaction conditions (H_2 balloon, 110 °C), promoted by a bimetallic nanocatalyst composed of copper and palladium nanoparticles (5:1 weight ratio) supported on mesostructured silica (MCM-48). The Cu-PdNPS@MCM-48 catalyst, which demonstrated to be highly chemoselective towards the alkyne functionality, is readily prepared from commercial materials and can be recovered and reused after thermal treatment followed by reduction under H_2 atmosphere.

Key words alkynes, semi-hydrogenation, heterogeneous catalysis, bimetallic nanoparticles, copper, palladium

Partial hydrogenation of alkynes is a significant transformation in fine chemistry, both at laboratory and industrial scale, because it leads to *cis*-, *trans*- or terminal alkene products that are fundamental building blocks for the synthesis of organic structures, which are of interest to a wide variety of fields, ranging from pharmaceuticals to materials science.[1] The catalytic partial hydrogenation of the C≡C bond has been accomplished either by using homogeneous or heterogeneous catalysts,[2] among them those based on the use of Pd as active metal have been by far the most studied ones. However, palladium is expensive and, in homogeneous catalytic systems, needs to be stabilized by phosphine ligands. Moreover, the selectivity of many palladium catalysts is limited by the formation of undesired overhydrogenation (alkane), isomerization (*cis* to *trans*), and oligomerization by-products,[3] mainly at high conversions. In the search for more selective, cheaper and/or environmentally friendly catalysts, the use of a wide range of transition metals have been reported in the last decade,[4] most of them showing that it is not easy to match both the activity and selectivity of some palladium catalysts. Thus, metals with high activity (e.g., Ni, Pt), frequently exhibit poor selectivity to the alkene product, and those that present high selectivity (e.g., Ag, Au) are far from being competitive in terms of activity.[5]

Heterogeneous catalysts based on earth-abundant and low-cost metals (e.g., Cu, Fe) are the more attractive ones for industrial implementation, but even when several heterogeneous catalytic systems for alkyne total hydrogenation are known, partial and selective hydrogenation remains a challenging issue. In this scenario, the use of metal nanoparticles (MNPs), both naked or supported, as catalysts for alkyne hydrogenation has attracted the interest of many research groups in the last years.[6] The possibility to control the shape, size, and structure at the nanometer level in the synthesis of MNPs, in some cases has allowed for a rational design of new nanocatalysts. A clear example is the BASF registered trademark NanoSelect Pd catalysts,[7] which have been shown to be highly selective in alkyne semi-hydrogenation.[8] On the other hand, the use of bare metal NPs is also of interest because it can sometimes help to understand the role of support during the catalytic process.[9]

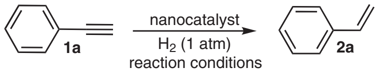
Bimetallic NPs have emerged as promising catalysts for important synthetic transformations, including hydrogenation reactions.[4b,10] It is known that bimetallic nanostructures offer the possibility of enhancing the catalytic properties, mainly through synergistic effects between both metals involved.[11] As mentioned above, the superior performance of palladium catalysts in hydrogenation reactions, makes it difficult to avoid the use of this metal in most of the hydrogenation catalysts. In this scenario, the search for new Pd-based bimetallic nanocatalysts with low palladium loading has been the goal of many research groups in recent years.[9,12] The Ag-Pd couple is by far the most commonly used for the semi-hydrogenation of acetylene,[13] however, from an economic point of view, first row transition metals (e.g., Fe, Co, Ni, Cu) are much more attractive than silver as palladium partners for bimetallic catalysts. Among them, Cu has been widely applied in partial hydrogenation reactions due to its excellent ethylene selectivity,[12] which is attributed to a favorable desorption of the C=C bond. These experimental observations about the selectivity of some Cu-based nanocatalysts have also been supported by DFT calculations.[14]

Based on our continuing interest in the development of new copper-based nanocatalysts for their application in selective and useful synthetic transformations,[15] we want to report herein our results on the performance of a bimetallic Cu-Pd nanocatalyst, consisting of copper and palladium NPs (5:1 weight ratio, 8.5:1 molar ratio) supported on mesoporous silica (MCM-48), in the selective semi-hydrogenation of alkynes.

We began our study by testing different nanocatalysts in the partial hydrogenation of phenyl acetylene (**1a**) as model alkyne. Supported and unsupported mono- and bimetallic NPs were prepared by fast reduction of the corresponding metal chlorides mediated by Li-DTBB (cat.), as previously reported by us (see Supporting Information).[15] For the preparation of supported nanocatalysts, the amount of metal NP precursors ($CuCl_2$ and $PdCl_2$) was calculated to obtain a nominal total metal loading of 18 wt%. As shown in Table 1, different materials considered as inert supports and some metal oxides were selected as carriers for the NPs. A Cu/Pd weight ratio of 3:1 was initially selected for testing both the activity and the selectivity of the bimetallic catalytic systems. Reactions were performed in toluene as solvent, at 110 °C, under H_2 atmosphere (balloon). As can be seen from Table 1, Cu-PdNPs immobilized in different materials (Table 1, entries 1–5) gave the alkene product **2a** with excellent selectivity, but most of them showed modest activity values. The best catalytic performance was obtained with the Cu-PdNPs@MCM-48 nanocatalyst, although the selectivity to the alkene product was not high enough (entry 5).

With the aim to improve the selectivity without loss of activity, the Cu/Pd ratio was varied. As shown in Table 1 (entry 6) a Cu/Pd weight ratio of 5:1 (8.5:1 molar ratio) was found to be optimal to maintain the high activity and to improve the selectivity of this catalyst in the semi-hydrogenation process. The optimal amount of catalyst was found to be 10 mg (see Table 1, entry 6, footnotes e and f), which means a 4.7 mol% of copper and a 0.5 mol% of palladium loading, referred to the starting alkyne. For the sake of comparison, monometallic Cu and Pd nanocatalysts were also tested. Thus, CuNPs@MCM-48 catalyst showed very low activity in the hydrogenation reaction (entry 7), whereas monometallic PdNPs@MCM-48 catalyst proved to be highly active but exhibited low selectivity to the semi-hydrogenation product, giving a mixture of ethylbenzene together with oligomerization by-products after 4 hours (entry 8). Finally, bimetallic unsupported Cu-PdNPs (Cu/Pd weight ratio: 5:1) showed very low hydrogenation activity, probably due to sintering after high-temperature stirring (entry 9).

Table 1 Screening of MNPs Catalysts[a]



Entry	Catalyst	Conversion (%)[b]	Selectivity (%)[c]
1	Cu-PdNPs@MagSilica	55	98
2	Cu-PdNPs@Celite	72	100
3	Cu-PdNPs@ZnO	38	100
4	Cu-PdNPs@MgO	45	100
5	Cu-PdNPs@MCM-48	93	90
6	**Cu-PdNPs@MCM-48**[d]	**97** (81[e], 98[f])	**100** (100[e], 89[f])
7	CuNPs@MCM-48	18	100
8	PdNPs@MCM-48	100	65[g], 5[h]
9	Cu-PdNPs (unsupported)	5	ND

[a] Reaction conditions: **1a** (0.5 mmol), nanocatalyst (10 mg, Cu/Pd weight ratio: 3:1, 4.25 mol% Cu and 0.8 mol% Pd), in toluene (5 mL), at 110 °C, 4 h, under H_2 atmosphere (1 atm, balloon).

[b] GC-MS conversion of the starting phenylacetylene, using dodecane as internal standard.

[c] Selectivity expressed as yield (%) of styrene based on starting **1a**.

[d] Catalyst Cu/Pd weight ratio: 5:1 (10 mg, 4.7 mol% Cu and 0.5 mol% Pd).

[e] Reaction performed by using 5 mg of catalyst (2.35 mol% Cu and 0.25 mol% Pd).

[f] Reaction performed by using 20 mg of catalyst (9.4 mol% Cu and 1.0 mol% Pd).

[g] Selectivity after 1 h of reaction time.

[h] Selectivity after 4 h of reaction time.

Analysis by TEM of the Cu-PdNPs@MCM-48 catalyst showed spherical nanoparticles with an average size of 4 ± 2 nm (Figure 1).

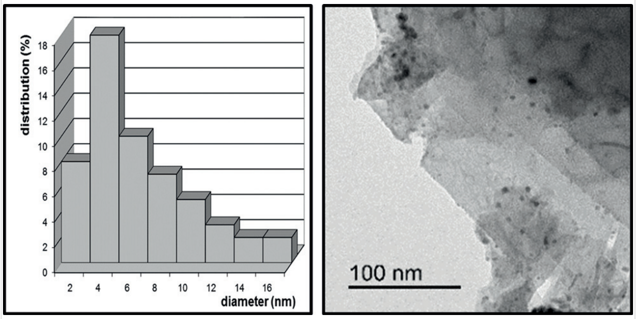


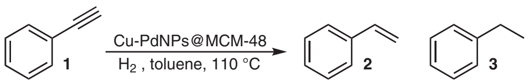
Figure 1 TEM micrograph and size distribution graphic for Cu-PdNPs@MCM-48 catalyst

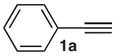
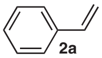
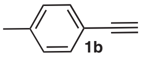
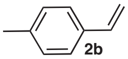
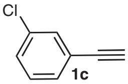
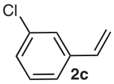
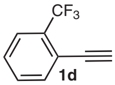
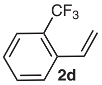
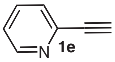
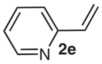
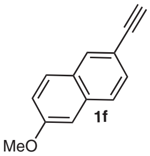
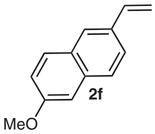
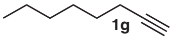
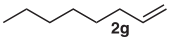
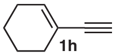
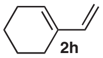
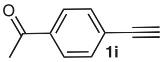
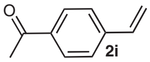
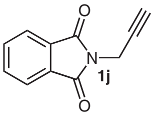
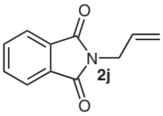
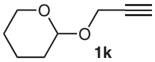
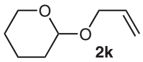
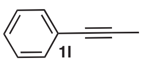
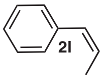
XPS analysis of Cu-PdNPs@MCM-48 revealed the presence of Pd 3d5/2 and Pd 3d3/2 peaks. Two contributions for each Pd peak arose after deconvolution, at 336.2/337.6 eV for Pd 3d5/2, and at 341.3/342.9 eV for Pd 3d3/2 peak. On the other hand, XPS spectrum showed Cu 2p3/2 peaks at 932.3, 934.6, 936.2, 941.5 and 944.7 eV, the last two transitions being a satellite shake-up feature characteristic of Cu^{2+} species. From these results it could be concluded that metallic copper and palladium coexist with the corresponding oxidized counterparts at the surface of the nanocatalyst.

In order to study the nature of the copper-palladium interaction in the bimetallic catalyst, characterization by Temperature Programmed Reduction (TPR) of the Cu-PdNPs@MCM-48 sample and of their monometallic counterparts was carried out (Figure 5 in Supporting Information). The results corresponding to the monometallic Pd sample indicate a reduction peak with a maximum at 17 °C. Besides the β-hydride decomposition is also detected as an evolution of hydrogen at 73 °C. Both features were previously observed for palladium supported catalysts.[16] The TPR profile of monometallic CuNPS@MCM-48 sample shows two peaks at 252 and 274 °C, which are both ascribed to the reduction of CuO. The reduction temperatures observed for copper species are quite similar to those corresponding to other copper-based catalysts supported on silica or on siliceous supports.[17] In the case of the bimetallic Cu-PdNPs@MCM-48, a hydrogen consumption between 100 and 184 °C is detected, as well as a low hydrogen uptake at lower temperature. The profile of the bimetallic sample does not result from the linear combination of those originated by the monometallic catalysts. It could be concluded that the close proximity of the metals conforming the bimetallic Cu-Pd nanoparticles gives rises to noticeable modification of the redox properties of palladium and copper. Thus, isolated monometallic Pd or Cu particles would not be present in the Cu-PdNPs@MCM-48 sample, and on the contrary, Cu-Pd bimetallic crystals are likely to be formed in the binary sample.

Then, the scope of the catalytic system was studied. Initially, a range of terminal alkynes were reacted under the optimized conditions. As shown in Table 2, phenylacetylenes substituted with electron-donating or electron-withdrawing groups (Table 2, entries 2–4) both gave the corresponding styrene derivatives in good yield, the catalyst showing high selectivity to the alkene product. A significant lower activity was observed for the hydrogenation of 2-ethynylpyridine (entry 5), as markedly longer reaction time was required to obtain 2-vinylpyridine in good yield. This could be ascribed to partial poisoning of the catalyst due to the presence of a pyridine ring in the starting alkyne. Nevertheless, it should be noted that selectivity to the alkene product was maintained after 24 hours of reaction time. Similar lack of activity, accompanied by high selectivity, was observed in the hydrogenation of 2-ethynyl-6-methoxynaphthalene (entry 6). Unfortunately in this case the conversion into 2-vinyl-6-methoxynaphthalene could not be improved even after 24 hours of reaction time. With regard to the hydrogenation of alkylacetylenes, working un-

Table 2 Hydrogenation of Alkynes Catalyzed by Cu-PdNPs@MCM-48[a]



Entry	Starting alkyne **1**	Alkene product **2**	X (%)[b]/S (%)[c]
1	 1a	 2a	97/100
2	 1b	 2b	92 (81)/98
3	 1c	 2c	99 (87)/97
4	 1d	 2d	95/93
5	 1e	 2e	20/99 94 (82)/96[d]
6	 1f	 2f	44/99 58 (50)/97[d]
7	 1g	 2g	99/97
8	 1h	 2h	95/89
9	 1i	 2i	98 (88)/95
10	 1j	 2j	52/99 99 (91)/87[d]
11	 1k	 2k	99/98
12	 1l	 2l	26/88 32/78[d] 97/45[e]

[a] Reaction conditions: starting alkyne (0.5 mmol), catalyst (10 mg, 4.7 mol% Cu and 0.5 mol% Pd), in toluene (5 mL), stirred at 110 °C, 4 h, under H_2 atmosphere (1 atm, balloon), unless otherwise stated.
[b] Conversion of the starting alkyne determined by GC-MS, using dodecane as internal standard. Isolated yield in parentheses.
[c] Selectivity towards the alkene product **2** (expressed as moles of alkene **2** × 100/moles of alkyne **1** converted).
[d] Reaction time: 24 h.
[e] Reaction performed by using 20 mg of catalyst (9.4 mol% Cu and 1.0 mol% Pd).

der the optimized conditions the reaction of 1-octyne quantitatively rendered 1-octene after 4 hours, with high selectivity to the alkene product (entry 7).

Then, the chemoselectivity of the catalytic system was studied by testing the hydrogenation of acetylenes bearing other reducible functional groups. Under the optimized conditions, the conjugated enyne 1-ethynylcyclohex-1-ene was converted into the corresponding conjugated diene, 1-vinylcyclohex-1-ene, in 95% yield and with 89% selectivity (Table 2, entry 8). Taking into account the broad synthetic interest for the selective reduction of the C≡C bond in the presence of carbonyl groups, we carried out the hydrogenation of 1-(4-ethynylphenyl)ethan-1-one (entry 9). The catalytic system showed to be highly selective, giving 95% of 1-(4-vinylphenyl)ethan-1-one as the major product, accompanied by only 5% of 1-(4-ethylphenyl)ethan-1-one without reduction of the C=O group. In the case of 2-ethynylisoindoline-1,3-dione (entry 10) the selectivity towards the hydrogenation of the C≡C bond was also remarkable, whereas the need for longer reaction times led to a lower selectivity, giving near 10% of the totally hydrogenated product. On the other hand, hydrogenation of 2-(ethynyloxy)tetrahydro-2*H*-pyran (entry 11) gave the corresponding vinyl derivative as the only reaction product in excellent yield.

With regard to the hydrogenation of internal alkynes, the catalytic system showed to be considerable less efficient. Unfortunately, very low catalytic activity was observed in the hydrogenation of prop-1-yn-1-ylbenzene (Table 2, entry 12). Extending the reaction time and/or doubling the amount of catalyst used, allowed to improve the conversion but also significantly lowered the selectivity to the alkene product. This poor catalyst performance with internal alkynes could be related to steric and accessibility constraints.[6]

We then studied the recyclability of the CuPdNPs/MCM-48 catalyst, an important issue of any heterogeneous catalyst. Unfortunately, the activity of the Cu-PdNPs@MCM-48 catalyst dropped in the second cycle, giving 53% of conversion for the semi-hydrogenation of phenylacetylene (**1a**). However, calcination of the spent catalyst at moderate temperature (150 °C) followed of reduction treatment under H_2 atmosphere, allowed to improve the catalyst activity in a second cycle (85% conversion) retaining the same selectivity to the alkene product as in the first cycle (99%).

We have also analyzed the possible leaching of the catalyst in the reaction media. In pursuing this, the concentration of copper and palladium in the liquid media after the hydrogenation of phenylacetylene over the Cu-PdNPs@MCM-48 catalyst was determined by ICP-AES. The results indicated extremely low levels of leached metal species (1.0 ppm of Pd, and 2.2 ppm of Cu) showing that the reaction mainly occurs over the heterogeneous surface of the catalyst.

In summary, we have presented herein a new bimetallic catalyst composed of copper and palladium nanoparticles (5:1 weight ratio) supported on mesostructured silica (MCM-48) that allows the partial hydrogenation of terminal alkynes with excellent selectivity to the alkene products. The experimental results and the catalyst characterization are in line with the presence of bimetallic Cu-Pd nanoparticles of around 4 nm in diameter and with a narrow size distribution. Additionally, this new bimetallic Cu-PdNPs@MCM-48 catalyst demonstrated to be highly chemoselective, allowing the hydrogenation process to be selectively carried out at the C≡C bond even in the presence of other reducible functionalities. Finally, the bimetallic Cu-Pd nanocatalyst could be recovered and reused upon thermal treatment followed by reduction under hydrogen atmosphere.

The preparation of Cu and Pd nanoparticles were carried out under N_2 atmosphere. Anhyd THF used as solvent was freshly distilled from Na/benzophenone ketyl. Other solvents were treated prior to use by standard methods. All starting materials were of the best available grade (Aldrich, Merck) and were used without further purification. Commercially available $PdCl_2$ was used for the preparation of PdNPs and Cu-PdNPs. $CuCl_2·2H_2O$ was dehydrated upon heating in an oven (150 °C, 45 min) prior to use for the preparation of CuNPs and Cu-PdNPs. Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm, 240–400 mesh). Reactions were monitored by TLC on silica gel plates (60F-254) visualized under UV light and/or using 5% phosphomolybdic acid in EtOH. NMR spectra were recorded on a Bruker ARX-300 spectrometer using $CDCl_3$ as the solvent and TMS as internal reference. Chemical shifts (δ) are reported in ppm from TMS using the residual solvent resonance ($CDCl_3$: 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR). Standard abbreviations are used to denote the multiplicities. Mass spectra (EI) were obtained at 70 eV on a Agilent 7890B GC/MS instrument equipped with a Agilent 5977A selective mass detector. FT-IR spectra were obtained on a Nicolet-Nexus spectrophotometer. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a HP-6890 instrument equipped with a flame-ionization detector and a 30 m column (HP-5MS, 0.25 mm, 0.25 μm), using N_2 as carrier gas.

The freshly prepared catalyst was characterized by Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). Cu and Pd content in the supported catalysts were determined by Atomic Absorption Spectroscopy (AAS) (see Supporting Information).

Semi-Hydrogenation of Alkynes 1a–l; General Procedure

The starting alkyne **1** (0.5 mmol) and dodecane as internal standard (0.22 mmol, 50 μL) were added to a suspension of the Cu-PdNPs/MCM-48 catalyst (10 mg) in toluene (5 mL). All reactions were carried out in a Schlenk-type flask, fitted with a reflux condenser and sealed with a rubber septum. The reaction flask was purged and filled with H_2 (1 atm) through a balloon connected to the flask by a needle, and then heated at 110 °C. Then, the reaction mixture was centrifuged and the supernatant removed. The solvent was evaporated in vacuo, and the crude product was purified by flash column chromatography (silica gel, hexane/EtOAc). The recovered solid catalyst was washed with toluene (3 × 2 mL), dried in an oven, calcined at 150 °C (4 h), and reduced in H_2 atmosphere at 200 °C before its reuse. The following known compounds included in Table 2 were characterized by comparison of their chromatographic and spectroscopic data (FT-IR, ^{1}H NMR, ^{13}C NMR, and MS) with those described in the literature.

Styrene (2a)[18]

Yield: 46 mg (0.44 mmol, 89%); colorless liquid.

IR (film): 3082, 3060, 3027, 1630, 1496, 1449, 992, 909, 777, 698 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.35 (m, 2 H), 7.25 (m, 3 H), 6.7 (dd, *J* = 10.8, 17.1 Hz, 1 H), 5.71 (d, *J* = 17.1 Hz, 1 H), 5.20 (d, *J* = 10.8 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.5, 128.5, 127.7, 126.1, 136.9, 113.7.

MS: *m*/*z* (%) = 104 (100, [M$^+$]), 103 (40), 78 (35), 77 (17), 51 (17).

1-Methyl-4-vinylbenzene (2b)[19]

Yield: 50 mg (0.43 mmol, 85%); colorless liquid.

IR (KBr): 3007, 1629, 1511, 1403, 990, 904, 824, 730 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.35 (d, *J* = 8.0 Hz, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 6.74 (dd, *J* = 17.7, 10.7 Hz, 1 H), 5.74 (d, *J* = 17.5 Hz, 1 H), 5.23 (d, *J* = 10.9 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.5, 136.6, 134.8, 129.1, 126.0, 112.7, 21.1.

MS: *m*/*z* (%) = 118 (100, [M$^+$]), 117 (90), 115 (23), 91 (26).

1-Chloro-3-vinylbenzene (2c)[19]

Yield: 64 mg (0.47 mmol, 94%); pale yellow liquid.

IR (KBr): 3063, 1594, 1564, 1474, 1414, 1396, 1202, 966, 914, 881, 847, 840, 788, 710, 685, 649 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.40 (s, 1 H), 7.20–7.31 (m, 3 H), 6.66 (dd, *J* = 17.5, 10.9 Hz, 1 H), 5.76 (d, *J* = 17.5 Hz, 1 H), 5.31 (d, *J* = 10.9 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 115.3, 124.2, 126.1, 127.7, 129.7, 134.4, 135.5, 139.3.

MS: *m*/*z* (%) = 140 (32, [M$^+$ + 2]), 139 (10, [M$^+$ + 1]), 138 (100, [M$^+$]), 103 (75), 102 (16), 77 (25), 75 (11), 51 (22), 50 (11).

1-(Trifluoromethyl)-2-vinylbenzene (2d)[20]

Yield: 77 mg (0.45 mmol, 90%); colorless liquid.

IR (film): 3010, 1670, 1486, 1310, 1180, 1156, 1124, 1070, 1028, 976, 770, 695 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.66 (d, *J* = 7.8 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.36 (t, *J* = 7.7 Hz, 1 H), 7.10 (ddd, *J* = 17.3, 11.0, 2.5 Hz, 1 H), 5.75 (d, *J* = 17.1 Hz, 1 H), 5.42 (dd, *J* = 11.0, 1.2 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.0, 133.3, 132.1, 127.7, 127.3, 125.8 (q), 125.6, 123.4, 118.2.

MS: *m*/*z* (%) = 172 (83, [M$^+$]), 171 (48), 153 (22), 152 (38), 151 (100), 133 (33), 127 (12), 126 (10), 125 (13), 122 (25), 103 (26), 102 (12), 101 (13), 77 (16), 76 (10), 75 (26), 74 (19), 69 (15), 63 (13), 51 (22), 50 (22).

2-Vinylpyridine (2e)[21]

Yield: 46 mg (0.44 mmol, 87%); colorless liquid.

IR (film): 3016, 1588, 1564, 1474, 1435, 989, 802, 746 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.57 (d, *J* = 4.8 Hz, 1 H), 7.64 (dt, *J* = 8.0, 2.0 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 1 H), 7.17–7.13 (m, 1 H), 6.82 (dd, *J* = 17.6, 10.8 Hz, 1 H), 6.20 (dd, *J* = 17.6, 1.2 Hz, 1 H), 5.48 (dd, *J* = 10.8, 1.2 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 155.6, 149.4, 136.8, 136.5, 122.4, 121.2, 118.2.

MS: *m*/*z* (%) = 105 (100, [M$^+$]), 105 (55), 79 (80), 78 (16), 52 (22), 51 (20), 50 (11).

2-Methoxy-6-vinylnaphthalene (2f)[22]

Yield: 50 mg (0.29 mmol, 58%); pale yellow solid; mp 93–95 °C.

IR (KBr): 3054, 2838, 1633, 1597, 1482, 1258 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.72–7.68 (m, 3 H), 7.62 (d, *J* = 8.5 Hz, 1 H), 7.14 (d, *J* = 8.13 Hz, 2 H), 6.89 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.85 (d, *J* = 17.6 Hz, 1 H), 5.29 (d, *J* = 10.9 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 157.7, 136.9, 134.2, 132.9, 129.5, 128.8, 126.9, 126.1, 123.7, 118.9, 113.0, 105.7, 55.2.

MS: *m*/*z* (%) = 184 (100, [M$^+$]), 169 (17), 141 (50), 115 (19).

1-Octene (2g)[23]

Yield: 52 mg (0.46 mmol, 93%); colorless liquid.

IR (film): 2959, 2928, 2857, 910 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.76–5.86 (m, 1 H), 4.90–5.20 (m, 2 H), 2.04 (dd, *J* = 14.8, 6.4 Hz, 2 H), 1.21–1.46 (m, 8 H), 0.87 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 138.5, 115.4, 114.0, 33.8, 31.7, 28.6, 22.6, 14.0.

MS: *m*/*z* (%) = 112 (20, [M$^+$]), 84 (22), 83 (34), 71 (12), 70 (86), 69 (44), 57 (19), 56 (87), 55 (99), 43 (100), 42 (66), 41 (82), 39 (28), 29 (35), 27 (25).

1-Vinylcyclohexene (2h)[24]

Yield: 47 mg (0.43 mmol, 87%); colorless liquid.

IR (neat): 3088, 3003, 2926, 2859, 2835, 1641, 1605, 1449, 1436, 1349, 1314, 1269, 1186, 1136, 1080, 1024, 988, 916, 890, 845, 802 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.34 (dd, *J* = 17.52, 28.19 Hz, 1 H), 5.76 (s, 1 H), 5.06 (d, *J* = 17.69 Hz, 1 H), 4.88 (d, *J* = 10.8 Hz, 1 H), 2.09–2.18 (m, 4 H), 1.55–1.73 (m, 4 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 140.4 136.2, 130.0, 109.7, 25.9, 23.9, 22.7, 22.5.

MS: *m*/*z* (%) = 108 (33, [M$^+$]), 93 (64), 91 (29), 80 (21), 79 (100), 78 (14), 77 (35), 67 (14), 65 (13), 51 (15), 41 (17), 39 (26).

1-(4-Vinylphenyl)ethan-1-one (2i)[25]

Yield: 68.6 mg (0.47 mmol, 94%); colorless oil.

IR (film): 3029, 2926, 1683, 1611, 1456, 1377, 1366, 1265, 954, 827 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.93 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1 H), 5.90 (d, *J* = 17.6 Hz, 1 H), 5.41 (d, *J* = 10.9 Hz, 1 H), 2.59 (s, 3 H).

^{13}C NMR (75 MHz, CDCl$_3$): δ = 197.7, 142.2, 136.4, 136.0, 128.8, 128.6, 126.4, 116.8, 26.7.

MS: *m*/*z* (%) = 146 (42, [M$^+$]), 131 (100), 103 (64).

2-Allylisoindoline-1,3-dione (2j)[26]

Yield: 79 mg (0.42 mmol, 84%); white solid, mp 58–59 °C.

IR (neat): 2956, 1701, 1681, 1470, 1430, 1392, 1108, 963, 731 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.85–7.87 (m, 2 H), 7.72–7.75 (m, 2 H), 5.86–5.93 (m, 1 H), 5.25 (d, J = 17 Hz, 1 H), 5.20 (d, J = 10.5 Hz, 1 H), 4.30 (d, J = 5.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 133.7, 131.8, 131.3, 123.0, 117.4, 39.8.

MS: m/z (%) = 188 (13, [M^+ + 1]), 187 (100, [M^+]), 169 (37), 160 (19), 130 (16), 105 (10), 104 (17), 76 (14).

2-(Allyloxy)tetrahydro-2*H*-pyran (2k)[27]

Yield: 65 mg (0.46 mmol, 92%); pale yellow liquid.

IR (film): 2948, 1124, 1078, 1035, 870 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.98–5.90 (m, 1 H), 5.30 (qd, J = 16.5, 1.5 Hz, 1 H), 5.17 (qd, J = 10.5, 1.5 Hz, 1 H), 4.65 (dd, J = 4.0, 3.5 Hz, 1 H), 4.24 (tdd, J = 13.0, 5.5, 1.5 Hz, 1 H), 3.99 (tdd, J = 13.0, 5.5, 1.5 Hz, 1 H), 3.97–3.85 (m, 1 H), 3.53–3.49 (m, 1 H), 1.89–1.82 (m, 1 H), 1.76–1.70 (m, 1 H), 1.64–1.50 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.7, 116.7, 97.9, 68.0, 62.2, 30.6, 25.4, 19.4.

MS: m/z (%) = 142 (2, [M^+]), 101 (10), 85 (100), 67 (16), 57 (24), 56 (19), 55 (33).

(*Z*)-Prop-1-en-1-ylbenzene (2l)[28]

Yield: 18 mg (0.15 mmol, 30%); colorless liquid.

IR (film): 3020, 2937, 1494, 1443, 962, 912, 764, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.20 (m, 5 H), 6.48-6.40 (dd, J = 12, 1.6 Hz, 1 H), 5.86–5.72 (dq, J = 11.6, 7.2 Hz, 1 H), 1.90 (dd, J = 7.2, 2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 129.9, 128.8, 128.1, 126.8, 126.4, 14.6.

MS: m/z (%) = 117 (100, [M^+]), 103 (11), 91 (40), 77 (11), 63 (13), 51 (17).

Funding Information

This work was generously supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PIP-2011-268), Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT, Prest. BID, PICT-2014-2171), and Universidad Nacional del Sur (UNS, PGI 24/Q072) from Argentina.

Acknowledgment

E.B. thanks the CONICET for a postdoctoral fellowship.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610318.

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