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Highly selective hydrogenation of multiple carbon–carbon bonds promoted by nickel(0) nanoparticles

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This paper is dedicated to Professor D. A. Evans on the occasion of his 65th anniversary

Abstract—A new method for the highly stereoselective cis semihydrogenation of internal alkynes, semihydrogenation of terminal alkynes, reduction of dienes to alkenes, and reduction of alkynes and alkenes to alkanes is described based on in situ generated both Ni(0) nanoparticles and molecular hydrogen.

1. Introduction

The selective transformation of hydrocarbons with multiple carbon–carbon bonds (i.e., alkynes and dienes) to monoolefins is of fundamental importance both in laboratory practice and fine chemicals production. It is also a crucial step in industrial polymerization processes with the aim of the complete elimination of alkynes and dienes from alkene feedstocks. Heterogeneous catalytic hydrogenation continues to be the most useful technique for the addition of molecular hydrogen to carbon–carbon double and triple bonds, particularly if the objective involves chemo-, regio-, and stereoselectivities.[1] In particular, the semihydrogenation of the carbon–carbon triple bond is a very valuable reaction in synthetic organic chemistry. The difficulty to control the stereochemistry and to minimize the formation of overreduced products make it a challenging transformation. In the last decades, different general methods have been developed for this purpose and applied depending on the stereochemistry desired for the final product, including: (a) heterogeneous catalytic hydrogenation,[1a] (b) homogeneous catalytic hydrogenation,[2] and (c) non-catalytic chemical methods[3a] (e.g., reduction by diimide,[3b] dissolving metals,[3c,d] low-valent metal species,[3e] hydroalumination,[3f] or metal hydride–transition-metal halide combinations[3g]).

Concerning the cis semireduction of alkynes and that of terminal alkynes, Lindlar catalyst,[4] trialkylammonium formates under palladium catalysis,[5] complex reducing agents of the type NaH–NaOR–MX_n,[6] and dispersed nickel on graphite,[7] are some of the formerly utilized reducing systems, but not always leading to an optimum selectivity. In fact, partial isomerization of the (*Z*)-alkene to the (*E*)-alkene, shift of the double bond, overreduction to the alkane, and problems with reproducibility were observed, especially in Lindlar's catalyst. In the more recent literature, noteworthy is the higher selectivity achieved with a montmorillonite-supported complex,[8] nickel boride or palladium catalysts on borohydride exchange resin,[9] a homogeneous palladium(0) catalyst,[10] palladium on pumice,[11] or using a variant of Lindlar's catalyst.[12] At any rate, most of the above mentioned methods are not general but applied to a specific type of substrate. Therefore, any new and efficient method for the semihydrogenation of alkynes is welcome.

Selective reduction of dienes was accomplished by heterogeneous catalytic hydrogenation with Pd supported on poly(*N*-vinyl-2-pyrrolidone) in methanol, $Pd/CaCO_3$ or Pd black in the presence of phenylacetaldehyde,[1a] by homogeneous catalytic hydrogenation with a variety of transition-metal complexes,[2] by alkali metals (for conjugated dienes),[13] or more recently by SmI_2/H_2O/amine.[14]

For the reduction of alkenes to alkanes heterogeneous catalytic hydrogenation[1] is preferred due to the mild reaction conditions mostly required and the easy separation of the catalyst. Among the many catalysts available, nickel catalysts[15] are universal and widely used both in the laboratory and in industry. However, Raney nickel is probably by far

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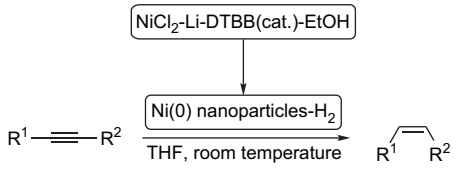
the most used nickel catalyst because of its high activity, being able to reduce practically any function.[16] Its main disadvantages are: (a) the difficulty in calculating the dosage (it is usually measured as a suspension rather than by weight); (b) ferromagnetic properties that preclude the use of magnetic stirring; (c) it is potentially hazardous (pyrophoric); (d) it becomes inactive after prolonged storage, presumably because it loses hydrogen slowly.

On the other hand, we have recently reported the fast synthesis of nickel(0) nanoparticles with diameters of 2.5±1.5 nm by reduction of anhydrous nickel(II) chloride with lithium powder and a catalytic amount of DTBB (4,4′-di-*tert*-butylbiphenyl) in THF at room temperature.[17] The high reactivity of these nanoparticles was demonstrated in the catalytic hydrogenation of a variety of organic compounds, including carbon–carbon multiple-bond-containing compounds.[18,19] Moreover, similar reduction systems to $NiCl_2$–Li–DTBB(cat.) such as $NiCl_2$–Li–copolymer(cat.),[20] $NiCl_2\cdot 2H_2O$–Li–DTBB(cat.),[19] $NiCl_2$–Li–DTBB(cat.)–EtOH, or $NiCl_2$–Li–copolymer(cat.)–EtOH,[20] also generate nanosized metallic nickel[21] with demonstrated or potential applicability in organic chemistry. We have recently communicated that the introduction of an alcohol (ethanol or isopropanol) as a source of hydrogen in the reducing system [i.e., $NiCl_2$–Li–DTBB(cat.)–ROH] is a very convenient method for the highly stereoselective cis semihydrogenation of internal alkynes and the semihydrogenation of terminal alkynes under mild reaction conditions.[22] One of the main advantages of this methodology is that the handling of external molecular hydrogen is avoided since it is generated in situ in the reaction flask.

2. Results and discussion

2.1. Semihydrogenation of internal alkynes

In a previous study, we applied the system composed of $NiCl_2\cdot 2H_2O$–Li–arene(cat.) to the reduction of alkynes. A variety of substrates could be completely reduced to the corresponding alkanes, whereas the semihydrogenation reaction could be only controlled in a few cases without a general product stereochemistry.[23] The more versatile system, $NiCl_2$–Li–DTBB(cat.)–EtOH was applied to a wide range of internal alkynes with a high selectivity and under very mild reaction conditions (Scheme 1 and Table 1). The role of the different components of the reducing system mentioned above is as follows: (a) nickel(II) chloride is the source of Ni(0) nanoparticles, (b) lithium has got a double role, the reduction of Ni(II) to Ni(0) and the in situ generation of molecular hydrogen by reaction with the alcohol, (c) DTBB is used in catalytic amounts and acts as an electron carrier from lithium to nickel(II) chloride, and (d) EtOH is the source of hydrogen.



Scheme 1.

Concerning the semihydrogenation of internal alkynes (Table 1), symmetrical dialkyl substituted alkynes (Table 1, entries 1 and 3) as well as cyclooctyne (Table 1, entry 5) were reduced to the corresponding alkenes with excellent conversions and yields and with exclusive cis stereochemistry. Several hydroxyalkyl substituted internal alkynes were also successfully converted into the corresponding *cis*-olefins (Table 1, entries 6–8). It is noteworthy that even the more labile and prone-to-isomerization oct-2-en-1-ol was obtained in a 93:7 *Z*/*E* diastereomeric ratio without any trace of the isomerized byproduct octanal (Table 1, entry 8). Alkynes bearing an alkoxy moiety (Table 1, entries 10, 12, and 13) were nicely semireduced, the reaction conditions being compatible with the presence of the benzyloxy group, which did not undergo hydrogenolysis. Furthermore, several propargylic amines could be also transformed into the corresponding *cis*-allylic amines with high conversions and isolated yields (Table 1, entries 14–16). The stereochemistry in all the products was confirmed by NOESY experiments.

Alternatively, a polymer-supported arene,[18b,24] prepared by radical copolymerization of 4-vinylbiphenyl and divinylbenzene (mixture of regioisomers),[24b] was utilized as an electron carrier instead of DTBB. Very similar results were obtained with this copolymer in the reduction of oct-4-yne and dec-5-yne (Table 1, entries 2 and 4, respectively), though the reaction times were longer due to its lower solubility in the reaction medium. In the case of 1-methoxydec-3-yne, however, a clear improvement in both the conversion and isolated yield was observed (compare entries 10 and 11 in Table 1). Nonetheless, by using the copolymer instead of DTBB the work-up was easier, since the arene is removed by simple filtration, and cleaner reaction crudes were obtained in all cases.

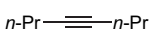
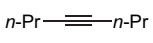
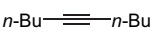
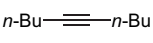
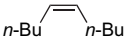
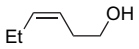
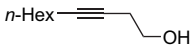
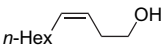
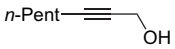
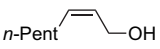
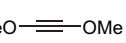
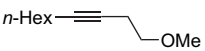
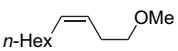
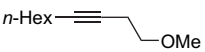
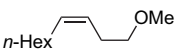
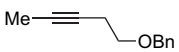
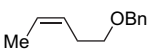
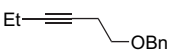
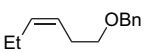
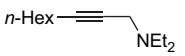
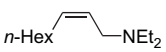
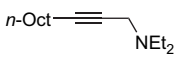
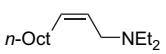
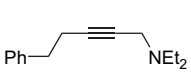
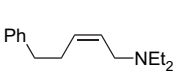
2.2. Semihydrogenation of terminal alkynes

The above methodology also found application in the generally less studied and more difficult to control semihydrogenation of terminal alkynes. In this case, *i*-PrOH showed to be more effective than EtOH as a hydrogen source. Thus, a variety of terminal alkynes bearing alkyl, alkoxyalkyl, and arylaminoalkyl substituents were reduced to the corresponding terminal alkenes in good yields albeit with variable amounts of the overreduced alkanes (10–15%) (Table 2). It is worthy to note that also in this case, the benzyloxy group remained untouched under the reaction conditions (Table 2, entry 3).

2.3. Complete hydrogenation of alkynes

The versatility of this reducing system was demonstrated in the complete hydrogenation of both internal and terminal alkynes (Table 3). In this case, EtOH was used as the hydrogen source in the presence of a 4-vinylbiphenyl/divinylbenzene copolymer as an electron carrier. By using a slight excess of lithium and EtOH (i.e., to generate 2.5 equiv of molecular hydrogen), diphenylacetylene and diphenyltrimethylsilylacetylene were transformed into 1,2-diphenylethane and trimethylphenethylsilane in high yields and short reaction times (Table 3, entries 1 and 2, respectively). The latter could be also obtained in high yield by using

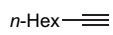
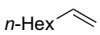
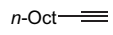
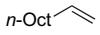
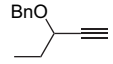
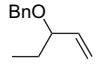
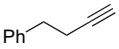
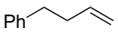
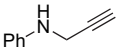
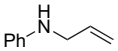
Table 1. Selective semihydrogenation of internal alkynes

Entry	Starting alkyne	t (h)[a]	Product	Conversion (%)[b]	Yield (%)[c]
1		2		100	99[d]
2		24[e]		100	99[d]
3		4		100	98[d]
4		24[e]		100	99[d]
5		3		100	95[d]
6		8		100	83[d]
7		4		100	62
8		24		77	65[f] (96[d])
9		4[g]		84	97[d]
10		2		92	85
11		24[e,g]		100	93
12		24		100	73
13		2		100	79
14		7		83	90
15		8		100	87
16		7		100	94

[a] Reaction carried out at room temperature with EtOH as the hydrogen source and DTBB as electron carrier, unless otherwise stated.
[b] Conversion determined by analytical GLC.
[c] Isolated yield of the olefin after column chromatography [silica gel (entries 7, 8, and 10–13) or neutral alumina (entries 14–16), hexane or hexane/EtOAc], unless otherwise stated. For conversions lower than 100% the corresponding yield refers to the amount of starting material converted.
[d] Yield determined using analytical GLC and *n*-dodecane as an internal standard.
[e] Reaction carried out with a 4-vinylbiphenyl/divinylbenzene copolymer as an electron carrier.
[f] *Z*/*E*=93:7.
[g] Reaction performed at 0 °C.

DTBB instead of the supported copolymer. However, purification by column chromatography of the resulting mixture was necessary with DTBB, whereas the reaction crude obtained with the supported copolymer was pure enough not requiring any further purification. Other internal alkynes, such as those bearing a dialkylaminomethyl and carboxy

Table 2. Selective semihydrogenation of terminal alkynes

Entry	Starting alkyne	t (h)[a]	Product	Conversion (%)[b]	Yield (%)[c]
1		24		100	85
2		24		100	85
3		7		79	74[d]
4		24		87	87
5		24		100	79[d]

[a] Reaction carried out at room temperature with *i*-PrOH as the hydrogen source and DTBB as the electron carrier, unless otherwise stated.
[b] Conversion determined by analytical GLC.
[c] Yield determined using analytical GLC and *n*-dodecane as an internal standard, unless otherwise stated.
[d] Isolated yield of the olefin after column chromatography (silica gel, hexane/EtOAc). For conversions lower than 100% the corresponding yield refers to the amount of starting material converted.

groups, were also completely reduced in high yields (Table 3, entries 4 and 5). A tertiary propargylic alcohol and hex-6-ynoic acid are some examples of the effective reduction of terminal alkynes to the corresponding alkanes (Table 3, entries 6 and 7).

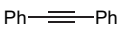
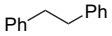
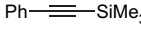
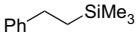
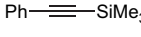
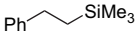
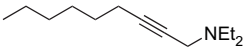
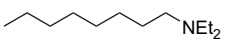
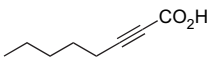
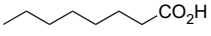
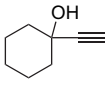
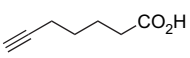
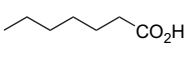
2.4. Semihydrogenation of dienes

The good results obtained in the semihydrogenation of alkynes prompted us to study the possible selectivity of the reducing system in the semihydrogenation of dienes. Thus, both the isolated diene cycloocta-1,5-diene and the conjugated one cyclohepta-1,3-diene were selectively reduced in excellent yields to the corresponding cycloalkenes at room temperature, using EtOH as the hydrogen source and DTBB as the electron carrier (Table 4, entries 1 and 2, respectively). High selectivity was also observed in the reduction of dicyclopentadiene, where only one of the two disubstituted carbon–carbon double bonds was reduced (Table 4, entry 3). In this case, the use of the copolymer as an electron carrier slightly improved the yield but the cleaner reaction crude did not need any further purification (Table 4, entry 4). Selective reduction of the exocyclic carbon–carbon double bond of (*R*)-(+)-limonene furnished (*R*)-(+)-*p*-menth-1-ene in high yield, independent of the electron carrier used (Table 4, entries 5 and 6).

2.5. Hydrogenation of alkenes

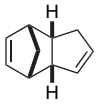
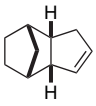
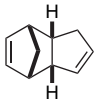
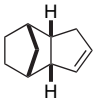
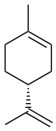
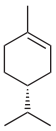
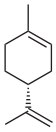
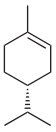
Finally, and in order to complete this study on the hydrogenation of multiple carbon–carbon bonds, we explored the reduction of a variety of alkenes, including a diene, to the corresponding alkanes (Table 5). Stilbene and 1,4-diphenylbuta-1,3-diene were reduced to the corresponding alkanes in high yields using EtOH as the hydrogen source and DTBB as the electron carrier (Table 5, entries 1 and 3). Once again, higher yields were obtained when using the copolymer as

Table 3. Complete hydrogenation of alkynes

Entry	Starting alkyne	t (h)[a]	Product	Yield (%)[b]
1		2		99
2		3		93[c]
3		5[d]		92
4		12		99
5		12		93[d]
6		12		95
7		12		95[d]

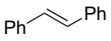
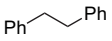
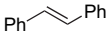
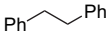
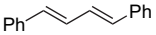
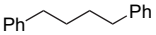
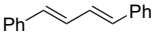
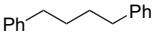
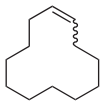
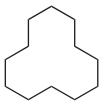
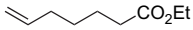
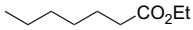
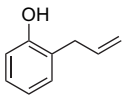
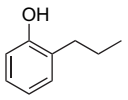
[a] Reaction carried out at room temperature with EtOH as the hydrogen source and a 4-vinylbiphenyl/divinylbenzene copolymer as electron carrier, unless otherwise stated.
[b] Isolated yield of the alkane after column chromatography [silica gel (entries 1, 3, and 6) or neutral alumina (entry 4), hexane or hexane/EtOAc], unless otherwise stated.
[c] Isolated yield from the reaction crude.
[d] Reaction carried out with DTBB as an electron carrier.

Table 4. Selective semihydrogenation of dienes

Entry	Starting diene	t (h)[a]	Product	Yield (%)[b]
1		24		95
2		21		99
3		22		88[c]
4		20[d]		90[e]
5		22		99
6		20[d]		92[c]

[a] Reaction carried out at room temperature with EtOH as the hydrogen source and DTBB as the electron carrier, unless otherwise stated.
[b] Yield determined using analytical GLC and *n*-dodecane as an internal standard, unless otherwise stated.
[c] Isolated yield of the alkene after column chromatography (silica gel, hexane).
[d] Reaction carried out with a 4-vinylbiphenyl/divinylbenzene copolymer as the electron carrier.
[e] Isolated yield from the reaction crude.

Table 5. Hydrogenation of alkenes

Entry	Starting alkene	t (h)[a]	Product	Yield (%)[b]
1		7		96
2		12[c]		99[d]
3		5		96
4		4[c]		99[d]
5		1		99
6		24		86[e]
7		24		79[e]
8		12		99

[a] Reaction carried out at room temperature with EtOH as the hydrogen source and DTBB as electron carrier, unless otherwise stated.
[b] Isolated yield of the alkene after column chromatography (silica gel, hexane or hexane/EtOAc).
[c] Reaction carried out with a 4-vinylbiphenyl/divinylbenzene copolymer as the electron carrier.
[d] Isolated yield from the reaction crude.
[e] Yield determined using analytical GLC and *n*-dodecane as an internal standard.

an electron carrier together with simpler product purification (Table 5, entries 2 and 4). As an example of an isolated alkene, cyclododecene was quantitatively reduced to cyclododecane in a short reaction time (Table 5, entry 5). In general, longer reaction times were needed for the reduction of the functionalized alkenes (*E*)-ethyl hex-3-enoate, ethyl hept-6-enoate, and *o*-allylphenol, which also proceeded with a good performance.

3. Conclusion

In summary, the in situ generated both Ni(0) nanoparticles and molecular hydrogen from the system $NiCl_2$–Li–DTBB–ROH is a new mild and simple methodology for the efficient stereoselective cis semihydrogenation of alkynes. This methodology has also found application in the semihydrogenation of terminal alkynes and dienes, as well as in the reduction of alkynes and alkenes to alkanes. The use of a polymer-supported arene as the electron carrier instead of DTBB represents a clear advantage making the work-up simpler and providing, in general, higher yields and cleaner reaction crudes. The above system is more advantageous than the previously reported $NiCl_2$–Li–arene–H_2 and $NiCl_2\cdot 2H_2O$–Li–arene systems since it is more selective in the semihydrogenation of alkynes and more compatible with the presence of a variety of functional groups.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker Avance 300 and Bruker Avance 400 (300 and 400 MHz for ^1H NMR, and 75 and 100 MHz for ^{13}C NMR, respectively) using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in δ (ppm) and coupling constants (J) in hertz. Mass spectra (EI) were obtained at 70 eV on a Shimadzu QP-5000 and Agilent 5973 spectrometers, fragment ions are given in m/z with relative intensities (%) in parenthesis. HR-MS analyses were carried out on a Finnigan MAT95S spectrometer. Determination of the purity of volatile compounds and chromatographic analyses (GLC) were performed with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and a 30 m capillary column (0.32 mm diameter, 0.25 μm film thickness), using nitrogen (2 mL/min) as carrier gas, $T_{injector}$=275 °C, T_{column}=60 °C (3 min) and 60–270 °C (15 °C/min), using *n*-dodecane as an internal standard. Flash column

chromatography was performed using silica gel 60 of 40–60 μm. THF was directly used without any purification (Acros, 99.9%). Anhydrous nickel chloride (Aldrich) and lithium powder were (MEDALCHEMY S. L.) commercially available.

Alkynes in entries 1–4 and 6–9 in Table 1, 1, 2, 4 in Table 2, 1–3, 5–7 in Table 3, all dienes in Table 4, and all alkenes in Table 5 were commercially available. Alkynes in entries 10–13 in Table 1, 3 and 5 in Table 2 were obtained by standard alkylation reactions from the starting alcohols (see below) and aniline. Cyclooctyne (Table 1, entry 5) was prepared by bromination of cyclooctene followed by two successive dehydrobrominations with KO-*t*-Bu and LDA.[25] The diethylaminomethyl alkynes (entries 14–16) were prepared following literature procedures (see below).[26] The 4-vinylbiphenyl/divinylbenzene copolymer was prepared by radical copolymerization of the corresponding monomers according to the published procedure.[27]

4.2. Preparation of the starting acetylenic methyl and benzyl ether derivatives. General procedure

The corresponding alcohol (1 mmol) was added to a white suspension of NaH (3 mmol) in THF (10 mL) at room temperature under argon. After stirring for 30 min, methyl iodide or benzyl bromide (3 mmol) was added and the reaction was monitored by GLC. Then, the resulting mixture was quenched with water (10 mL) and extracted with $CHCl_3$ (3×10 mL). The organic phase was dried with anhydrous Na_2SO_4 and the solvent evaporated (15 Torr) to give an oil. Purification by flash column chromatography (silica gel, hexane) afforded the corresponding alkylated products. New compounds or those for which spectroscopic data have not been found or are incomplete, follow.

4.2.1. 1-Methoxydec-3-yne (Table 1, entry 10).[28] Yield: 97%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t, J=6.8 Hz, 3H, CH_3), 1.21–1.52 [m, 8H, $(CH_2)_4CH_3$], 2.12–2.16, 2.40–2.45 [2m, 4H, $CH_2(CH_2)_4CH_3$, CH_2CH_2O], 3.37 (s, 3H, CH_3O), 3.47 (t, J=7.0 Hz, 2H, CH_2O); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (CH_3), 18.7, 19.9, 22.5, 28.5, 28.9, 31.3 [$(CH_2)_5CH_2$, CH_2CH_2O], 58.5 (CH_3O), 71.3 (CH_2O), 76.4 [$C{\equiv}C(CH_2)_2O$], 81.3 [$C{\equiv}C(CH_2)_2O$]; IR (film): ν=1459 ($C{\equiv}CCH_2$), 1119 (C–O) cm^{-1}; MS (EI): m/z (%)=167 (M^+-1, 1), 153 (11), 125 (24), 123 (11), 121 (21), 112 (10), 111 (22), 108 (12), 107 (47), 101 (14), 99 (13), 98 (29), 97 (100), 95 (23), 94 (19), 93 (58), 91 (22), 85 (15), 84 (10), 83 (68), 82 (10), 81 (47), 80 (20), 79 (79), 77 (27), 72 (11), 71 (11), 69 (28), 68 (96), 67 (73), 66 (17), 65 (18), 55 (30), 53 (21), 52 (15), 51 (11); HR-MS: calcd for $C_{11}H_{20}O$: 168.1514; found: 168.1495.

4.2.2. 5-Benzyloxypent-2-yne (Table 1, entry 12).[29] Yield: 91%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.76 (t, J=2.5 Hz, 3H, CH_3), 2.39–2.46 (m, 2H, CH_2CH_2O), 3.53 (t, J=7.0 Hz, 2H, CH_2CH_2O), 4.52 (s, 2H, CH_2Ph), 7.24–7.33 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=3.3 (CH_3), 20.0 (CH_2CH_2O), 68.7, 72.7 (CH_2CH_2O, CH_2Ph), 75.7, 76.5 ($CH_3C{\equiv}CCH_2$, $CH_3C{\equiv}CCH_2$), 127.4, 127.5, 128.2, 138.1 (6×ArC); IR (film): ν=3087, 3063, 3029, 737, 698 (HC=C), 1454 ($C{\equiv}CCH_2$), 1104 (C–O) cm^{-1}; MS (EI): m/z (%)=174 (M^+, 1), 173 (M^+-1, 5), 160 (6), 159 (51), 146 (3), 145 (4), 131 (4), 130 (2), 129 (13), 128 (3), 105 (5), 92 (8), 91 (100), 89 (3), 77 (3), 67 (3), 65 (12), 63 (2), 53 (3), 51 (3); HR-MS: calcd for $C_{12}H_{14}O$: 174.1045; found: 174.1006.

4.2.3. 1-Benzyloxyhex-3-yne (Table 1, entry 13).[29] Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.11 (t, J=7.5 Hz, 3H, CH_3), 2.11–2.20 (m, 2H, CH_2CH_3), 2.43–2.49 (m, 2H, CH_2CH_2O), 3.55 (t, J=7.1 Hz, 2H, CH_2CH_2O), 4.54 (s, 2H, CH_2Ph), 7.23–7.34 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.3 (CH_2CH_3), 14.1 (CH_3), 20.1 (CH_2CH_2O), 68.8, 72.8 (CH_2CH_2OBn, CH_2Ph), 75.9 ($CH_3CH_2C{\equiv}C$), 82.7 ($CH_3CH_2C{\equiv}C$), 127.5, 127.6, 128.3, 138.2 (6×ArC); IR (film): ν=3087, 3063, 3029, 736, 698 (HC=C), 1454 ($C{\equiv}CCH_2$), 1104 (C–O) cm^{-1}; MS (EI): m/z (%)=187 (M^+-1, 2), 173 (5), 160 (7), 159 (60), 145 (2), 143 (3), 131 (2), 130 (2), 129 (14), 128 (3), 105 (5), 92 (8), 91 (100), 89 (2), 79 (3), 77 (3), 67 (3), 65 (11), 63 (2), 53 (2), 51 (3); HR-MS: calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1154.

4.2.4. 3-Benzyloxypent-1-yne (Table 2, entry 3). Yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.01 (t, J=7.4 Hz, 3H, CH_3), 1.73–1.83 (m, 2H, CH_2CH_3), 2.45 (s, 1H, HC≡C), 4.01 (t, J=6.4 Hz, 1H, CHO), 4.49, 4.80 (AB system, J=11.8 Hz, 2H, CH_2O), 7.24–7.37 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=9.5 (CH_3), 28.7 (CH_2CH_3), 69.6 (CHO), 70.4 (CH_2O), 73.8 ($C{\equiv}CH$), 82.7 ($HC{\equiv}C$), 127.6, 127.9, 128.3, 137.9 (6×ArC); IR (film): ν=3299 (HC≡C), 3088, 3064, 3031, 737, 698 (HC=C), 1069 (C–O) cm^{-1}; MS (EI): m/z (%)=145 (7), 144 (3), 117 (3), 107 (10), 105 (5), 92 (28), 91 (100), 79 (8), 77 (8), 67 (3), 65 (10), 51 (4); HR-MS: calcd for $C_{12}H_{14}O$: 174.1045; found: 174.1018.

4.3. Synthesis of the starting acetylenic diethylamino derivatives. General procedure[26]

In a round-bottomed flask fitted with a reflux condenser diethylamine (10.4 mL, 7.3 g) was added in three portions at room temperature over a solution of paraformaldehyde (0.1 mol, 3 g) in dioxane (25 mL). The temperature of the mixture rose gradually to 45 °C after each addition. Thus, after cooling to room temperature a second portion of diethylamine was added. When the ensuing exothermic reaction had subsided, the last portion was added. The conversion was completed by heating the mixture for 30 min at 50 °C. The reaction mixture was cooled to room temperature and CuBr (4.6 mmol, 660 mg) was added. Then, the mixture was heated at 85 °C and the corresponding acetylene (0.1 mol) was added in portions over 30 min. The reaction mixture was cooled to room temperature after an additional period of 2–2.5 h. In all cases the reaction mixture was poured into 500 mL of water and extracted with Et_2O (3×40 mL). The organic phase was dried with anhydrous Na_2SO_4 and concentrated in vacuo (15 Torr). The resulting residue was purified by flash column chromatography (silica gel, hexane) affording the corresponding acetylenes. New compounds or those for which spectroscopic data have not been found, follow.

4.3.1. *N,N*-Diethylnon-2-yn-1-amine (Table 1, entry 14).[30] Yield: 91%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (t,

J=6.7 Hz, 3H, CH_3CH$_2$CH$_2$), 1.06 (t, J=7.2 Hz, 6H, 2×CH_3CH$_2$N), 1.13–1.54 [m, 8H, (CH_2)$_4$CH$_3$], 2.16–2.20 [m, 2H, CH_2C≡CH$_2$N], 2.52 (q, J=7.2 Hz, 4H, 2×NCH_2CH$_3$), 3.38 (t, J=2.0 Hz, 2H, C≡CH_2N); ^{13}C NMR (75 MHz, CDCl$_3$): δ=12.4 (2×CH$_3$CH$_2$N), 13.8 (CH_3CH$_2$CH$_2$), 18.5, 22.4, 28.4, 28.8, 31.2 [(CH$_2$)$_5$CH$_3$], 40.8 (C≡CCH_2N), 46.9 (2×NCH$_2$CH$_3$), 74.1 (C≡CCH$_2$N), 84.7 (C≡CCH$_2$N); IR (film): ν=1463 (C≡CCH$_2$) cm^{-1}; MS (EI): m/z (%)=195 (M$^+$, 6), 194 (M$^+$−1, 4), 181 (13), 180 (100), 112 (2), 108 (2), 86 (3), 81 (7), 79 (3), 77 (2), 67 (3), 58 (7), 56 (2), 55 (2), 53 (2); HR-MS: calcd for C$_{13}$H$_{25}$N: 195.1987; found: 195.1987.

4.3.2. *N,N*-Diethylundec-2-yn-1-amine (Table 1, entry 15).[31] Yield: 93%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.88 (t, J=6.7 Hz, 3H, CH$_3$), 1.06 (t, J=7.2 Hz, 6H, 2×CH_3CH$_2$N), 1.28–1.52 [m, 12H, (CH_2)$_6$CH$_3$], 2.16–2.18 (m, 2H, CH_2C≡CCH$_2$N), 2.53 (q, J=7.2 Hz, 4H, 2×NCH_2CH$_3$), 3.38 (s, 2H, C≡CCH_2N); ^{13}C NMR (75 MHz, CDCl$_3$): δ= 12.4 (2×CH$_3$CH$_2$N), 13.9 (CH_3CH$_2$CH$_2$), 18.5, 22.5, 28.7, 28.9, 29.0, 29.1, 31.7 [CH$_3$(CH$_2$)$_7$], 40.8 (C≡CCH$_2$N), 47.0 (2×NCH$_2$CH$_3$), 74.2 (C≡CCH$_2$N), 84.7 (C≡CCH$_2$N); IR (film): ν=1463 (C≡CCH$_2$) cm^{-1}; MS (EI): m/z (%)= 223 (M$^+$, 5), 222 (M$^+$−1, 4), 209 (15), 208 (100), 95 (2), 86 (2), 81 (3), 79 (2), 67 (3), 58 (5), 56 (2), 55 (2); HR-MS: calcd for C$_{15}$H$_{29}$N: 223.2300; found: 223.2298.

4.3.3. *N,N*-Diethyl-5-phenylpent-2-yn-1-amine (Table 1, entry 16). Yield: 85%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=1.03 (t, J=7.2 Hz, 6H, 2×CH_3CH$_2$), 2.47 (q, J=7.2 Hz, 4H, 2×CH_2CH$_3$; t, J=7.5 Hz, 2H, CH$_2$Ph), 2.81 (t, J=7.5 Hz, 2H, CH_2CH$_2$Ph), 3.34 [d, J=2.0 Hz, 2H, CH_2N(CH$_2$CH$_3$)$_2$], 7.17–7.30 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, CDCl$_3$): δ=12.5 (2×CH$_3$CH$_2$), 20.7 (CH$_2$CH$_2$Ph), 35.3 (CH$_2$Ph), 40.8 [CH$_2$N(CH$_2$CH$_3$)$_2$], 46.9 (2×CH$_2$CH$_3$), 75.1 (C≡CCH$_2$N), 84.0 (C≡CCH$_2$N), 126.1, 128.2, 128.4, 140.7 (6×ArC); IR (film): ν=3086, 3063, 3027 (HC=C), 1454 (C≡CCH$_2$) cm^{-1}; MS (EI): m/z (%)=215 (M$^+$, 7), 214 (M$^+$−1, 5), 201 (17), 200 (100), 142 (2), 141 (4), 129 (5), 128 (26), 127 (4), 115 (7), 108 (3), 92 (3), 91 (31), 65 (5), 58 (8), 56 (4), 51 (2); HR-MS: calcd for C$_{15}$H$_{21}$N: 215.1674; found: 215.1677.

4.4. Semihydrogenation of alkynes

In a 30 mL reaction tube, nickel chloride (130 mg, 1 mmol) was added over a suspension of lithium (28 mg, 4 mmol) and DTBB (13 mg, 0.05 mmol) or 4-vinylbiphenyl/divinylbenzene copolymer (40 mg, 0.2 mmol) in THF (2 mL) at room temperature under argon. The reaction mixture, which was initially dark green, changed to black indicating that nickel(0) was formed. After 10 min, THF (18 mL), EtOH (0.12 mL, 2 mmol, for internal alkynes) or *i*-PrOH (0.15 mL, 2 mmol, for terminal alkynes), and the corresponding alkyne (1 mmol) were consecutively added. The needle of the argon inlet was removed and the septum was sealed with insulated tape. The progress of the reaction was monitored by GLC–MS. After total conversion of the starting material, the resulting suspension was diluted with Et$_2$O (10 mL) and filtered through a pad containing silica gel (lower layer) and Celite (upper layer) (ca. 3:1). The residue obtained was purified by flash column chromatography (silica gel, hexane/EtOAc 9:1 for entries 7, 8, and 10–13 in Table 1 or neutral alumina, hexane/EtOAc 8:2 for entries 14–16 in Table 1) to give the corresponding alkenes. For volatile products, the dried organic layer was analyzed by GLC using *n*-dodecane as an internal standard. *cis*-Hex-3-ene-1-ol, oct-1-ene, dec-1-ene, 4-phenylbut-1-ene, and *N*-allylaniline were characterized by comparison of their physical and spectroscopic data with those of commercially available samples (Aldrich). The products *cis*-oct-4-ene, *cis*-dec-5-ene, and *cis*-1,2-dimethoxyethene were characterized by comparison of their physical and spectroscopic data with those of authentic samples prepared by semihydrogenation using Lindlar catalyst.[4b] New products or those for which spectroscopic data have not been found or are incomplete, follow.

4.4.1. (*Z*)-Dec-3-en-1-ol (Table 1, entry 7).[32] Yield: 62%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.88 (t, J=6.6 Hz, 3H, CH$_3$), 1.22–1.50 [m, 8H, (CH_2)$_4$CH$_3$], 1.70 (s, 1H, OH), 2.06 (td, J=6.8, 6.6 Hz, 2H, CH_2(CH$_2$)$_4$CH$_3$), 2.33 (td, J=6.6, 6.5 Hz, 2H, CH_2CH$_2$OH), 3.64 (td, J=5.8, 5.7 Hz, 2H, CH_2OH), 5.32–5.40 (m, 1H, HC=CHCH$_2$CH$_2$OH), 5.52–5.61 (m, 1H, CH=CHCH$_2$CH$_2$OH); ^{13}C NMR (75 MHz, CDCl$_3$): δ=14.0 (CH$_3$), 22.6, 27.3, 28.9, 29.6, 30.8, 31.7 [(CH$_2$)$_5$, CH$_2$CH$_2$OH], 62.3 (CH$_2$OH), 124.9 (CH=CHCH$_2$CH$_2$OH), 133.5 (CH=CHCH$_2$CH$_2$OH); IR (film): ν=3373 (OH), 3009 (HC=CH), 1048 (C–O) cm^{-1}; MS (EI): m/z (%)=138 (M$^+$−18, 7), 110 (16), 109 (17), 96 (26), 95 (35), 83 (26), 82 (51), 81 (79), 79 (13), 77 (3), 71 (12), 70 (17), 69 (52), 68 (100), 67 (82), 66 (8), 65 (5), 58 (2), 57 (25), 56 (24), 55 (93), 54 (40), 53 (15), 51 (2); HR-MS: calcd for C$_{10}$H$_{20}$O: 156.1514, 138.1671 (M$^+$−H$_2$O); found: 138.1431.

4.4.2. (*Z*)-Oct-2-en-1-ol (Table 1, entry 8).[33] Yield: 65%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.89 (t, J=6.8 Hz, 3H, CH$_3$), 1.21–1.41 [m, 6H, (CH_2)$_3$CH$_3$], 1.51 (s, 1H, OH), 2.07 (td, J=6.9, 6.8 Hz, 2H, CH_2(CH$_2$)$_3$CH$_3$), 4.20 (d, J=5.6 Hz, 2H, CH_2OH), 5.50–5.73 (m, 2H, CH=CH); ^{13}C NMR (75 MHz, CDCl$_3$): δ=14.0 (CH$_3$), 22.5, 27.4, 29.2, 31.4 [(CH$_2$)$_4$], 58.5 (CH$_2$OH), 128.2 (CH=CHCH$_2$OH), 133.3 (CH=CHCH$_2$OH); IR (film): ν=3357 (OH), 3014, 758 (HC=C), 1119 (C–O) cm^{-1}; MS (EI): m/z (%)=111 (M$^+$−17, 2), 110 (M$^+$−18, 21), 95 (12), 85 (7), 84 (4), 83 (3), 82 (22), 81 (35), 79 (4), 72 (4), 71 (11), 70 (7), 69 (22), 68 (30), 67 (28), 66 (4), 65 (3), 58 (7), 57 (100), 56 (19), 55 (41), 54 (32), 53 (8), 51 (3).

4.4.3. (*Z*)-1-Methoxydec-3-ene (Table 1, entry 10). Yield: 93%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.88 (t, J=6.9 Hz, 3H, CH_3CH$_2$), 1.23–1.43 [m, 8H, (CH_2)$_4$CH$_3$], 2.04 (td, J=6.7, 6.6 Hz, 2H, CH_2(CH$_2$)$_4$CH$_3$), 2.33 (td, J=6.8, 6.7 Hz, 2H, CH_2CH$_2$O), 3.34 (s, 3H, CH$_3$O), 3.38 (t, J=7.0 Hz, 2H, CH$_2$O), 5.32–5.40 (m, 1H, CH=CHCH$_2$CH$_2$O), 5.43–5.52 (m, 1H, CH=CHCH$_2$CH$_2$O); ^{13}C NMR (75 MHz, CDCl$_3$): δ=14.0 (CH$_3$CH$_2$), 22.6, 27.3, 27.7, 28.9, 29.5, 31.7 [(CH$_2$)$_5$, CH$_2$CH$_2$O], 58.5 (CH$_3$O), 72.4 (CH$_2$O), 125.3 (CH=CHCH$_2$CH$_2$O), 132.0 (CH=CHCH$_2$CH$_2$O); IR (film): ν=3008, 724 (HC=C), 1119 cm^{-1}; MS (EI): m/z (%)=170 (M$^+$, 2), 142 (2), 139 (6), 138 (53), 127 (2), 110 (15), 109 (20), 97 (8), 96 (37), 95 (33), 85 (4), 84 (2), 83 (16), 82 (55), 81 (68), 80 (3), 79 (10), 77 (4), 71 (21), 70 (4), 69 (29), 68 (100), 67 (72), 66 (10), 65 (4), 59 (3), 58 (17), 57 (5), 56 (6), 55 (48), 54 (42), 53 (12), 51 (2); HR-MS: calcd for C$_{11}$H$_{22}$O: 170.1671; found: 170.1660.

4.4.4. (*Z*)-5-Benzyloxypent-2-ene (Table 1, entry 12).[29] Yield: 73%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.62 (d, J=6.5 Hz, 3H, CH_3), 2.38 (td, J=7.0, 6.9 Hz, 2H, CH_2CH_2O), 3.47 (t, J=6.9 Hz, 2H, CH_2CH_2O), 4.51 (s, 2H, CH_2Ph), 5.38–5.46 (m, 1H, CH_3CH=CH), 5.49–5.59 (m, 1H, CH_3CH=C*H*), 7.24–7.33 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.8 (CH_3), 27.6 (CH_2CH_2O), 69.8, 72.8 (CH_2CH_2O, CH_2Ph), 125.8, 126.4, 127.4, 127.5, 128.3, 138.5 (ArC, CH_3CH=CH, CH_3CH=C*H*); IR (film): ν=3086, 3064, 735, 697 (HC=C), 1101 (C–O) cm^{-1}; MS (EI): *m*/*z* (%)=176 (M^+, 4), 175 (M^+-1, 5), 132 (3), 107 (3), 105 (3), 104 (4), 92 (10), 91 (100), 89 (2), 77 (2), 65 (8), 55 (3), 51 (2); HR-MS: calcd for $C_{12}H_{16}O$: 176.1201; found: 176.1231.

4.4.5. (*Z*)-1-Benzyloxyhex-3-ene (Table 1, entry 13).[34] Yield: 79%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.96 (t, J=7.5 Hz, 3H, CH_3), 2.06 (td, J=14.8, 7.3 Hz, 2H, CH_2CH_3), 2.37 (td, J=7.1, 6.8 Hz, 2H, CH_2CH_2O), 3.47 (t, J=7.1 Hz, 2H, CH_2CH_2O), 4.51 (s, 2H, CH_2Ph), 5.32–5.40 (m, 1H, CH_3CH_2CH=CH), 5.43–5.51 (m, 1H, CH_3CH_2CH=C*H*), 7.22–7.34 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2 (CH_3), 20.6 (CH_2CH_3), 27.8 (CH_2CH_2O), 70.0, 72.8 (CH_2CH_2O, CH_2Ph), 124.8, 127.4, 127.5, 128.3, 133.6, 138.5 (6×ArC, CH=CH); IR (film): ν=3087, 3064, 735, 696 (HC=C), 1102 (C–O) cm^{-1}; MS (EI): *m*/*z* (%)=190 (M^+, 2), 189 (M^+-1, 2), 161 (6), 107 (6), 104 (3), 99 (3), 92 (11), 91 (100), 89 (2), 82 (2), 81 (2), 77 (2), 69 (4), 68 (3), 67 (2), 65 (7), 55 (3), 51 (2); HR-MS: calcd for $C_{13}H_{18}O$: 190.1358; found: 190.1343.

4.4.6. (*Z*)-*N*,*N*-Diethylnon-2-en-1-amine (Table 1, entry 14).[35] Yield: 90%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, J=6.4 Hz, 3H, $CH_3CH_2CH_2$), 1.04 (t, J=7.2 Hz, 6H, 2×CH_3CH_2N), 1.09–1.49 [m, 8H, $(CH_2)_4CH_3$], 2.07 [t, J=6.5 Hz, 2H, $CH_2(CH_2)_4CH_3$], 2.52 (q, J=7.2 Hz, 4H, 2×NCH_2CH_3), 3.11 [d, J=5.8 Hz, 2H, $CH_2N(CH_2CH_3)_2$], 5.42–5.56 (m, 2H, CH=CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.8 (2×CH_3CH_2N), 14.1 ($CH_3CH_2CH_2$), 22.6, 27.5, 28.9, 29.6, 31.7 [$(CH_2)_5$], 46.7 (2×NCH_2CH_3), 49.6 [$CH_2N(CH_2CH_3)_2$], 126.7 (CH=$CHCH_2N$), 132.5 (CH=$CHCH_2N$); IR (film): ν=3012, 1655, 756 (HC=C) cm^{-1}; MS (EI): *m*/*z* (%)=197 (M^+, 6), 196 (M^+-1, 3), 183 (3), 182 (21), 126 (3), 112 (17), 110 (3), 98 (2), 96 (3), 86 (20), 84 (2), 83 (9), 82 (2), 81 (2), 74 (4), 73 (28), 72 (12), 70 (2), 69 (16), 68 (2), 67 (5), 59 (3), 58 (100), 57 (4), 56 (10), 55 (15), 54 (3), 53 (2); HR-MS: calcd for $C_{13}H_{27}N$: 197.2143; found: 197.2156.

4.4.7. (*Z*)-*N*,*N*-Diethylundec-2-en-1-amine (Table 1, entry 15).[36] Yield: 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, J=6.6 Hz, 3H, $CH_3CH_2CH_2$), 1.04 (t, J=7.2 Hz, 6H, 2×CH_3CH_2N), 1.20–1.49 [m, 12H, $(CH_2)_6CH_3$], 2.02–2.07 [m, 2H, $CH_2(CH_2)_6CH_3$], 2.52 (q, J=7.2 Hz, 4H, 2×NCH_2CH_3), 3.10 [d, J=5.8 Hz, 2H, $CH_2N(CH_2CH_3)_2$], 5.42–5.56 (m, 2H, CH=CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.8 (2×CH_3CH_2N), 14.1 ($CH_3CH_2CH_2$), 22.7, 27.5, 29.3, 29.5, 29.6, 29.6, 31.9 [$(CH_2)_7CH_3$], 46.7 (2×NCH_2CH_3), 49.6 [$CH_2N(CH_2CH_3)_2$], 126.7 (CH=$CHCH_2N$), 132.5 (CH=$CHCH_2N$); IR (film): ν=3012, 1650, 756 (HC=C) cm^{-1}; MS (EI): *m*/*z* (%)=226 (M^++1, 2), 225 (M^+, 16), 224 (M^+-1, 9), 211 (9), 210 (63), 196 (4), 138 (2), 126 (5), 124 (2), 112 (20), 110 (5), 98 (3), 97 (7), 96 (4), 86 (27), 84 (3), 83 (9), 82 (3), 81 (3), 79 (2), 74 (6), 73 (47), 72 (16), 71 (3), 70 (2), 69 (11), 68 (3), 67 (7), 59 (3), 58 (100), 57 (5), 56 (8), 55 (16), 54 (3), 53 (2); HR-MS: calcd for $C_{15}H_{31}N$: 225.2457; found: 225.2500.

4.4.8. (*Z*)-*N*,*N*-Diethyl-5-phenylpent-2-en-1-amine (Table 1, entry 16). Yield: 94%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.00 (t, J=7.1 Hz, 6H, 2×CH_3), 2.35–2.52 (m, 6H, 2×CH_2CH_3, CH_2Ph), 2.67 (t, J=7.6 Hz, 2H, CH_2CH_2Ph), 3.03 [d, J=5.9 Hz, 2H, $CH_2N(CH_2CH_3)_2$], 5.45–5.60 (m, 2H, CH=CH), 7.18–7.30 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.7 (2×CH_3), 29.5, 35.8 (CH_2CH_2Ph), 46.7 (2×NCH_2CH_3), 49.6 [$CH_2N(CH_2CH_3)_2$], 125.8, 127.7, 128.3, 128.4, 131.1 (6×ArC, CH=CH); IR (film): ν=3062, 3025, 698 (HC=C) cm^{-1}; MS (EI): *m*/*z* (%)=217 (M^+, 9), 216 (M^+-1, 3), 203 (3), 202 (21), 188 (4), 145 (6), 144 (3), 143 (4), 130 (2), 129 (14), 128 (5), 127 (2), 124 (2), 115 (4), 112 (12), 110 (6), 96 (4), 92 (8), 91 (100), 89 (2), 86 (21), 82 (2), 77 (2), 74 (8), 73 (36), 72 (13), 67 (3), 66 (2), 65 (9), 59 (3), 58 (67), 57 (2), 56 (7), 55 (2), 54 (2), 53 (2), 51 (2); HR-MS: calcd for $C_{15}H_{23}N$: 217.1830; found: 217.1819.

4.4.9. 3-Benzyloxypent-1-ene (Table 2, entry 3).[37] Yield: 74%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (t, J=7.5 Hz, 3H, CH_3), 1.48–1.60 (m, 1H, $CH_aH_bCH_3$), 1.62–1.74 (m, 1H, $CH_aH_bCH_3$), 3.62 (td, J=6.9, 6.8 Hz, 1H, CHO), 4.33, 4.57 (AB system, J=12.0 Hz, 2H, CH_2O), 5.14–5.21 (m, 2H, CH_2=CH), 5.64–5.76 (m, 1H, CH=CH_2), 7.19–7.33 (m, 5H, 5×ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=9.6 (CH_3), 28.2 (CH_2CH_3), 69.9 (CH_2O), 81.8 (CHO), 117.0 (CH_2=CH), 127.2, 127.5, 128.2, 138.7, 138.8 (6×ArC, CH=CH_2); IR (film): ν=3065, 3030, 994, 735, 697 (HC=CH) cm^{-1}; MS (EI): *m*/*z* (%)=148 (M^+-28, 2), 147 (20), 107 (6), 92 (11), 91 (100), 79 (3), 77 (4), 65 (7), 55 (3), 51 (2); HR-MS: calcd for $C_{12}H_{16}O$: 176.1201; found: 176.1206.

4.5. Complete hydrogenation of alkynes

The reaction was performed according to the procedure described for the semireduction of alkynes but using the following amounts of reactants: nickel chloride (130 mg, 1 mmol), lithium (70 mg, 10 mmol), 4-vinylbiphenyl/divinylbenzene copolymer (40 mg, 0.2 mmol) or DTBB (13 mg, 0.05 mmol), EtOH (0.29 mL, 5 mmol), and the alkyne (1 mmol). The residue obtained was purified by flash column chromatography (silica gel, hexane or hexane/EtOAc 9:1 for entries 1, 3, and 6 in Table 3) or neutral alumina (hexane/EtOAc 8:2 for entry 4 in Table 3) to give the corresponding alkanes. For the carboxylic acids in entries 5 and 7 (Table 3), 2 M HCl (15 mL) was added, the resulting mixture being extracted with CH_2Cl_2 (3×10 mL).

n-Heptanoic and *n*-octanoic acids were characterized by comparison of their physical and spectroscopic data with those of commercially available samples (Aldrich). 1,2-Diphenylethane, trimethylphenethylsilane, and 1-ethylcyclohexanol gave satisfactory analyses by comparison of their physical and spectroscopic data with those of authentic samples.[38]

4.5.1. *N,N*-Diethylnonan-1-amine (Table 3, entry 4).[39] Yield: 98%; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (t, J=6.5 Hz, 3H, $CH_3CH_2CH_2$), 1.02 (t, J=7.2 Hz, 6H, 2×CH_3CH_2N), 1.20–1.40 [m, 14H, $(CH_2)_7CH_3$], 2.40 (t, J=7.7 Hz, 2H, NCH_2CH_2), 2.52 (q, J=7.1 Hz, 4H, 2×NCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.5 (2×CH_3CH_2N), 14.0 ($CH_3CH_2CH_2$), 22.6, 26.8, 27.7, 29.3, 29.5, 29.6, 31.8 [$(CH_2)_7CH_3$], 46.8 (2×NCH_2CH_3), 52.9 (NCH_2CH_2); IR (film): ν=1380 (C–N) cm^{-1}; MS (EI): m/z (%)=199 (M^+, 4), 198 (M^+-1, 1), 184 (5), 87 (6), 86 (100), 84 (1), 72 (5), 58 (4), 57 (1), 56 (2), 55 (2).

4.6. Semihydrogenation of dienes

The reaction was performed according to the procedure described for the semireduction of alkynes but using the following amounts of reactants: nickel chloride (130 mg, 1 mmol), lithium (31 mg, 4.4 mmol), DTBB (13 mg, 0.05 mmol) or 4-vinylbiphenyl/divinylbenzene copolymer (40 mg, 0.2 mmol), EtOH (0.14 mL, 2.4 mmol), and the diene (1 mmol). The residue obtained was purified by flash column chromatography (silica gel, hexane) to give the corresponding alkenes.

Cyclooctene and cycloheptene were characterized by comparison of their physical and spectroscopic data with those of commercially available samples (Aldrich). (*R*)-(+)-*p*-Menth-1-ene[40] and 3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-indene[38] were characterized by comparison of their physical and spectroscopic data with those described in the literature.

4.7. Hydrogenation of alkenes

The reaction was performed according to the procedure described for the semireduction of alkynes but using the following amounts of reactants: nickel chloride anhydrate (130 mg, 1 mmol), lithium [35 mg, 5 mmol (for entries 1, 2, 5, and 8 in Table 5), 70 mg, 10 mmol (for entries 3 and 4 in Table 5), 29 mg, 4.2 mmol (for entries 6 and 7 in Table 5)], and DTBB (13 mg, 0.05 mmol) or 4-vinylbiphenyl/divinylbenzene copolymer (40 mg, 0.2 mmol), EtOH [0.17 mL, 3 mmol (for entries 1, 2, 5, and 8 in Table 5), 0.28 mL, 5 mmol (for entries 3 and 4 in Table 5), 0.12 mL, 2.2 mmol (for entries 6 and 7 in Table 5)], and the alkene or diene (1 mmol). The residue obtained was purified by flash column chromatography (silica gel, hexane or hexane/EtOAc 9:1) to give the corresponding alkane.

Cyclododecane, ethyl heptanoate, ethyl octanoate, and 2-ethylphenol were characterized by comparison of their physical and spectroscopic data with those of commercially available samples (Aldrich). 1,2-Diphenylethane and 1,4-diphenylbutane gave satisfactory analyses by comparison of their physical and spectroscopic data with those of authentic samples.[38]

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