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Nickel Catalyzed Hydrovinylation of Arylethylenes: General Method of Synthesis of α-Arylpropionic Acids Intermediates

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Abstract—The hydrovinylation of arylethylenes catalyzed by $[Ni(MeCN)_6][BF_4]_2/AlEt_2Cl/PPh_3$ was modulated to obtain 3-aryl-1-butenes in high yields and selectivities. A wide variety of arylethylenes containing electron-donating or electron-withdrawing groups and Lewis basic group, can be hydrovinylated at room temperature and under mild conditions by changing the relative ratios of the three-component catalyst. Similar activities and selectivities were observed for *o*-, *m*- and *p*-substituted styrenes. Also, the hydrovinylation of olefins with substituents in the vinyl fragment, such as α-methylstyrene and indene, can be accomplished.

Introduction

α-Arylpropionic acids have emerged as an important class of non-steroidal anti-inflammatory agents over the past two decades. There are several reports showing considerable efforts in order to synthesize this class of drugs.[1] In particular, hydrovinylation reaction of arylethylenes have been investigated most extensively because of the importance of 3-aryl-1-butenes as potential intermediates for this drug.[2]The selective arylethylene hydrovinylation can be achieved by a catalyst-based reaction, employing a transition metal complex, especially Ni and Pd, as catalyst. Catalysts based on Rh[3] and Ru[4] have also been used, but they are less selective in 3-aryl-1-butenes. Typically (η^3-allyl) nickel halides activated by Lewis acids,[5] cationic Ni-mesityl complexes[6] and (η^3-allyl) nickel[7]or (η^3-allyl) palladium[8] halides, where halide anion is abstracted by a silver salt with a noncoordinating anion, have been applied in the catalytic arylethylene hydrovinylation reactions.

Several α-aryl propionic acids of pharmaceutical interest have Lewis basic centers and in some cases only one of the enantiomers has biological activity. As a special requirement for a general method of synthesis of these compounds the hydrovinylation must tolerate Lewis basic substrates and the employed catalytic system has to be stereoselective as well as chemo- and regioselective. Indeed, catalysts that fulfil these requirements have already been reported. The enantioselective hydrovinylation of styrene or Lewis basic vinylarenes was performed by a nickel allyl/organoaluminum catalyst, in the presence of a chiral azaphospholene at low temperatures (−70°C).[9] Recently, RajanBabu and coworkers presented a versatile allyl nickel halide based catalytic system that performs enantioselective hydrovinylations of 2-vinyl-6-methoxynaphthalene and other substrates at −56°C.[7a] Ceder reported a catalyst able to codimerize Lewis basic arylethylenes with ethylene.[6] We have worked on a dicationic nickel complex/$AlEt_2Cl$ catalyst for arylethylene hydrovinylation under mild conditions.[10] Our system appeared to be active, chemo- and regioselective when styrene was used as substrate, but poorly active for substrates with Lewis basic centers. These initial results encouraged us to proceed on the optimization of the catalytic system in order to enhance its activity and its applicability range. In this work we present our progress using $[Ni(MeCN)_6][BF_4]_2/AlEt_2Cl/PPh_3$ optimized for styrene hydrovinylation and for other vinylarene substrates.

Results and Discussion

Styrene hydrovinylation optimization

In our previous report we worked on a $[Ni(MeCN)_6][BF_4]_2/AlEt_2Cl$ catalyst system for arylethylenes hydrovinylation. In these types of catalysts the alkylaluminum is believed to play an essential role by forming an initial Ni–C bond and acting as counterion for the catalytic $[Ni–H]^+$ formed.[11] After trying several alkylaluminum compounds as cocatalysts for the reaction, we concluded that $AlEt_2Cl$ could be used with the best results.

The catalytically active species is believed to be $[Ni–H]^+$,

Keywords: nickel; hydrovinylation; α-arylpropionic acids; codimerization; styrene.

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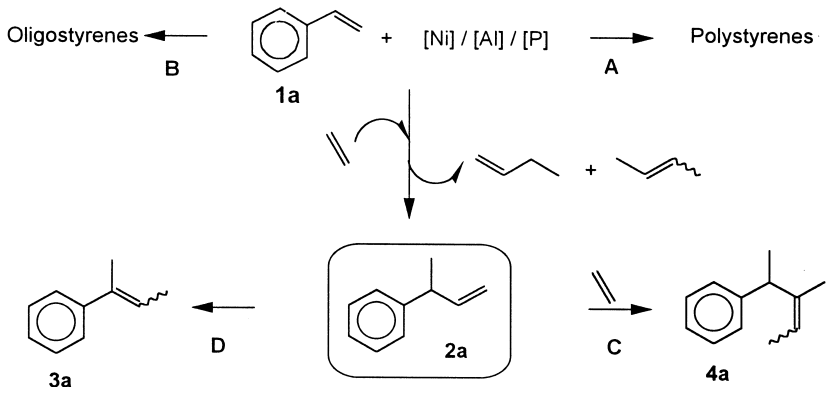


Scheme 1.

and several side reactions can be observed in the arylethylene hydrovinylation. Scheme 1 shows the observed byproducts formed in styrene hydrovinylation reactions.

The dimerization of ethylene to yield variable amounts of butenes catalyzed by the same system has already been report by us[12] and was observed for all the hydrovinylation runs. Aiming towards chemo- and regioselectivity in 3-phenyl-1-butene (**2a**), we have to consider (a) the noncatalyzed styrene thermal polymerization (path A, Scheme 1), (b) $[Ni–H]^+$ catalyzed styrene oligomerization (path B), (c) the recoordination of **2a** to the metallic center and subsequent hydrovinylation yielding methyl-phenylpentenes (**4a**) (path C) and (d) 2a isomerization to *E*- and *Z*-2-phenyl-2-butenes (**3a**) (path D).

Table 1 shows the optimization of the reaction conditions in order to achieve the best catalyst performances for the styrene (**1a**) hydrovinylation.

It can be seen that all the attempts with PPh_3 show total conversion of styrene and that the selectivity towards 3-phenyl-1-butene is easily improved by changing the reaction times and temperatures (entries 1–4). By lowering reaction temperature the styrene polymerization ceases and we could observe that all the other byproducts appeared in decreased amounts.

Table 1. Optimization of the reaction conditions towards **2a** (0.1 mmol $[Ni(MeCN)_6][BF_4]_2$; P=10 bar; 20 mL CH_2Cl_2, [Al]/[Ni]=5). Unless otherwise noted, total conversion of styrene was observed

Entry	Time (min)	Sty/Ni	T (°C)	L	[L]/[Ni]	Yield (%)[a]
1	240	400	50	PPh_3	2	2
2	60	400	50	PPh_3	2	4
3	60	400	25	PPh_3	2	20
4	30	400	25	PPh_3	2	61
5	60	400	25	PPh_3	4	96
6	50	400	25	PPh_3	4	98
7[b]	360	1500	25	PPh_3	4	93
8[c]	360	6600	25	PPh_3	4	92
9[d]	75	200	25	dppe[e]	1	96
10[f,g]	40	200	25	ppfa[h]	1	89

[a] GC yields.
[b] P=30 bar.
[c] P=35 bar, [Al]/[Ni]=8.
[d] [Al]/[Ni]=20.
[e] dppe=1,2-bis-(diphenylphosphino)ethane.
[f] [Al]/[Ni]=15.
[g] Conversion=92%.
[h] ppfa=*N*,*N*-dimethyl-1-[2-(diphenylphosphino)ferrocenyl]-ethylamine.

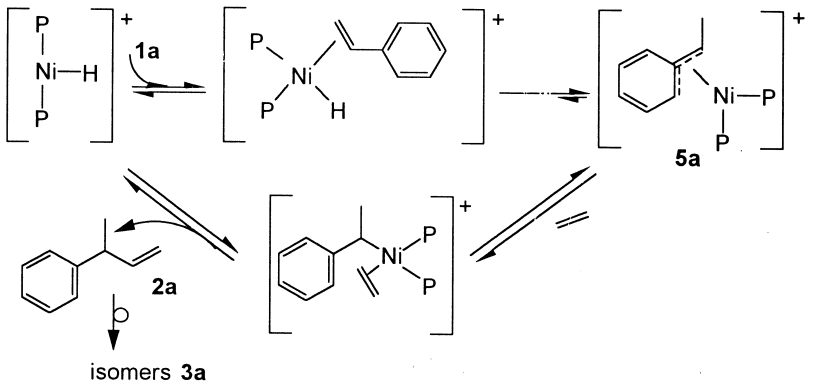
The regiochemistry of the $[Ni–H]^+$ catalyzed styrene hydrovinylation to 3-phenyl-1-butene has been explained in terms of the stability of a cationic η^3-benzylic intermediate (**5a**) (Scheme 2).[6,7a] In fact it was already reported that a $[Ni(\eta^3\text{-}CH_2Ph)(PPh_3)][PF_6]$ catalyzes the regioselective styrene oligomerization.[13] The increase of the [P]/[Ni] molar ratio (entries 5 and 6) could also increase the 3-phenyl-1-butene selectivity by stabilizing the intermediate **5a**. This apparently also had an effect on the isomerization of **2a** to **3a**.

The high activity and selectivity towards **2a** are maintained when larger amounts of styrene compared to the catalyst amount are employed. For entries 7 and 8 the reactor was pressurized to around 30 bar and additional ethylene was added periodically to maintain the pressure above 10 bar. Pressures higher than 10 bar were applied in order to assure that ethylene could always be available for hydrovinylation. This procedure can prevent 3-phenyl-1-butene isomerization, maintaining the selectivity for the reaction at high levels. For the entry 8, 22.7 mg (0.047 mmol) of the catalyst were used to produce 39 g (29.5 mmol) of 3-phenyl-1-butene (90% isolated yield).

Chelating diphosphines and aminophosphines have been shown to be inactive in hydrovinylation reaction.[6,7a] One of the claimed reasons for this behavior is that the active species is believed to contain only one molecule of ligand.[5a] In fact, in our conditions no reaction at all was observed when dppe and ppfa were used in conjunction with the complexes $[(\eta^3\text{-}C_4H_7)Ni(COD)][PF_6]$ and $[(\eta^3\text{-}C_4H_7)PdCl]_2/AgBF_4$.[8] In sharp contrast, the catalytic system described here is active and selective for the hydrovinylation of styrene. High activity and selectivities in 3-phenyl-1-butene were observed when $[Ni(MeCN)_6][BF_4]_2$ was used in conjunction with $AlEt_2Cl$ and a diphosphine (entry 9) or an aminophosphine (entry 10).

Hydrovinylation of styrene derivatives

Although our earlier studies using sytrene derivatives containing Lewis basic centers did not exhibit encouraging results,[10] our current studies present a more versatile system,

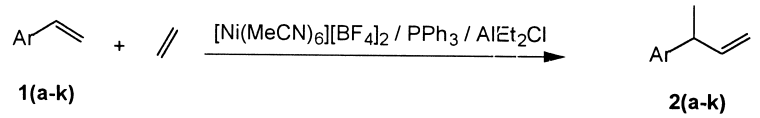


Scheme 2.

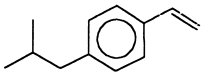
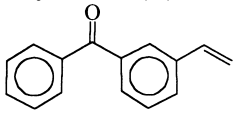
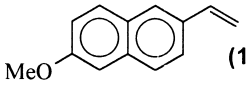
capable of performing active and selective styrene hydrovinylations. Examining the optimization of the hydrovinylation of styrene (Table 1) it is evident that it is possible to improve the reaction performance by working on the catalyst and by tailoring the system composition and reaction conditions. This feature led us to concentrate our efforts on a $[Ni(MeCN)_6][BF_4]_2/AlEt_2Cl$/phosphine catalyst capable of yielding 3-aryl-1-butenes in high yields regardless of the arylethylene employed as substrate.

The hydrovinylation of styrene derivatives substituted in the aromatic ring can be accomplished with similar results to those observed with styrene by changing the [Al]/[Ni] molar ratio (Table 2). In the case of the alkyl substituted styrene and vinylnaphthalene, only by increasing the [Al]/[Ni] molar ratio is it possible to achieve a good catalyst activity without losing selectivity. However, for the styrene derivatives with Lewis basic centers (entries 6–11 in Table 2) this alternative was not enough. These substrates did not undergo hydrovinylation reaction using the procedure described for the other substrates (see Experimental section). Hence, we decided to change the order of the addition of the reactants, since we believed this was occurring because the Lewis acid used as cocatalyst could be reacting with the substrate, precluding formation of the active species. The hydrovinylation reactions were performed with high yields and selectivities for this kind of substrate, by adding $AlEt_2Cl$ immediately after the introduction of the solution of the nickel complex and the phosphine into the reaction vessel under ethylene atmosphere. In terms of reactivity and selectivity, few differences were observed not only with substituted styrenes containing

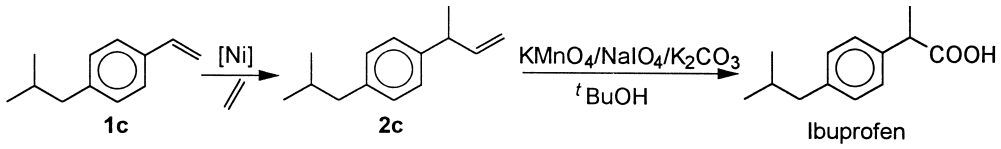
Table 2. Hydrovinylation of arylethylenes (reactions were carried out at room temperature in 20 mL CH_2Cl_2, 10 bar of ethylene, 0.025 mmol $[Ni(MeCN)_6][BF_4]_2$; and [P]/[Ni]=4)



1(a-k) 2(a-k)

Entry	Substrate	*T* (min)	[Al]/[Ni]	[subst.]/[Ni]	Conversion (%)[a]	Sel (%)[b]	Yield (%)
1	Styrene (**1a**)	60	5	400	100	96	96[c] (87)[d]
2	4-Methylstyrene (**1b**)	60	5	400	98	86	84
3	 (**1c**)	30	10	200	100	95	95(68)
4	2-Vinylnaphthalene (**1d**)	40	10	100	97	96	93(66)
5	Vinylferrocene (**1e**)	45	5	100	100	99	99(71)
6	 (**1f**)	60	38	100	100	>99	99(84)
7	4-Benzoylstyrene (**1g**)	60	38	100	100	88	88(74)
8	3-Chlorostyrene (**1h**)	60	7	400	95	98	93(75)
9	2-Chlorostyrene (**1i**)	60	6	300	93	95	88(59)
10	4-Methoxystyrene (**1j**)	60	10	350	100	95	95(76)
11	 (**1k**)	40	20	100	97	99	96(76)

[a] Determined by GC.
[b] Selectivity towards 3-aryl-1-butene=3-aryl-1-butene/converted arylethylene.
[c] GC yield.
[d] Isolated yields.



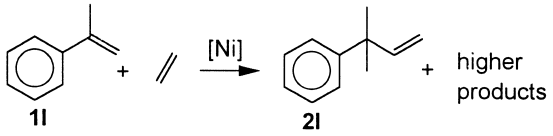
Scheme 3.

substituents in the *meta* and *para* (entries 6,7) but also in *meta* and *ortho* (entries 8,9). Vinylferrocene exhibits similar behavior to styrene and undergoes hydrovinylation in high yield and selectivity (entry 5).

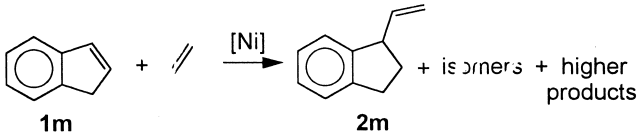
4-Isobutylstyrene, 3-vinylbenzophenone, and 2-methoxy-6-vinylnaphtalene, all potential precursors for anti-inflammatory agents gave excellent yields of the expected hydrovinylation products. We ran the oxidation of **1c** according to the procedure described by us for the Ketoprofen[14] using strong oxidants such as $KMnO_4$ and $NaIO_4$ (Scheme 3). This procedure affords Ibuprofen in 71% of yield.

Substitution at the α- or β-carbons of the styrene generally leads to poor conversions and yields.[15] We are pleased to find out that by using the catalytic system described here, α-methylstyrene (**1l**) was hydrovinylated in moderated yields (58–68%), which to the best of our knowledge is the best result described at this point. A considerable amount of ethylene is consumed in the formation of butenes. This greater butene formation has already been observed in other catalytic systems and can be associated with the steric effect of the methyl fragment. The coordination of the more hindered double bond at the Ni–H species is more difficult and consequently the ethylene dimerization to butenes prevails. We have observed metallic nickel at the end of these reactions indicating that the species formed with this olefin should be more unstable than those formed with styrene. The results are less reproducible probably due to this instability. For instance, using an Al/Ni ratio=15, α-methylstyrene was consumed in 78–100% with a selectivity in 3,3-methyl-phenyl-1-butene (**2l**) of 68–74%. Besides butenes, the only byproducts observed were formed from the reaction of α-methylstyrene (**1l**) with two molecules of ethylene (Scheme 4).

Poorer results were found in the indene (**1m**) hydrovinylation. The best results obtained were an indene (**1m**) conversion of 60% and a very good selectivity of 95% in



Scheme 4.



Scheme 5.

ethylene–indene codimers. However, only 60% of this fraction was 1-vinylindane. Further studies have shown that 1-vinylindane is the initial product and that the hydrovinylation catalytic system is also active in the isomerization of this olefin to internal isomers (Scheme 5). When higher conversions were obtained (83–100%), the selectivity in ethylene–indene codimers decreased (70–92%) to some extend but the content of **2m** was drastically reduced (2–30%).

Finally, in order to extend the scope of our work we tried the hydrovinylation of 2-vinylpyridine (**1n**). In spite of changing the order of the addition of the reactants or the [Al]/[Ni] molar ratio, we observed no codimerization products. Besides the total consumption of the olefin, only polymerization products were observed.

In conclusion, a wide variety of arylethylenes containing electron-donating or electron-withdrawing groups and Lewis basic groups, can be hydrovinylated at room temperature and under mild conditions by changing the relative ratios of the three-catalyst components and using a suitable protocol. Similar activities and selectivities were observed for *o*-, *m*- and *p*-substituted styrenes. Also, the hydrovinylation of olefins with substituents on the vinyl fragment, such as α-methylstyrene and indene, can be accomplished. In opposition to previous catalytic systems, chelating phosphines can be used in conjunction with $[Ni(MeCN)_6][BF_4]_2$ and $AlEt_2Cl$ affording good activities and selectivities. The catalytic activity observed in the presence of chelating phosphines opens a possibility to explore the widely available chiral chelating ligands in the asymmetric hydrovinylation reaction. This work is now in progress.

Experimental

General

Standard techniques for the manipulation of air-sensitive compounds were used. Catalytic reactions were carried out under ethylene pressure in a 100 ml- or 500 ml-stainless steel autoclave. NMR spectra were recorded on a Varian VXR-200 or Varian XL 300 spectrometer. Infrared spectra were recorded on a Bomem B-102 spectrometer. Mass spectra were recorded on a GC/MS Shimadzu QP-5050 (EI, 70 eV). Gas chromatographic analyses were carried out on a Varian 3400 CX or HP 5890 GC equipped with a capillary column L&M — 1 (Polydimethylsiloxane) and Simplicity-5 (Polydiphenylsiloxane), respectively, using hydrogen flame ionization detection. Peak areas were measured by using the internal integration with tetradecane as the standard and were corrected to accommodate different detector response factors.

Materials

Solvents and reagents were dried over suitable drying agents and distilled prior to use. Compounds **1a**, **1b**, **1h**, **1i**, **1l**, **1m**, and **1n** were purchased from Aldrich. $[Ni(MeCN)_6][BF_4]_2$[16], **1c**[17] were synthesized as described in the literature. (**1-d**,**f**,**g**,**j**,**k**)[18] were prepared by an adapted procedure of a Heck reaction and **1e** by a Wittig reaction.

General procedure for arylethylenes hydrovinylation

3-Phenyl-1-butene (2a). A solution of 27.3 mg of $[Ni(MeCN)_6][BF_4]_2$ (0.057 mmol) and 60.4 mg of PPh_3 (0.23 mmol) in 20 mL of dry CH_2Cl_2 was placed in a 100 mL stainless steel autoclave under argon. Then 2.65 g (25.44 mmol) of styrene, 0.43 g of tetradecane (internal standard) and 0.79 mL of $AlEt_2Cl$ 0.36 M solution in toluene were added to the system. The autoclave was closed and the resulting mixture was stirred at room temperature for 1 h under 10 bar of ethylene. After releasing the excess of ethylene, the autoclave was opened and 1 mL of methanol was added. The reaction mixture was distilled using a bulb to bulb technique (70°C, 2 mm Hg) to afford 2.9 g of a colorless oil (87%; >97% pure based upon GC). ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ=1.37 (d, J=6.9 Hz, 3H), 3.44–3.49 (m, 1H), 5.01–5.09 (m, 2H), 5.98–6.07 (m, 1H), 7.19–7.30 (m, 5H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 20°C): δ=20.5 (CH_3), 43.1 (CH), 113.0 ($CH_{2\ olef.}$), 126.1, 127.2, 128.4 (CH_{arom}), 143.2 ($CH_{olef.}$), 145.5 (C_q). IR(KCl/film) ν= 1638, 1602, 998, 915 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=132 (M^+, 21%), 117 (100), 105 (8), 91 (27), 77 (18), 65 (9), 51 (17), 39 (12). Analytical data: Calculated: C=90.85%, H=9.15%. Found: C=90.68%, H=9.23%.

The following compounds were prepared and isolated in a similar manner (all compounds were judged to be >97% pure based upon GC).

3-(4-Isobutylphenyl)-1-butene (2c). Colorless liquid. Kugelrohr distilled (90–100°C, 2 mm Hg), 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ=0.82 (d, J=6.6 Hz, 6H), 1.28 (d, J=6.9 Hz, 3H), 1.77 (septet, J=6.7 Hz, 1H), 2.37 (d, J=7.1 Hz, 2H), 3.38 (quintet, J=6.8 Hz, 1H), 4.91–5.00 (m, 2H), 5.87–5.99 (m, 1H), 7.02 (AB, J=8.2 Hz, $\Delta\nu$=12, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, 20°C): δ=20.7 (CH_3), 22.4 ($2CH_3$), 30.2 (CH), 42.8 (CH), 45.0 (CH_2), 112.8 ($CH_{2\ olef.}$), 126.9, 129.1 (CH_{arom}), 139.4 (C_q), 142.7 (C_q), 143.5 ($CH_{olef.}$). IR(KCl/film) ν=3082, 3052, 2957, 2868, 1637, 1512, 1465, 1368, 1017, 912, 844, 797 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=188 (M^+, 29%), 189 (M^+1, 5) 145 (100), 131 (93), 117 (40), 115 (27), 105 (15), 91 (28), 57 (47). Analytical data: Calculated: C=89.30%, H=10.70%. Found: C=89.55%, H=10.76%.

3-(β-Naphthyl)-1-butene (2d). Pale yellow liquid. The reaction mixture was filtered and the volatiles were removed under reduced pressure, 66% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ=1.36 (d, J=6.8 Hz, 3H), 3.54 (quintet, J=6.8 Hz, 1H), 4.96–5.15 (m, 2H), 5.91–6.08 (m, 1H), 7.28–7.72 (m, 7H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 20°C): δ=20.7 (CH_3), 43.2 (CH), 113.4 ($CH_{2\ olef.}$), 125.2, 125.3, 125.9, 126.2, 127.5, 127.6, 127.9 (CH_{arom}), 132.2, 133.7, 143.0 (C_q), 143.1 ($CH_{olef.}$). IR(KCl/film) ν=3054, 2966, 2872, 1632, 1600, 1507, 1453, 1271, 914, 817, 748 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=182 (M^+, 48), 167 (100), 166 (21), 165 (44), 152 (31), 153 (14), 82 (27). Analytical data: Calculated: C=92.26%, H=7.74%. Found: C=92.39%, H=7.84%.

3-Ferrocenyl-1-butene (2e). Orange oil. Flash chromatography with hexane/dichloromethane (90:10, v/v) as eluent, 71% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ=1.22 (d, J=7.0 Hz, 3H), 3.07 (quintet, J=7.1 Hz, 1H), 3.96–4.24 (m, 9H), 4.86–4.96 (m, 2H), 5.81–5.99 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$, 20°C): δ=21.0 (CH_3), 37.4 (CH), 66.7, 66.9, 67.4, 67.5, 68.6 (CH_{arom}), 93.8 (C_q), 112.9 ($CH_{2\ olef.}$), 143.8 ($CH_{olef.}$). IR(KCl/film) ν=3093, 2967, 1635, 1453, 1106, 1000, 914, 816 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=240 (M^+, 52), 238 (6), 225 (30), 223 (8), 121 (34), 57 (7), 56 (100). Analytical data: Calculated: C=70.03%, H=6.72%. Found: C=69.91%, H=6.81%.

3-Methyl-3-phenyl-1-butene (2l). Colorless liquid. Kugelrohr distilled (110–120°C, 2 mm Hg). ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ=1.49 (s, 6H), 5.11–5.17 (m, 2H), 6.12 (dd, J=11.0 and 16.8 Hz, 1H), 7.23–7.45 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$, 20°C): δ=28.5 ($2CH_3$), 47.8 (C_q), 110.9 ($CH_{2\ olef.}$), 126.1, 126.4, 128.4 (CH_{arom}), 148.3 ($CH_{olef.}$) 148.8 (C_q). IR(KCl/film) ν=3085, 3060, 2967, 1636, 1600, 1494, 1445, 1362, 912, 763, 699 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=146 (M^+, 29), 131 (100), 129 (14), 116 (16), 115 (16), 103 (7), 91 (55), 65(22), 51 (16). Analytical data: Calculated: C=90.35%, H=9.65%. Found: C=90.51%, H=9.77%.

3-(3-Benzoylphenyl)-1-butene (2f). A solution of 6.8 mg of $[Ni(MeCN)_6][BF_4]_2$ (0.0132 mmol) and 14.8 mg of PPh_3 (0.0564 mmol) in 15 mL of dry CH_2Cl_2 was placed in a 100 mL stainless steel autoclave under argon. Then the autoclave was purged with ethylene and 0.2 mL of $AlEt_2Cl$ 1.8 M solution in toluene was added to the system. The autoclave was closed and the mixture was stirred at room temperature for 10 min under ethylene atmosphere. After this time, a solution of 269 mg of **1f** (1.29 mmol) in 5 mL of dry CH_2Cl_2 was added and the resulting mixture was stirred at room temperature for 1 h at 10 bar of ethylene. After releasing the excess of ethylene, the autoclave was opened and 1 mL of methanol was added. The reaction mixture was Kugelrohr distilled (135°C, 2 mm Hg) to afford 239 mg of **2f** as colorless oil (80%). ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ=1.32 (d, J=7.2 Hz, 3H), 3.48 (quintet, J=6.6 Hz, 1H), 4.96–5.04 (m, 2H), 5.86–6.03 (m, 1H), 6.99–7.83 (m, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$, 20°C): δ=20.7 (CH_3), 43.0 (CH), 113.8 ($CH_{2\ olef.}$), 128.1, 128.2, 128.4, 128.8, 130.0, 131.4, 132.3 (CH_{arom}), 137.7 (C_q), 142.6 ($CH_{olef.}$), 145.9 (C_q), 196.8 (C=O). IR(KCl/film) ν=3082, 3076, 2965, 1733, 1660, 1598, 1578, 1448, 1282, 915, 715, 701 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=236 (M^+, 22), 159 (27), 131 (80), 105 (100), 91 (15), 77 (66), 51 (22). Analytical data: Calculated: C= 86.41%, H=6.82%. Found: C=86.37%, H=6.89%.

The following compounds were prepared and isolated in a similar manner.

3-(4-Benzoylphenyl)-1-butene (2g). Pale yellow liquid.

Kugelrohr distilled (150°C, 2 mm Hg), 74% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ=1.40 (d, J=7.0 Hz, 3H), 3.55 (quintet, J=6.8 Hz, 1H), 5.05–5.14 (m, 2H), 5.93–6.09 (m, 1H), 7.29–7.81 (m, 9H). ^{13}C NMR (75.4 MHz, $CDCl_3$, 20°C): δ=20.5 (CH_3), 43.2 (CH), 113.9 ($CH_{2\ olef.}$), 127.1, 128.0, 128.1, 128.4, 129.9, 130.0, 130.1, 130.4, 132.1 (CH_{arom}), 135.5 (C_q), 137.8 (C_q), 142.2 ($CH_{olef.}$), 150.5 (C_q), 196.3 (C=O). IR(KCl/film) ν=3082, 3058, 2968, 2872, 1659, 1605, 1447, 1440, 1316, 1279, 851, 702 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=237 (M^++1, 7%), 236 (M^+, 38), 159 (44), 131 (30), 115 (15), 105 (100), 77 (75), 51 (24). Analytical data: Calculated: C=86.41%, H=6.82%. Found: C=86.58%, H=7.00%.

3-(3-Chlorophenyl)-1-butene (2h). Colorless liquid. Kugelrohr distilled (65–75°C, 2 mm Hg), 75% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ=1.43 (d, J=7.1 Hz, 3H), 3.52 (quintet, J=7.0 Hz, 1H), 5.09–5.19 (m, 2H), 5.96–6.12 (m, 1H), 7.14–7.33 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, 20°C): δ=20.5 (CH_3), 42.8 (CH), 113.7 ($CH_{2\ olef.}$), 125.5, 126.2, 127.4, 129.6 (CH_{arom}), 134.1 (C_q), 142.3 ($CH_{olef.}$), 147.6 (C_q). IR(KCl/film) ν=3082, 2970, 2878, 1638, 1596, 1573, 1477, 1421, 1080, 917, 783 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=166 (M^+, 26%), 151 (25), 131 (100), 115 (51), 116 (44), 103 (12), 91 (23), 77 (16), 51 (21). Analytical data: Calculated: C=72.07%, H=6.65%. Found: C=72.30%, H=6.69%.

3-(2-Chlorophenyl)-1-butene (2i). Colorless liquid. Kugelrohr distilled (50–65°C, 2 mm Hg), 59% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ=1.26 (d, J=7.0 Hz, 3H), 3.93 (quintet, J=7.1 Hz, 1H), 4.95–5.05 (m, 2H), 5.83–6.00 (m, 1H), 6.97–7.28 (m, 4H). ^{13}C NMR (50.3 MHz, $CDCl_3$, 20°C): δ=19.3 (CH_3), 38.8 (CH), 113.9 ($CH_{2\ olef.}$), 126.9, 127.3, 128.1, 129.5 (CH_{arom}), 133.6 (C_q), 141.4 ($CH_{olef.}$), 142.8 (C_q). IR(KCl/film) ν=3082, 3064, 2969, 1638, 1590, 1572, 1440, 1410, 1032, 996, 916, 753 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=166 (M^+, 56%), 151 (60), 131 (81), 115 (75), 103 (100), 91 (25), 77 (36), 51 (56). Analytical data: Calculated: C=72.07%, H=6.65%. Found: C=71.89%, H=6.57%.

3-(4-Methoxyphenyl)-1-butene (2j). Colorless liquid. Kugelrohr distilled (75°C, 2 mmHg), 76% yield. ^{1}H NMR (200 MHz, $CDCl_3$, 20°C): δ=1.33 (d, J=7.0 Hz, 3H), 3.35–3.52 (m, 1H), 3.78 (s, 3H), 4.97–5.10 (m, 2H), 5.89–6.10 (m, 1H), 6.84 (d, J=8.8 Hz, 2H), 7.13 (d, J=8.8 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, 20°C): δ=20.8 (CH_3), 42.3 (CH), 55.2 (CH_3), 112.2 ($CH_{2\ olef.}$), 113.8, 128.1 (CH_{arom}), 137.6 (C_q), 143.6 ($CH_{olef.}$), 157.9 (C_q). IR(KCl/film) ν=3076, 3034, 2964, 1632, 1611, 1583, 1247, 1179, 1037, 913, 830 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=161 (M^+−1, 11%), 162 (M^+, 40), 147 (100), 131 (18), 115 (24), 103 (12), 91 (58), 77 (20), 51 (19). Analytical data: Calculated: C=81.44%, H=8.70%. Found: C=81.57%, H=8.65%.

3-(6-Methoxynaphthyl)-1-butene (2k). Pale yellow liquid. The reaction mixture was filtered and the volatiles were removed under reduced pressure, 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ=1.43 (d, J=6.8 Hz, 3H), 3.59 (quintet, J=6.8 Hz, 1H), 3.89 (s, 3H), 5.05–5.11 (m, 2H), 6.05–6.12 (m, 1H), 7.10–7.74 (m, 6H). ^{13}C (75.4 MHz, $CDCl_3$, 20°C): δ=20.7 (CH_3), 43.0 (CH), 55.2 (CH_3), 105.2(CH_{arom}), 113.2 ($CH_{2\ olef.}$), 118.6, 125.0, 126.7, 126.8, 129.1 (CH_{arom}), 133.2 (C_q), 140.6 (C_q), 143.3 ($CH_{olef.}$), 157.3 (C_q). IR(KCl/film) ν=3052, 2963, 2842, 1634, 1605, 1505, 1484, 1266, 1231, 1033, 852, 808 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=212 (M^+, 88), 197 (100), 182 (30), 165 (73), 153 (35), 141 (15), 115 (21), 76 (12), 63(14), 51(11). Analytical data: Calculated: C=84.87%, H=7.60%. Found: C=85.03%, H=7.72%.

α-(4-Isobutylphenyl) propionic acid (Ibuprofen).[14] To a solution of **2c** (71 mg, 0.38 mmol) in 10 mL of ^{t}BuOH and 20 mL of water, $KMnO_4$ (185 mg, 1.17 mmol), $NaIO_4$ (1.46 g, 6.86 mmol) and K_2CO_3 (366 mg, 2.64 mmol) were added. The pH of the solution was adjusted to 8 with 3 M NaOH aqueous solution and then the reaction mixture was stirred for 3 h at room temperature. After this time the pH of the mixture was adjusted to 1 with concentrated HCl and $NaHSO_3$ was added to reduce MnO_2. The mixture was washed with ether and the ethereal layer was extracted with 3 M NaOH aqueous solution. The aqueous layer was acidified with concentrated HCl and then extracted with ether. The organic layer was dried over $MgSO_4$, filtered and the volatiles were removed under reduced pressure, yielding Ibuprofen as a white powder (56 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ=0.81 (d, J=6.4 Hz, 6H), 1.45 (d, J=6.9 Hz, 3H), 1.76 (septet, J=6.9 Hz, 1H), 2.36 (d, J=7.2 Hz, 2H), 3.62 (q, J=6.9 Hz, 1H), 7.08 (AB, J=8.1 Hz, $\Delta\upsilon$=35, 4H). IR(KCl/Nujol mull) ν=3000–2500, 1719, 1508, 1462, 1420, 1231, 1184, 780 cm^{-1}. GC/MS (EI, 70 eV): m/z (%)=206 (M^+, 45%), 161 (100), 163 (90), 119 (56), 117 (56), 107 (58), 91 (93), 77 (17).

Determination of the structure of 2m

The ^{1}H NMR of a complex mixture of $C_{11}H_{12}$ and $C_{13}H_{16}$ isomers resulting of the hydrovinylation of indene (**1m**) showed a quartet at 3.75 ppm (J=8.0 Hz), revealing the presence of 1-vinylindane.[15a] The mixture of $C_{11}H_{12}$ and $C_{13}H_{16}$ isomers was placed in a stainless steel autoclave with Pd/C and charged with 10 atm of hydrogen. The reaction was followed by GC/MS. The hydrogenation of the $C_{11}H_{12}$ fraction gave only one product indicating that 1-vinylindane was the former species formed in the hydrovinylation reaction.

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