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Scope, limitations and mechanistic aspects in the selective homogeneous palladium-catalyzed reduction of alkenes under transfer hydrogen conditions

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Abstract—A new and efficient mild Pd/P(*t*-Bu)$_3$ catalyst for selective reduction of various alkenes under transfer hydrogen conditions has been developed leading to the corresponding saturated derivatives in chemical yields varying from 65 to 98%. Mechanistic rationale of this reaction has been also demonstrated.

1. Introduction

The growing importance of green chemistry and the concept of atom economy in organic synthesis have increased the search for transformations resulting in less waste.[1,2] An important advance in this field is the development of multifunctional reagents capable of promoting one or more distinct transformations sequentially in the same pot. Such reactions not only make better use of precious reagents but, as an added benefit, eliminates inefficient separation and purification after each step.[3,4] In this context, palladium reagents, well known to provide a myriad of different reactions, appeared particularly well suited.[5,4b] Hydrogenation of unsaturated compounds is one of the most important reactions in organic chemistry and hence several reagents have been used for this purpose.[6] Addition of hydrogen to an alkene to form the corresponding alkane is highly thermodynamically favored. However, the reaction rate is negligible under ordinary conditions in the absence of a catalyst. Selective, mild, and effective reducing agents in transition metal-catalyzed transfer hydrogenation have been of considerable interest. Among the various available processes, catalytic transfer hydrogenation (CTH) is emerging as a viable alternative to the commonly used reduction processes involving hazardous molecular hydrogen or a metal hydride donor.[7] Nevertheless, to date only few homogeneous catalytic palladium systems have been reported for selective reduction of alkenes under transfer hydrogen conditions.[8] It has long been recognized that changing substituents on phosphorus ligands can cause marked changes in the behavior of the free ligands and of their transition metal complexes. Thus, it has appeared in this area that P(*t*-Bu)$_3$ (tri-*tert*-butyl phosphine) may have a singular behavior since numerous reactions can be only performed using this ligand.[9] In this context, we recently found its successful use as ligand in a homogeneous palladium-catalyzed reduction of numerous alkenes under transfer hydrogen conditions with high selectivities and isolated yields.[10] In continuation of our work, we report herein the scope, limitations, and mechanistic aspects of such a reaction.

A systematic analysis of solvent and ligand nature as well as temperature and palladium source involved has been realized since this reaction seems to be highly experimental conditions dependent as we have already noticed. Thus, 4-allylanisole **1** was chosen as test substrate and the reaction was carried out using HCO_2H as the hydrogen source under various experimental conditions (Table 1).

Although isolated chemical yield of up to 95% has been obtained performing the reaction in THF (Table 1, entry 6), it clearly appears that the nature of the solvent used has an important influence on the outcome of the reaction. Thus, polar solvents such as dioxane and diethylether led to the formation of the expected hydrogenated product in low chemical yields (Table 1, entries 5 and 6, 15 and 25% yield, respectively), whereas no conversion occurred using dichloromethane or acetonitrile as solvents (Table 1, entries 8 and 9).

In a second way, the influence of the phosphorus ligand involved on the outcome of the reaction has been studied (Table 2). Thus, the choice of the nature of the ligand appears crucial since only P(*t*-Bu)$_3$ afforded compound **2**, whereas

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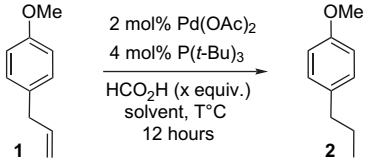
Table 1. Influence of the experimental conditions (solvent, temperature, HCOOH equivalents) on the Pd-catalyzed reduction of 4-allylanisole **1** under transfer hydrogen conditions



Entry[a]	Solvent	Temperature	HCOOH (equiv)	Isolated yield (%)
1	Toluene	Reflux to rt	5	18
2	CH_2Cl_2	Reflux to rt	5	<5
3	$CHCl_3$	Reflux to rt	5	<5
4	CH_3CN	Reflux to rt	5	<5
5	THF	Reflux to rt	1.2	93
6	*THF*	*Reflux to rt*	*5*	*95*
7	THF	rt	5	95
8	Dioxane	Reflux to rt	5	15
9	Et_2O	Reflux to rt	5	25
10	MeOH	Reflux to rt	5	<5
11	H_2O	Reflux to rt	5	<5
12	DMF	Reflux to rt	5	<5

[a] Reactions performed under argon on 1 mmol scale.

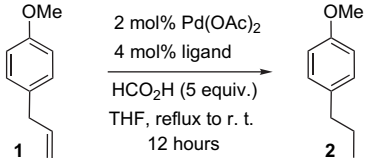
no conversion was observed using more classical P(*n*-Bu)$_3$, PPh_3, P(NMe$_2$)$_3$, and P(furyl)$_3$ ligands (Table 2, entries 2–5). Moreover, bidentate ligands such as dppe, BINAP, and DIOP do not afford the expected saturated derivative **2** (Table 2, entries 6–8).[11]

Finally the influence of the nature of the palladium source has been taken into consideration and it clearly appears that Pd(OAc)$_2$ and Pd$_2$(dba)$_3$ led to the best chemical yields, whereas $PdCl_2$ and $PdBr_2$ afforded compound **2** in moderate yields (Table 3).

Performing the reaction on various olefins under the best experimental conditions led in all cases to high chemical yields varying from 5 to 98% (Tables 4 and 5) depending on the nature of the considered substrate.

In the case of aromatic or non-functionalized substrates, the catalyst exhibits high activity (Table 4). Thus, *trans*-**3** and *cis*-**5** stilbenes are successfully converted into 1,2-diphenylethane **4** in 86 and 92% yield, respectively, suggesting a similar behavior of the two isomers toward the palladium catalyst. On the other hand, 2-vinyl naphthalene **6**

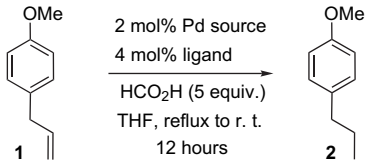
Table 2. Influence of the nature of the ligand on the Pd-catalyzed reduction of 4-allylanisole **1** under transfer hydrogen conditions



Entry[a]	Ligand	Isolated yield (%)
1	P(*t*-Bu)$_3$	95
2	P(*n*-Bu)$_3$	<5
3	PPh_3	<5
4	P(NMe$_2$)$_3$	<5
5	P(furyl)$_3$	<5
6[b]	dppe	<5
7[b]	BINAP	<5
8[b]	DIOP	<5

[a] Reactions performed under argon on 1 mmol scale.
[b] Reactions indifferently performed using 2 and 4 mol % of bidentate ligand.

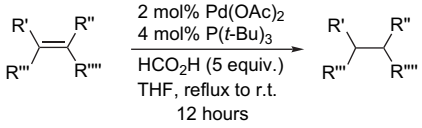
Table 3. Influence of the nature of the palladium source on the Pd-catalyzed reduction of 4-allylanisole **1** under transfer hydrogen conditions



Entry[a]	Palladium source	Isolated yield (%)
1	Pd(OAc)$_2$	95
2	$PdCl_2$	67
3	$PdBr_2$	56
4	Pd allyl	88
5[b]	Pd$_2$(dba)$_3$	92

[a] Reactions performed under argon on 1 mmol scale.
[b] Problems of reproducibility have been encountered in this case.

Table 4. Pd/P(*t*-Bu)$_3$-catalyzed reduction of various alkenes under transfer hydrogen conditions



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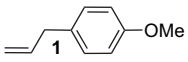
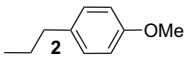
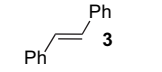
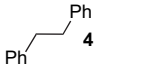
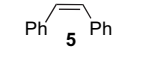
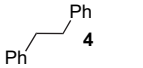
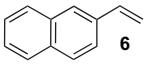
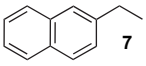
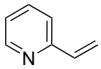
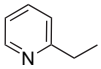
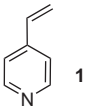
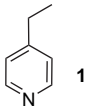
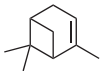
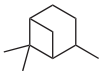
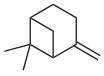
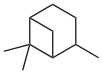
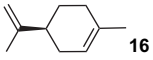
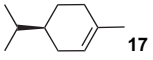
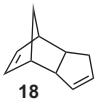
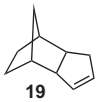
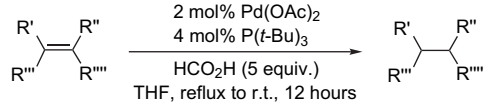
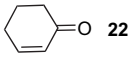
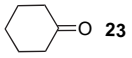
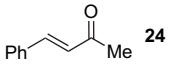
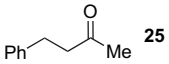
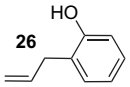
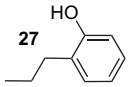
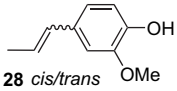
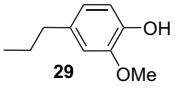
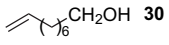
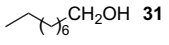
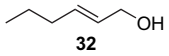
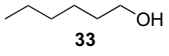
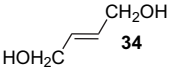
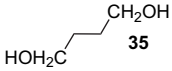
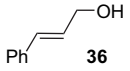
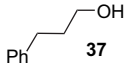
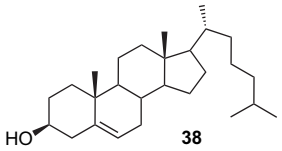
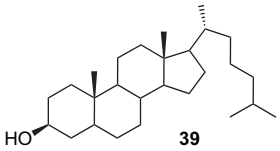
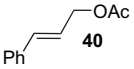
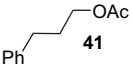
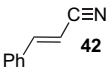
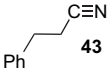
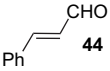
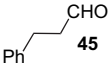
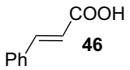
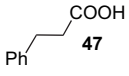
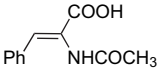
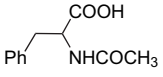
1			95
2			86
3			92
4			65
5			<5
6			83
7			<5
8			<5
9			<5
10			81
11			23

[a] Reactions performed under argon on 1 mmol scale.

Table 5. Pd/P(*t*-Bu)$_3$-catalyzed reduction of various functionalized alkenes under transfer hydrogen conditions



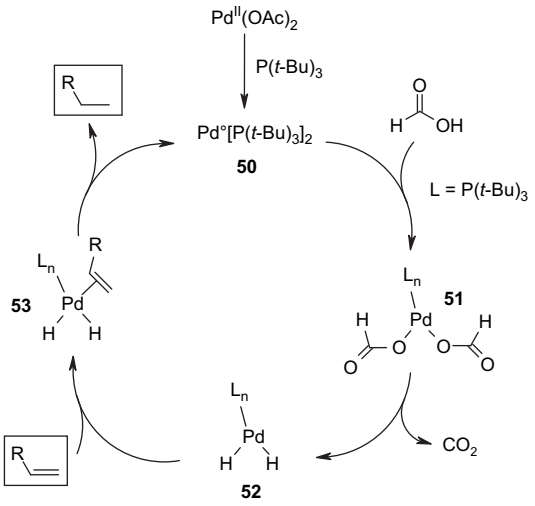
Entry[a]	Substrate	Product	Isolated yield (%)
1	 **22**	 **23**	78
2	 **24**	 **25**	95
3	 **26**	 **27**	98
4	 **28** *cis/trans*	 **29**	87
5	 **30**	 **31**	97
6	 **32**	 **33**	77
7	 **34**	 **35**	78
8	 **36**	 **37**	94
9	 **38**	 **39**	<5
10	 **40**	 **41**	93
11	 **42**	 **43**	86
12	 **44**	 **45**	79
13	 **46**	 **47**	79
14	 **48**	 **49**	<5

[a] Reactions performed under argon on 1 mmol scale.

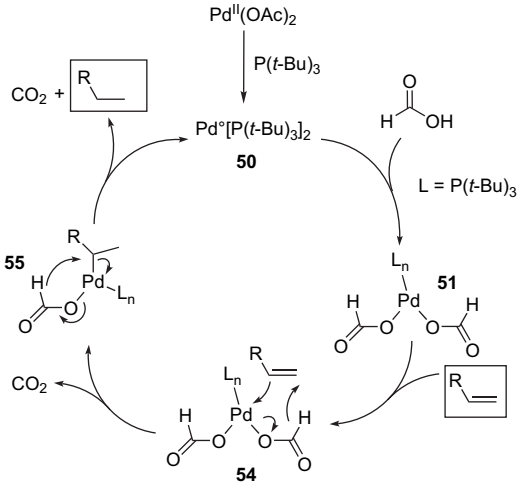
and 4-vinyl pyridine **8** led to the expected saturated compounds in excellent yields (Table 4, entries 4 and 6, 65 and 83% yield, respectively). Surprisingly, 2-vinyl pyridine **8** is not converted into its corresponding saturated derivative probably due to the presence of the pyridine group near the olefin moiety poisoning the palladium catalyst. Furthermore, no conversion occurs for disubstituted alkenes such as α- and β-pinene and limonene, whereas dicyclopentadiene **18** led to the formation of the monohydrogenated derivative **19** demonstrating the high selectivity of the catalyst since only one of the two double bonds has been reduced.

Moreover, this catalytic process is highly substrate tolerant since compounds possessing ketone, ether, phenol, alcohol, or nitrile functionalized groups are converted into the corresponding expected compound without significant loss of activity of the catalyst in moderate to excellent yields varying from 77 to 98% yield (Table 5, entries 1–15). Here again, it is noteworthy that disubstituted substrates such as cholesterol **38** and α-acetamidocinnamic acid **48** do not lead to the formation of the desired saturated product.

As already mentioned, transfer hydrogenation using formic acid as the hydrogen donor is a valuable alternative to traditional hydrogenation with hydrogen gas.[12] The development of heterogeneous catalysts for this reaction is of particular interest for industrial processes and numerous mechanisms have been postulated. In this context, Spencer and Yu have



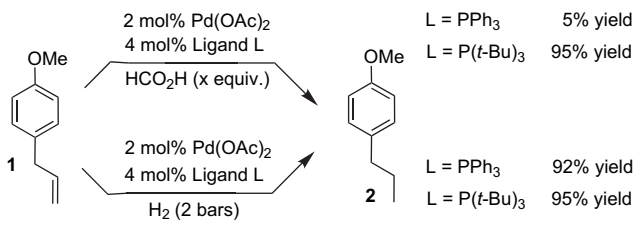
Scheme 1.



Scheme 3.

investigated the mechanism of transfer hydrogenation of methyl cinnamate with formic acid using heterogeneous Pd/C.[13] In this study, the authors propose that the delivery of formyl hydrogen is concerted with decarboxylation. Nevertheless, since no homogeneous palladium catalytic systems have been reported to date, we have envisioned three different mechanistic rationales rationalizing our experimental observations. First of all, according to mechanisms already proposed for heterogeneous transfer hydrogenation, a palladium diformate key intermediate **51** could be involved as illustrated in Scheme 1. This intermediate **51** could collapse to form the dihydrido metal species **52**, which could react with the unsaturated compound. In this context, the catalyst represented by the species **52** should be equivalent to that generated from hydrogen gas with the catalyst and should therefore have the same reactivity.

Performing the reaction using hydrogen gas as hydrogen donor (under 2 bar pressure) led to the formation of 4-propyl anisole **2** in 93% isolated yield suggesting in this case that such a mechanism cannot be totally excluded (Scheme 2). Thus in order to demonstrate the validity of such an hypothesis, the hydrogenation reaction was performed using PPh_3 ligand instead of P(*t*-Bu)$_3$ since no reaction occurred under our transfer hydrogen conditions in the presence of such a ligand. Nevertheless, in this case the hydrogenation of allylanisole **1** appears complete after 12 h and the expected hydrogenated product was obtained in 95% isolated yield. On the basis of these opposite results, the proposed mechanistic rationale illustrated in Scheme 1 and more precisely the formation of dihydrido metal species **52** cannot be



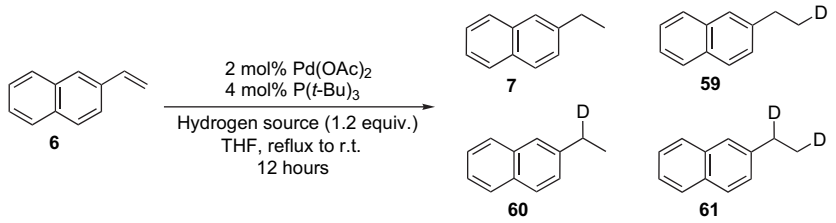
Scheme 2.

reasonably taken into consideration for our homogeneous palladium-catalyzed reduction of alkenes under transfer hydrogen conditions.

A second viable mechanism involving the same palladium diformate key intermediate **51** is depicted in Scheme 3. In this case, olefin coordination and hydropalladation followed by decarboxylation of the formate anion could lead to the formation of new formate palladium complex **55**. A subsequent reductive elimination will afford the expected saturated compound regenerating the active Pd(0) catalyst. If this proposed mechanism is operating then only one of the two hydrogen atoms from a formic acid molecule will always be transferred in one catalytic cycle. To investigate whether complex **54** is the active intermediate, several labeling experiments were performed (Table 6). Thus, the reduction of the double bond of 2-vinyl naphthalene was employed to trap the liberated hydrogen by the collapse of complex **54**. If differentially deuterium labeled formic acid (HCOOD or DCOOH) is used then the distribution of deuterium across the single bond can determine the origin of the hydrogen transferred to the double bond. When the reduction was carried out with HCOOD or DCOOH the results show that the products formed are indifferently monodeuterated ethyl naphthalenes **59** and **60**. In these two cases, no traces of the formation of non-labeled derivative **7** or bideuterated compound **61** have been noticed suggesting that the two hydrogen atoms came from the same molecule of formic acid. This fact is also in total agreement with the 95% isolated yield of the expected product **2** obtained using 1 equiv of formic acid with respect to the substrate in order to perform the transfer hydrogen reaction. Under these considerations, this mechanism cannot account for the results obtained experimentally.

The last mechanistic rationale envisioned is depicted in Scheme 4. Thus, the reaction may proceed via an oxidative addition of formic acid on Pd(0) with formation of key intermediate formato-(hydrido)palladium complex **56**. Activation of the olefin and hydride transfer followed by decarboxylation of the formate anion led to the formation of new hydrido palladium complex **58**. Subsequent migration of the hydride afforded the saturated expected compound and

Table 6. Palladium-catalyzed reduction of 2-vinyl naphthalene using deuterated formic acids as hydrogen source

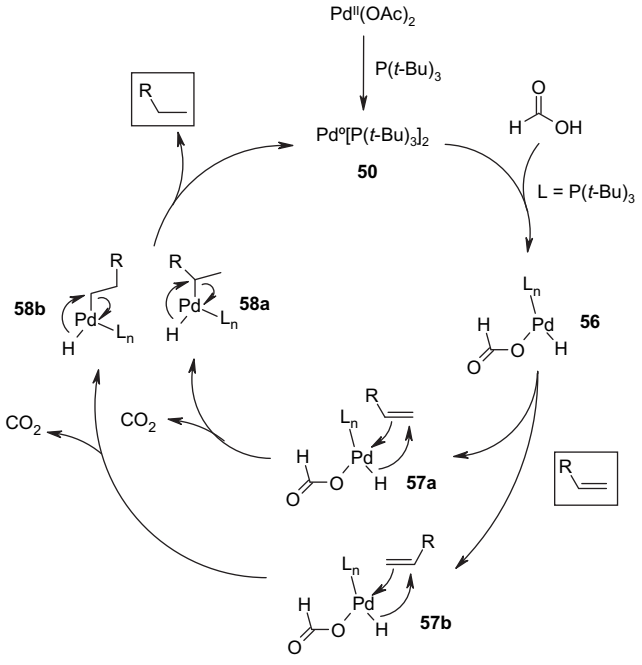


Hydrogen source	Product distribution (%)[a]			
	7	**59**	**60**	**61**
HCOOH	100	0	0	0
HCOOD	0	70	30	0
DCOOH	0	30	70	0
DCOOD	0	0	0	100

[a] ^{1}H NMR spectral data are available in Supplementary data.

regenerates the active Pd(0) catalyst. Moreover, an interesting distribution of deuterium across the single bond determining the origin of the hydrogen transferred to the double bond has been noticed (Table 6). Thus, when the reduction of vinyl naphthalene was carried out with HCOOD or DCOOH, 70:30 and 30:70 product distribution ratios (**59**:**60**) have been encountered, respectively (Fig. 1).[14] This observation suggests the formation of two transient palladium species **57a** and **57b** in a 70:30 distribution ratio, in favor of the transient palladium species **57a**, from palladium formate key intermediate **56** rationalizing the regioselectivity of the deuterium transfer. This latter mechanism is to date the most plausible and in total agreement with all the experimental observations.

In conclusion, a new and efficient mild Pd/P(*t*-Bu)$_3$ catalyst for selective reduction of various alkenes under transfer hydrogen conditions has been developed and applications of such a method in total organic synthesis will be reported in due course.



Scheme 4.

2. Experimental section

2.1. Materials and methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC300 spectrometer in $CDCl_3$ as solvent. The chemical shifts (parts per million) were determined relative to Me_4Si (^{1}H and ^{13}C). Toluene and tetrahydrofuran (THF) were purchased from SDS and distilled from sodium/benzophenone ketyl immediately prior to use. Ethylacetate and petroleum ether (35–60 °C) were purchased from SDS and used without any previous purification. Column chromatography was performed on SDS silica gel (70–230 mesh). High-resolution mass spectra were recorded on a API *III* Plus Sciex apparatus.

2.1.1. General procedure for the selective reduction of 4-allylanisole (1) under transfer hydrogen conditions (Table 4, entry 1). In a two necked round flask 5.4 mg of $Pd(OAc)_2$ (2.4×10^{-5} mol) in anhydrous freshly distilled THF (5 mL) was placed at 20 °C under argon. To this solution, 20 mg of P(*t*-Bu)$_3$ (10^{-4} mol) was successively added and the solution was heated to reflux for 10 min. To this mixture 148 mg of 4-allylanisole **1** (10^{-3} mol) and 230 mg of formic acid (5×10^{-3} mol) were added. The resulting solution was stirred for 15 min to reflux then cooled to 20 °C for 12 h. After filtration over Celite and evaporation of the solvents, the crude residue was purified by chromatography on a silica gel column using petroleum ether/ethylacetate (100:0→50:50) as eluent, affording the expected product **2** in 95% yield. Viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (t, J=9 Hz, 3H), 1.70 (m, 2H), 2.63 (m, 2H), 3.86 (s, 3H), 6.91–7.36 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.24, 25.28, 37.63, 55.62, 114.09, 123.85, 127.34, 129.76, 135.22, 158.14.

2.1.2. Synthesis of 1,2-diphenylethane (4) (Table 4, entries 2 and 3). White solid; 92% yield; ^{1}H NMR ($CDCl_3$,

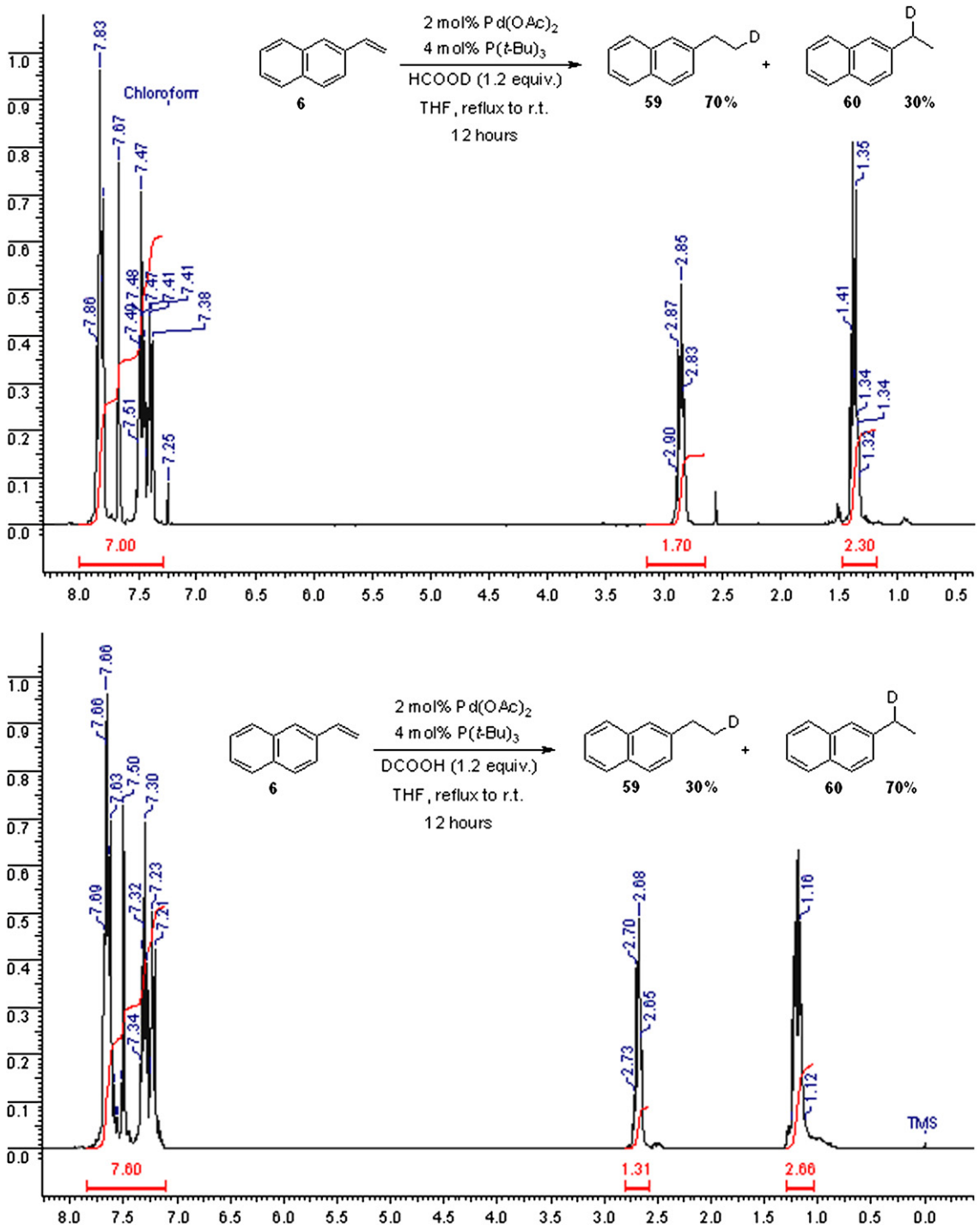


Figure 1.

300 MHz) δ 3.06 (s, 3H), 7.30–7.47 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.15, 126.13, 128.54, 128.66, 141.97.

2.1.3. Synthesis of 2-ethyl naphthalene (7) (Table 4, entry 4). Viscous oil; 65% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.45 (t, J=6 Hz, 3H), 2.92 (q, J=6 Hz, 2H), 7.45–7.93 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.50, 29.02, 124.98, 125.51, 127.05, 127.40, 127.57, 127.78, 128.10, 131.93, 133.70, 141.71.

2.1.4. Synthesis of 4-ethyl pyridine (11) (Table 4, entry 6). Viscous oil; 83% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (t, J=6 Hz, 3H), 2.73 (q, J=6 Hz, 2H), 7.28–7.32 (m, 2H), 8.53–8.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.48, 28.83, 124.69, 146.99, 165.55.

2.1.5. Synthesis of 3a,4,5,6,7,7a-hexahydro-1*H*-4,7-methano-indene (19) (Table 4, entry 19). Viscous oil; 81% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26–1.47 (m, 6H), 2.14–2.29 (m, 4H), 2.54 (m, 1H), 3.01 (m, 1H), 5.56 (m, 1H),

5.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.39, 25.03, 32.64, 39.95, 41.37, 41.55, 42.84, 53.33, 130.76, 133.31.

2.1.6. Synthesis of cyclohexanone (23) (Table 5, entry 1). Oil; 78% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.51–1.71 (m, 6H), 2.14 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.55, 26.60, 41.49, 211.25.

2.1.7. Synthesis of 4-phenyl-2-butanone (25) (Table 5, entry 2). Viscous oil; 95% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.15 (s, 3H), 2.76–2.95 (m, 4H), 7.20–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.14, 30.45, 45.54, 126.53, 128.72, 128.91, 141.43, 208.33.

2.1.8. Synthesis of 2-propyl phenol (27) (Table 5, entry 3). Viscous oil; 98% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (t, J=9 Hz, 3H), 1.70–1.82 (m, 2H), 2.71 (m, 2H), 5.73 (s, 1H), 6.84–7.24 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.47, 23.42, 32.48, 115.78, 121.14, 127.46, 129.19, 130.75, 154.03.

2.1.9. Synthesis of 2-methoxy-4-propyl phenol (29) (Table 5, entry 5). Viscous oil; 87% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.99 (m, 3H), 1.84 (m, 2H), 2.57 (m, 2H), 3.89 (s, 3H), 5.67 (s, 1H), 6.70–6.91 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.87, 24.95, 37.85, 55.91, 111.19, 114.27, 121.07, 134.77, 143.66, 146.45.

2.1.10. Synthesis of 1-nonanol (31) (Table 5, entry 6). Viscous oil; 97% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (m, 3H), 1.18–1.30 (m, 12H), 1.52–1.58 (m, 2H), 2.40 (s, 1H), 3.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.13, 22.73, 25.84, 29.39, 29.54, 29.70, 31.97, 32.70, 62.89.

2.1.11. Synthesis of 1-hexanol (33) (Table 5, entry 7). Viscous oil; 77% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (t, J=9 Hz, 3H), 1.23–1.50 (m, 8H), 3.51 (m, 2H), 3.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.09, 20.77, 23.62, 29.83, 30.73, 60.67.

2.1.12. Synthesis of 1,4-butanediol (35) (Table 5, entry 8). Viscous oil; 78% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (m, 4H), 3.62 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.19, 62.87.

2.1.13. Synthesis of 3-phenyl-propan-1-ol (37) (Table 5, entry 9). Viscous oil; 94% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.96 (m, 2H), 2.76 (m, 2H), 3.71 (m, 2H), 4.25 (s, 1H), 7.24–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.47, 34.48, 62.51, 126.30, 128.84, 142.26.

2.1.14. Synthesis of 3-phenyl-propan-1-acetate (41) (Table 5, entry 11). Viscous oil; 93% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00 (m, 2H), 2.08 (s, 3H), 2.73 (t, J=6 Hz, 2H), 4.13 (t, J=6 Hz, 2H), 7.21–7.54 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.79, 30.04, 32.04, 63.68, 125.87, 128.25, 141.06, 170.98.

2.1.15. Synthesis of 3-phenyl propionitrile (43) (Table 5, entry 12). Viscous oil; 86% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.60 (m, 2H), 2.94 (m, 2H), 7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.67, 31.90, 118.66, 127.61, 127.83, 129.54, 138.59.

2.1.16. Synthesis of 3-phenyl propionic acid (47) (Table 5, entry 14). Viscous oil; 79% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.72–3.05 (m, 4H), 7.26–7.40 (m, 5H), 11.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.01, 36.11, 126.83, 128.72, 129.02, 140.61, 179.93.

Supplementary data

^{1}H and ^{13}C NMR spectral data as well as MS spectroscopic measurements of the synthesized products are provided. Ordering information is given on any current masterhead page. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.01.053.

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14. Such an observation has been noticed by Spencer and Yu (Ref. 13) demonstrating that DCOOH produced a 70:30 mixture of deuteration at the benzylic versus C-2 position of methyl cinnamate using Pd/C heterogeneous catalyst under transfer hydrogen conditions.