Dalton Transactions

PAPER



Cite this: Dalton Trans., 2016, 45, 6124

Received 2nd October 2015, Accepted 2nd November 2015 DOI: 10.1039/c5dt03857j

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Introduction

Microwave-assisted FLP-catalyzed hydrogenations

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FLP-catalyzed hydrogenations of 15 substrates were compared using microwave irradiation and conventional heating. The direct comparison revealed that a rate acceleration of up to 2.5 was achieved in the presence of microwaves. This heating method is particularly promising for the hydrogenation of nitrogencontaining heterocycles. Acridine, quinines and especially 1-methyl indole were reduced very efficiently under mild conditions and only 4 bar hydrogen pressure in high yields.

 $B(C_6F_5)_3$

Lewis acids

Lewis bases

The reduction of organic molecules by frustrated Lewis pairs (FLP) using molecular hydrogen (H_2) has emerged to be a powerful tool for organic synthesis.¹ Electron-deficient as well as electron-rich compounds have been successfully hydrogenated² and even asymmetric reductions of prochiral substrates were achieved.3 Usually such reactions are conducted in closed reaction systems e.g. thick-walled vials, pressure tubes including NMR-tubes or steel bomb autoclaves. The appropriate reactor must be selected with regard to the required H₂pressure. The closed reaction systems are typically heated in oil baths or with heating jackets above the boiling point of the solvent.4 The same specifications hold true for microwavereactors including the advantage of the fast equilibration of the temperature and inverted temperature gradients.⁵ Microwave-assisted transition-metal catalyzed hydrogenations and transfer hydrogenations were reported⁶ rendering this method attractive for FLP-catalyzed hydrogenations. Interestingly, the application of microwave heating in FLP-catalyzed hydrogenations has not been reported yet.

Herein we report the first microwave-assisted FLP-catalyzed hydrogenation of imines, heterocycles, enamines, silyl enol ethers, nitroolefins, malonates and olefins. This study focuses on the comparison of hydrogenations conducted under conventional and microwave heating. Therefore reported catalyst systems (Lewis acids 1–3 and Lewis bases 4–8, Chart 1) and known substrates susceptible to FLP-catalyzed hydrogenation were investigated.

Results and discussion

We initiated our studies with the well-established FLP-catalyzed hydrogenation of *N*-benzylidene-*tert* butyl amine^{1c,7} (9)

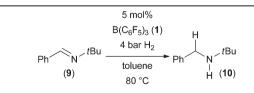
4 P(-) P(-

Chart 1 Lewis acids and Lewis bases for FLP-mediated hydrogen activation.

using conventional and microwave heating. A solution of imine **9** in toluene (0.2 M) and 5 mol% $B(C_6F_5)_3$ was prepared and split into two identical thick walled glass vessels. The vessels were sealed and pressurized with 4 bar of hydrogen. One sample was immersed into a preheated oil bath and the second sample was introduced into a CEM microwave reactor with a power setting to 150 W. Both reactions were heated to 80 °C for the indicated time (see Table 1).

 Table 1
 FLP-catalyzed
 hydrogenation
 of
 N-benzylidene-tertbutyl

 amine (9)
 using
 conventional (oil bath) and microwave heating in
 toluene (0.2 M)



Time [min]	Oil bath	Microwave (150 W)		
Time [min]	Yield [%]			
10	22	60		
15	42	82		
20	47	99		

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X = F(2), H(3)

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The hydrogenation product **10** was obtained with both heating methods however in very different yields. The reaction using microwave irradiation gave the product in 60% yield after 10 minutes while using conventional heating furnished only 22% yield. The microwave-assisted reaction went to full conversion with prolongation of the reaction time to 20 minutes while the oil bath heated reaction provided **10** in 47% yield. We attribute this significant rate increase to more efficient heating of the reaction by microwave irradiation.

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Encouraged by these results we investigated other substrates bearing polarized double bonds in the microwave-assisted reaction. We selected substrates, which are susceptible to FLPcatalyzed hydrogenation under conventional heating and compared them with yields obtained from microwave experiments.

The standard conditions for the hydrogenations using microwave-assisted and conventional heating were benzene as solvent (0.2 M), 4 bar hydrogen and 150 W power-level in CEM Discover microwave reactor with external IR temperature control or a preheated oil-bath respectively.¹² For best comparability thermal as well as microwave-assisted hydrogenations were conducted under identical conditions using stock-solutions, identical glassware, temperature, hydrogen pressure and reaction time. The reactions were stopped after 10 to 120 minutes and the yields were determined by ¹H NMR with hexamethylbenzene as internal standard. The results are summarized in Table 2. Generally, all substrates underwent FLPcatalyzed hydrogenation under microwave conditions most of them with pronounced rate acceleration. In accord with our observations for imine 9 we found two-fold rate increase for imines 11a and 11b (entries 1 and 2). The imine 11c underwent hydrogenation in comparable yields and diastereoselectivity irrespective of the heating method (entry 3). Particularly, the hydrogenation of nitrogen-containing heterocycles benefits from microwave-assisted heating (entries 4-7). The hydrogenation of acridin (11d), 8-methyl-quinolin (11e) and 2-methyl-quinoline (11f) proceeded in significantly higher yields (72-99%) compared to the reactions with conventional heating (7-68%). Notably, indol 11g was reduced in 57% yield in 40 minutes at 140 °C with only 4 bar of hydrogen pressure under microwave conditions whereas the hydrogenation was not achieved using conventional heating (entry 7). Although yields for the reaction using conventional heating were not reported^{2e} the decrease of the required pressure by almost 100 bar renders the application of microwave-assisted FLP-hydrogenation of indoles as very promising. We also investigated the core hydrogenation of diphenylamine with 20 mol% catalyst loading (11h).^{4b} However, even under forcing conditions only traces of the product could be observed irrespective of the heating techniques (entry 8). The electron-rich double bond in enamines^{7b} and silvl enol ethers^{3c,9,13} were reduced in good to excellent yields in only 10 to 40 minutes (entries 9-11). Again the microwave-assisted reactions provided the products in shorter reaction times compared to reactions using conventional heating. Densely functionalised malonates^{10,14} were hydrogenated in quantitative yield in 2 h at 80 °C (entry 12) compared to 12 h at room temperature. However, direct

$$Ar_{3}B + PAr'_{3} \underset{-H_{2}}{\overset{+H_{2}}{\longleftarrow}} [Ar_{3}B - H][H - PAr'_{3}]$$
(1)

According to an almost ergoneutral reaction the temperature increase shifts the equilibrium to the left side resulting in reduced concentrations of the H₂-activation products.^{7*c*,10,11,15} Consequently, substrates *e.g.* nitroolefins or olefins (entries 13 and 14), which require the application of highly reversible FLP-catalysts are less susceptible to microwave-assisted hydrogenations and conventional heating provides higher yields. The reduction of nitroolefin **11m** was achieved in 60% at 50 °C, but only 32% yield was obtained if the reaction was conducted at 80 °C (entry 13). Similar reactivity was observed for the hydrogenation of the olefin **11n** (entry 14). Nevertheless, microwave-assisted FLP-catalyzed hydrogenations are highly valuable for reactions, which require heating leading to a significant rate increase.

Conclusions

In summary we have shown that microwave-assisted heating significantly accelerates FLP-catalyzed hydrogenations rendering this methodology as useful tool in organic synthesis. The yields for the hydrogenation of fifteen common substrates under microwave irradiation and conventional heating were directly compared. Rate increase of 2–2.5 were observed for imines **9**, **11a** and **11b** using only 4 bar of hydrogen pressure. We attribute the reduced reaction times to more efficient heating of the reaction mixture. The hydrogenation of nitrogen-containing heterocycles *e.g.* acridine (**11d**), quinolines (**11e–f**) and 1-methyl indole (**11g**) proceeds in high yields under mild reaction conditions. Astonishingly, the indole derivative **11g** was reduced in 57% yield under only 4 bar hydrogen pressure while the reduction was absent using conventional heating.

Experimental

General information

All preparations were carried out in oven-dried glassware under an atmosphere of inert gas (Argon 5.0, Air Liquide) employing both Schlenk line techniques and a Glovebox Systems inert atmosphere glovebox. Microwave assisted reactions were carried out in a CEM Discover microwave system (model 908010) with external IR temperature control in 10 ml reaction vessels equipped with Teflon/rubber crimp caps. $[D_6]$ -deuterated benzene and toluene were degassed by 3

Table 2	Microwave-assisted FLP-catalyzed hydrogenations ^a
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$ m^{-1} h^{-1} h^{-1}$	Entry	Substrate		Catalyst	mol% cat.	Pressure H ₂ [bar]	Temp. [°C]	Time [min.]	Yield [%]	Ref
$\mathbf{m}^{-1} \mathbf{b}^{-1} \mathbf{m}_{110}^{-1} = \begin{bmatrix} \text{Cow, heating} & 1 & 5 & 4 & 80 & 20 & 60 & 99 & 72 & 60 & 60 & 99 & 72 & 10$	1	Ph	MW^b	1	5	4	80	20	12	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Ph N Ph 11a	Conv. heating ^c	1	5	4				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		114			5	5	120	60	99	7 <i>a</i>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	Me	MW	1	10	4	110	40	99	
$ = \sum_{n'} \sum_{m' \to m'} \sum_{n'} \sum_{n'' \to m'} \sum_{n'' \to m'} \sum_{n'' \to m''} \sum_{n'' \to m''' \to m'''} \sum_{n'' \to m''' \to m'' \to m''' \to$		Ph N ^{Ph} 11h	Conv. heating	1	10	4	110		45	
$m \rightarrow - m_{11c} \qquad \text{NW} \qquad 1 \qquad 5 \qquad 4 \qquad 80 \qquad 20 \qquad 20 \qquad 23 \qquad 27 (32.46) \\ 280 (48 h) \qquad 72 (35.46) \qquad 8 \\ \hline \qquad \qquad$	115	110			5	10	120	1320 (22 h)	68	3 <i>e</i>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	Me Me		1	5	4	80			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Ph N Ph 11c	Conv. heating	1	5					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					5	5	80	2880 (48 h)	72 (36 de)	8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					5	4	80	10	99	
$\int_{M_{m}}^{N_{m}} \int_{110}^{N_{m}} \int_{100}^{N$			conv. heating	1	5					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		11d			5	4	25	120	80	4 <i>c</i>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	5		MW	1	10	4	80	40	99	
$ \int_{M_{m}}^{M_{m}} \frac{1}{11e} $ $ \int_{M_{m}}^{M_{m}} \frac{1}{1e} = 10 4 80 360 (6 h) 88 4c 1c 1c 1c 1c 1c 1c 1c$								40		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		j N Me	0							4c
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		^{Me} 11e								
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	5		MW	1	5	4	80	40	75	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					5					
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	^{Me} 11f	✓ ^N ^{Me} 11f	0							4 <i>c</i>
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	7	Ме	N 41 X 7	1	-	4	140	40		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Ń	MW Conv. heating		5 5					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		11g	Conv. neuting	1						2e
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0								
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	3	NHPh	MW	1	20	4	140	120	4	
$100 4 \qquad 110 \qquad 5700 \ (96 \ h) \qquad 653 \qquad 42$ $p_{h} \stackrel{M_{e}}{\leftarrow} \stackrel{\Lambda_{e}}{\rightarrow} \stackrel{\Lambda_{e}}{=} 11 \qquad MW \qquad 1 \qquad 5 \qquad 4 \qquad 140 \qquad 40 \qquad 66 \qquad 66 \qquad 66 \qquad 66 \qquad 66 \qquad 66 \qquad $		11h	Conv. heating	1		4	140	120	0	
$\Pr \left(\begin{array}{c} Pn \\ Pn \\ Pn \\ fn \\ Pn \\ fn \\ $		• 1111			100	4	110	5760 (96 h)	65	4b
$P_{P} \longrightarrow N \longrightarrow_{11i} Conv. heating 1 5 4 140 40 43$ $P_{Ph} \longrightarrow_{Ph} \int_{Ph} \frac{11i}{11i} Conv. heating 1/4 10 4 80 20 73 10 99 20 4 80 10 99 20 76 10 99 10 90 10 99 10 99 10 90 10 99 10 99 10 90 10 99 10 99 10 90 10 99 10 90 10 99 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 99 10 90 10 99 10 99 10 90 10 99 10 90 10 99 10 99 10 90 10 99 10 99 10 90 10 99 10 99 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 90 10 99 10 90 1$)	Me	MW	1	5	4	140	40	66	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		Ph N 11i	Conv. heating	1	5	4	140	40	43	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$										
$1 \qquad Ph \qquad 11j \qquad Conv. heating \qquad 1/4 \qquad 10 \qquad 4 \qquad 80 \qquad 20 \qquad 76 \\ 1/5 \qquad 20 \qquad 5 \qquad 50 \qquad 1440 (24 h) \qquad 78 \qquad 9$ $1 \qquad \qquad 1/4 \qquad 10 \qquad 4 \qquad 80 \qquad 30 \qquad 55 \\ 11k \qquad MW \qquad 1/4 \qquad 10 \qquad 4 \qquad 80 \qquad 30 \qquad 55 \\ 11k \qquad MW \qquad 1/4 \qquad 10 \qquad 4 \qquad 80 \qquad 30 \qquad 55 \\ 11k \qquad 1/5 \qquad 20 \qquad 5 \qquad 50 \qquad 1440 (24 h) \qquad 74 \qquad 9$ $2 \qquad Ph \qquad -11i \qquad Conv. heating \qquad 3/7 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 99 \\ Ph \qquad -11i \qquad Conv. heating \qquad 3/7 \qquad 20 \qquad 4 \qquad 80 \qquad 40 \qquad 45 \\ 20 \qquad 4 \qquad 80 \qquad 40 \qquad 45 \\ 20 \qquad 4 \qquad 80 \qquad 40 \qquad 42 \\ 20 \qquad 4 \qquad 80 \qquad 40 \qquad 42 \\ 25 \qquad 720 (12 h) \qquad >95 \qquad 10 \\ 3 \qquad Ph \qquad N^{O_2} 11m \qquad MW \qquad 2/6 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 23 \\ Ph \qquad Conv. heating \qquad 2/6 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 17 \\ Conv. heating \qquad 2/6 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 17 \\ Conv. heating \qquad 2/6 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 17 \\ Conv. heating \qquad 2/6 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 17 \\ Conv. heating \qquad 2/6 \qquad 20 \qquad 4 \qquad 50 \qquad 120 \qquad 23 \\ 4 \qquad Ph \qquad 11n \qquad MW \qquad 1/8 \qquad 20 \qquad 4 \qquad 80 \qquad 60 \qquad 16 \\ 110 \qquad 60 \qquad 8 \\ Conv. heating \qquad 1/8 \qquad 20 \qquad 4 \qquad 80 \qquad 60 \qquad 16 \\ 110 \qquad 60 \qquad 8 \\ 110 \qquad 10 \qquad 10 \\ 110 \qquad 10 \qquad 10 \\ 110 \qquad 10 \qquad $	10		MW	1/4		4				
$1 \longrightarrow 1/5 \qquad 20 \qquad 4 \qquad 80 \qquad 20 \qquad 76 \qquad 9$ $1 \longrightarrow 1/5 \qquad 20 \qquad 5 \qquad 50 \qquad 1440 (24 \text{ h}) \qquad 78 \qquad 9$ $1 \longrightarrow 1/5 \qquad 20 \qquad 5 \qquad 50 \qquad 1440 (24 \text{ h}) \qquad 78 \qquad 9$ $1 \longrightarrow 1/5 \qquad 20 \qquad 5 \qquad 50 \qquad 1440 (24 \text{ h}) \qquad 74 \qquad 9$ $2 \longrightarrow 1/5 \qquad 20 \qquad 5 \qquad 50 \qquad 1440 (24 \text{ h}) \qquad 74 \qquad 9$ $2 \longrightarrow 1/5 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 99 \qquad 99$ $2 \longrightarrow 1/5 \qquad 20 \qquad 4 \qquad 80 \qquad 40 \qquad 45 \qquad 99$ $2 \longrightarrow 1/5 \qquad 20 \qquad 4 \qquad 80 \qquad 40 \qquad 45 \qquad 99 \qquad 99 \qquad 99 \qquad 99 \qquad 99 \qquad 99 \qquad 99$	Ph、 🔨	⁻ " ^{Ph} 11i								
$1 \qquad \qquad$,	Conv. heating							0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				1/5	20	5	50	1440 (24 h)	/8	9
11k 1/5 20 5 50 1440 (24 h) 74 9 $2 Ph + f + f + f + f + f + f + f + f + f +$	11	OSiPh ₂ Me	MW					30		
$2 \xrightarrow{\text{EtO}}_{Ph} \stackrel{\circ}{\leftarrow} \stackrel{\circ}{\int}_{OE'} \frac{MW}{1/8} \frac{3/7}{20} \stackrel{20}{\leftarrow} \frac{4}{4} \qquad \begin{array}{c} 80 & 120 & 99 \\ 80 & 40 & 45 \\ 20 & 4 & 80 & 40 & 42 \\ 80 & 40 & 42 \\ 25 & 720 (12 \text{ h}) & >95 & 10 \end{array}$ $3 \xrightarrow{Ph} \stackrel{\sim}{\leftarrow} \stackrel{NO_2}{11m} \frac{MW}{2/6} \stackrel{2/6}{20} \stackrel{20}{} \stackrel{4}{} \stackrel{80}{} \frac{120}{120} \stackrel{23}{} \stackrel{23}{} \stackrel{20}{} \stackrel{4}{} \stackrel{80}{} \stackrel{120}{} \stackrel{23}{} \stackrel{10}{} \stackrel{11}{} \stackrel{11}{} \stackrel{11}{} \stackrel{11}{} \stackrel{11}{} \stackrel{10}{} \stackrel{11}{} \stackrel{11}{$			Conv. heating							
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		11K		1/5	20	5	50	1440 (24 h)	74	9
Ph + for the term of ter	12	EtO	MW	3/7	20	4	80	120	99	
$4 Ph = 11n MW 1/8 20 4 80 40 42 \\ 20 4 25 720 (12 h) >95 10 \\ MW 1/8 20 4 80 120 23 \\ 20 4 80 120 17 \\ 20 4 80 120 17 \\ 20 5 40 1440 (24 h) >95 10 \\ 1440 (24 h) >95 10 \\ 20 4 80 60 16 \\ 20 4 80 60 16 \\ 20 4 80 60 57 8 \\ 110 60 8 \\ 20 4 80 60 57 8 \\ 110 60 8 \\ 110 10 10 10 10 10 10 1$		PhO								
$3 Ph \xrightarrow{NO_2} 11m \qquad MW \qquad 2/6 \qquad 20 \qquad 4 \qquad 50 \qquad 120 \qquad 23 \\ Conv. heating 2/6 \qquad 20 \qquad 4 \qquad 80 \qquad 120 \qquad 17 \\ 20 \qquad 4 \qquad 50 \qquad 120 \qquad 59 \\ 20 \qquad 5 \qquad 40 \qquad 1440 (24 h) >95 \qquad 10 \\ 4 Ph \underset{Ph}{\overset{Ph}{\longrightarrow}} 11n \qquad MW \qquad 1/8 \qquad 20 \qquad 4 \qquad 80 \qquad 60 \qquad 16 \\ Conv. heating 1/8 \qquad 20 \qquad 4 \qquad 80 \qquad 60 \qquad 57 \\ \end{array}$	OEt 111		Conv. heating	3/7	20	4	80	40	42	
$4 \xrightarrow{\text{Ph}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Conv. heating}} \underbrace{\frac{20}{20}}_{20} \underbrace{\frac{4}{50}}_{20} \underbrace{\frac{80}{120}}_{120} \underbrace{\frac{17}{59}}_{59} \underbrace{\frac{10}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{59}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{59}}_{100} \underbrace{\frac{17}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{100}}_{110} \underbrace{\frac{17}{100}}$		UET 11			20	4	25	720 (12 h)	>95	10
$4 \xrightarrow{\text{Ph}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Ph}} \underbrace{\frac{20}{10}}_{\text{Conv. heating}} \underbrace{\frac{20}{20}}_{20} \underbrace{\frac{4}{50}}_{20} \underbrace{\frac{80}{120}}_{120} \underbrace{\frac{17}{59}}_{59} \underbrace{\frac{10}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{59}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{59}}_{100} \underbrace{\frac{17}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{100}}_{1440} \underbrace{\frac{17}{24 \text{ h}}}_{20} \underbrace{\frac{17}{100}}_{110} \underbrace{\frac{17}{100}}$	13	Ph NO ₂	MW	2/6	20	4	50	120	23	
$4 \xrightarrow{\text{Ph}}_{\text{Ph}} \underbrace{11n}_{\text{Conv. heating}} \frac{2/6}{1/8} \underbrace{20}_{20} \underbrace{4}_{20} \underbrace{50}_{40} \underbrace{120}_{1440} \underbrace{59}_{1440} \underbrace{50}_{24} \underbrace{120}_{1440} \underbrace{59}_{20} \underbrace{1440}_{24} \underbrace{110}_{1440} \underbrace{60}_{16} \underbrace{80}_{1440} \underbrace{160}_{16} \underbrace{110}_{110} \underbrace{60}_{16} \underbrace{80}_{1440} \underbrace{160}_{1440} $	15 1	TTW						120		
$4 \xrightarrow{Ph}_{Ph} \underbrace{MW 1/8}_{20} \begin{array}{c} 20 \\ 20 \\ 0 \\ 0 \\ 0 \\ 0 \\ 110 \\ 0 \\ 0 \\ 10 \\ 10 \\ 60 \\ 8 \\ 60 \\ 57 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 1$			Conv. heating	2/6	20	4	50	120	59	
Ph 11n 20 4 110 60 8 Conv. heating 1/8 20 4 80 60 57					20	5	40	1440 (24 h)	>95	10
Ph 11n 20 4 110 60 8 Conv. heating 1/8 20 4 80 60 57	14	Ph	MW	1/8	20	4	80	60	16	
Conv. heating $1/8$ 20 4 80 60 57		Ph 11n			20	4	110	60	8	
20 4 25 1440 (24 h) 99 11	···· 1	111	Conv. heating	1/8				60		
					20	4	25	1440 (24 h)	99	11

^a Conditions: benzene, 150 W, 4 bar hydrogen pressure; 0.2 M. ^b MW: microwave reactor. ^c Conv. heating: conventional heating.

freeze-pump-thaw cycles, vacuum transferred from sodium/ benzophenone, dispensed into Straus flasks equipped with Young-type Teflon valve stop-cocks and stored over 4 Å molecular sieves. Hydrogen 6.0 (AirLiquide) was purified through a Johnson Matthey Model HIG 35XL gas purifier. Substrates for hydrogenation reactions were purchased from Sigma Aldrich or abcr and were recrystallized or distilled prior to use if necessary. Reagents for borane synthesis were used as received without further purification. $B(C_6F_2H_3)_3$ (3), $B(C_6F_3H_2)_3$ (2) were prepared as described earlier.¹⁰

General procedure for microwave assisted hydrogenation reactions

In a glovebox, $B(C_6F_5)_3$ (1) (5–10 mol%), hexamethylbenzene (1.6 mg, 0.01 mmol, 0.1 equiv.) and the corresponding substrate (0.1 mmol, 1.0 equiv.) were dissolved in 0.5 ml of deuterated solvent. The stock solution was divided in three parts, two portions of 0.2 ml were transferred into two 10 ml reaction vessels equipped with magnetic stir bars and were capped with PTFE/butyl rubber crimp caps. The third part of 0.1 ml of the stock solution was used as comparison sample and analysed by ¹H NMR spectroscopy. The reaction vessels were attached to an H₂/vacuum line via needle, immersed into liquid nitrogen (6 cm), freeze pump thawed for one cycle and charged with H_2 at 77 K. The reactions were carried out in two CEM Discover (model 908010) microwave systems using 150 W power at given times and temperatures. The cooled reaction mixtures were separately analysed by ¹H NMR spectroscopy. Yield as mean value of both measurements. Non-microwave control samples were completely immersed in a preheated oil bath. For substrates requiring an FLP, a suitable base was added matching the concentration of borane as indicated. For the domino hydrosilylation hydrogenation of enones HSiPh₂Me (0.1 mmol, 1.0 equiv.) was added prior to the addition of a suitable base as described earlier.9 Reactions of nitroolefins and malonates required the use of $B(2,6-F_2-C_6H_3)_3$ (3) or $B(2,4,6-F_3-C_6H_2)_3$ (2) (20 mol%).

The analytic data of all starting materials and hydrogenation products were reported in the literature. Yields were determined by ¹H NMR spectroscopy using hexamethylbenzene as internal standard.

Acknowledgements

The German Science Foundation (DFG) is gratefully acknowledged for financial support.

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