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Stereoselective Hydrosilylation of Enals and Enones Catalysed by Palladium Nanoparticles

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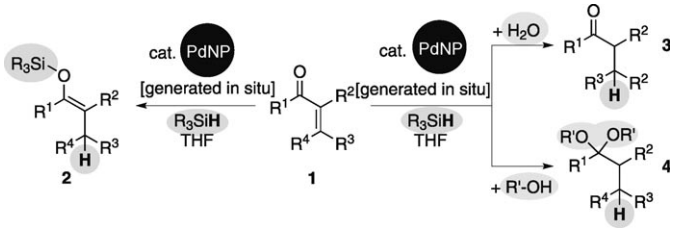
Abstract: A highly versatile and efficient hydrosilylation method by palladium nanoparticle catalysis allows the direct and chemoselective synthesis of 1) enolsilanes of high isomeric purity, 2) saturated aldehydes or ketones, or 3) the corresponding saturated acetals from α,β-unsaturated aldehydes or ketones. The choice of the product is determined by simply switching the solvent from THF to mixtures of THF/water or THF/alcohol.

Keywords: acetals · aldehydes · heterogeneous catalysis · hydrosilylation · nanoparticles · palladium

Introduction

The advantages of nanoparticles as catalysts are typically associated with their high efficiency in traditional reactions, such as oxidation and reduction, or as reservoirs of metals for homogeneous reactions.[1] However, stereoselective reactions catalysed by nanoparticles are still quite rare,[2] the substrate scopes of the reactions are often very limited[3] and, in many cases, these reactions have turned out to be catalysed by leached catalyst species in the solution phase.[4]

Herein, we report that palladium nanoparticles (PdNPs) can be used in a highly stereoselective hydrosilylation of unsaturated enals and enones catalysed by PdNPs with a wide substrate scope. By changing the composition of the solvent mixture of the reaction, it is also possible to access saturated aldehydes, ketones or acetals (Scheme 1).



Scheme 1. Three optional reactivity modes for the hydrosilylation of enals and enones with PdNPs.

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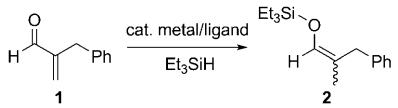
Stereo- and chemoselective reductions of α,β-unsaturated carbonyl compounds are highly important reactions in organic synthesis[5] due to the high utility of stereodefined enolsilanes as nucleophiles. 1,4-Hydrosilylation of enals and enones with modest stereoselectivities has been achieved with a number of metal catalysts, including copper,[6] palladium,[7] rhodium[8] and others.[9] Surprisingly, heterogeneous or nanoparticle catalysis with palladium has not been explored, although the presence of a reducing agent, such as a silane, and a reducible metal complex might readily lead to the formation of metallic (nano)particles that could act as the true catalysts.[10]

Results and Discussion

Highly stereoselective 1,4-hydrosilylation of enals and enones: We initiated our study with the palladium-catalysed hydrosilylation of α-substituted acroleins. These compounds are efficiently prepared by α-methylenation of aldehydes.[11] The α-benzyl acrolein **1a** was subjected to the optimised conditions described in the literature for the 1,4-hydrosilylation of enones.[8,12] Promising results were obtained with $Pd(OAc)_2$ and tricyclohexylphosphine (PCy_3); a catalyst combination described by Oshima et al. for the stereoselective 1,4-hydrosilylation of α,β-unsaturated ketones,[13] allowing us to isolate the desired enolsilane as a single *Z* isomer with a conversion of 63% (Table 1, entry 1). Superior yields and faster conversions were obtained with the $PdCl_2/PCy_3$ catalyst system (Table 1, entry 3). A solvent screen indicated THF as the optimal solvent; this allowed us to reduce the loading of silane to 110 mol% and significantly assisted the purification of the products.[14] The excellent results obtained with this catalyst system for α-benzyl acrolein (100% conversion in 3 h, 84% isolated yield, >50:1 *Z*/*E* selectivity; Table 1, entry 3) encouraged us to test the generality of this protocol with a range of unsaturated carbonyl compounds.

The results of the hydrosilylation experiments under optimised conditions are summarised in Table 2. The reaction

Table 1. Screening of the catalytic system.



Entry	Catalyst	Conditions[a]					Conv.[b] [%]	Z/E[c]
		M [mol%]	L [mol%]	Solvent	T	t [h]		
1	$Pd(OAc)_2/PCy_3$	5.0	10.0	toluene	RT	14	63[d]	>50:1
2	$Pd(OAc)_2/PCy_3$	1.5	3.0	THF	RT	3	50	>50:1
3	$PdCl_2/PCy_3$	1.5	3.0	THF	RT	3	>95[d]	>50:1
4	$PdCl_2/PPh_3$	1.5	3.0	THF	RT	3	20	>50:1

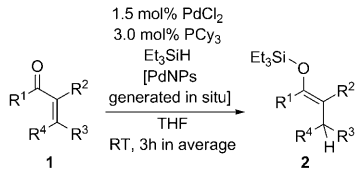
[a] M = metal, L = ligand. [b] The conversion was measured by GC. [c] The stereoselectivity was measured by ^{1}H NMR spectroscopy. [d] Traces of saturated aldehyde (5–10%) were also detected.

affords excellent stereoselectivities with α-monosubstituted enals (Table 2, entries 1–9), β-monosubstituted enals (Table 2, entries 10–12), as well as β,β-disubstituted enals (Table 2, entries 13–16) with alkyl or substituted alkyl substituents. For aldehydes with β-aryl groups, the reaction is not chemoselective. In these cases, the major product is the 1,2-hydrosilylation product.[15] However, cyclic and acyclic enones readily participate in the reaction without chemoselectivity problems (Table 2, entries 19 and 20).

Investigating the nature of the real catalyst: The formation of the *Z* isomer in the hydrosilylation reaction is not directly reconcilable with the mechanism proposed by Oshima and co-workers.[16] To shed light on the mechanism, kinetic studies were initiated. Although the reactions were typically completed within 1–2 h, an induction period was always observed and the rates did not show a clear dependence on the concentration of either substrate. We therefore suspected that the catalytically active black reaction mixture generated after addition of triethylsilane may not be a homogeneous system.[17] Additionally, we observed the slow deposition of black particles on the bottom of the reaction vessel. Centrifugation of the reaction mixture allowed us to separate the particles from the solution. After washing with THF, the re-suspended particles were still active hydrosilylation catalysts for up to six recycles.[14] Importantly, the supernatant liquor still contained some palladium (35 mg L^{-1}), but it was no longer an active catalyst.[14] These experiments confirmed the heterogeneity of the catalytic system.[18]

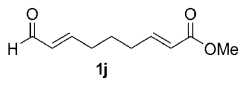
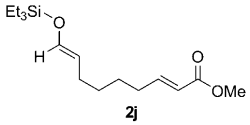
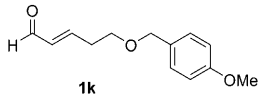
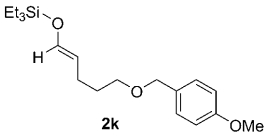
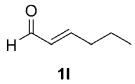
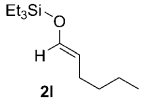
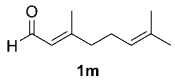
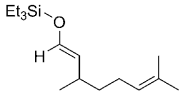
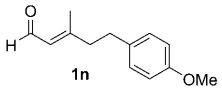
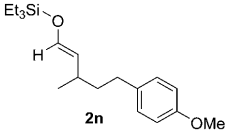
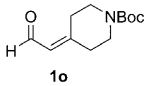
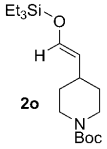
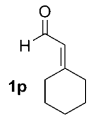
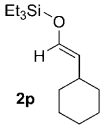
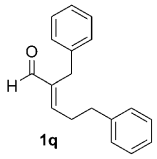
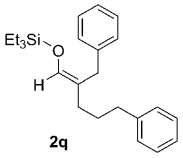
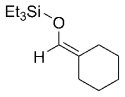
The TEM images of palladium particles formed in situ and isolated after completion of the hydrosilylation reaction and those of palladium particles formed ex situ are comparable. The particles are 6 to 9 nm in scale, but readily form aggregates (Figure 1). The isolated particles are still active in hydrosilylation and they display catalytic activity similar to that observed for related PdNPs. For example, they are active catalysts for hydrogenolysis and hydrogenation reactions.[19] To confirm that the hydrosilylation activity is not restricted to catalysts prepared with silane reduction, we also prepared poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilised PdNPs.[20] These PVP-stabilised PdNPs are also active catalysts for hydrosilylation, affording the same stereoselectivity for **2a** (>25:1 *Z*/*E* ratio) as our own in situ prepared PdNP catalyst, but with a lower chemoselectivity and reaction rate.[14] Al-

Table 2. Hydrosilylations of unsaturated aldehydes and ketones using the $PdCl_2/PCy_3$ catalytic system.



	Enal/Enone	Product	Yield[a] [%]	Z/E[b]
1	1a	2a	84	>50:1
2	1b	2b	98	20:1
3	1c	2c	93	>50:1
4	1d	2d	81	20:1
5	1e	2e	85	>50:1
6	1f	2f	84	20:1
7	1g	2g	84	>50:1
8	1h	2h	86	>50:1
9	1i	2i	86	13:1

Table 2. (Continued)

	Enal/Enone	Product	Yield[a] [%]	Z/E[b]
10	 1j	 2j	94	>1:50
11	 1k	 2k	87	>1:50
12	 1l	 2l	83	1:12
13	 1m	 2m	90	>1:50
14	 1n	 2n	95	>1:50
15	 1o	 2o	96	1:10
16	 1p	 2p	99	1:10
17	 1q	 2q	82	7:1
18	 1r	 2r	88	N/A
19	 1s	 2s	95	1:3
20	 1t	 2t	91	N/A

[a] Yields of isolated product. [b] Stereoselectivity measured by ^{1}H NMR spectroscopy.

though the PdNPs prepared by the silane reduction can be separated and recycled, we recommend in situ preparation for the hydrosilylation reaction for convenience and the best yields.[21]

Saturated aldehydes or ketones under aqueous conditions: The scope of the hydrosilylation is not restricted to nonaqueous conditions and the nanoparticles retain their activity in water. As such, when the hydrosilylation is performed in aqueous THF, saturated aldehydes or ketones are generated rapidly (Table 3). A control experiment with the enolsilane **2a** indicated that the enolsilane is stable under the reaction conditions,[14] and therefore, it appears likely that the saturated aldehydes and ketones are generated directly in the process in the presence of water. Furthermore, the reactions are significantly accelerated in the presence of water when compared with nonaqueous conditions.[14]

The scope of the reduction under aqueous conditions was screened with different α-substituted acroleins (Table 3, entries 1–5), β-substituted enals (Table 3, entries 6 and 7) and α,β-disubstituted enal (Table 3, entry 8) as well as both aliphatic and aromatic ketones (Table 3, entries 9 and 10). Importantly, this reduction proceeds under mild conditions (RT) and typically takes only 1 h to complete, affording the products cleanly. No 1,2-reduction products were detected; even chalcone **1v** afforded clean 1,4-reduction. The reactions can also be readily scaled up: the reduction of **1a** at the 10 mmol scale affords **3a** in 93% yield (1.37 g).[22]

Direct formation of acetals with alcohols: Finally, by using methanol or ethylene glycol as the co-solvent instead of water, the corresponding saturated acetals can be accessed directly (Table 4). The formation of acetals is attributed to traces of HCl generated during the PdNP formation.[23] The conditions are mild enough to preserve potentially labile protecting groups, such as cyclic acetals (Table 4, entry 3) or Boc groups (Table 4, entry 5). For all of the substrates tested (Table 4), the reaction was completed after only 15–30 min and afforded an essentially pure acetal; the only significant side products were the silylated alcohols (e.g., $Et_3SiOCH_2CH_2OH$). For both aldehydes and ketones, this protocol affords the saturated acetals rapidly and in high yields.

Mechanistic aspects: The high stereoselectivities obtained in this process and the (seemingly) opposite stereoselectivities obtained with α- and β-substituted enals suggest that the mechanism may involve a selective trapping of the *s-trans* conformation of the enal with the hydrosilylating catalyst, resulting in an enolsilane in which the hydride-bearing carbon and the enolate are *trans* to each other. This is the pattern universally observed in the hydrosilylations. Furthermore, the results under aqueous conditions indicate that the

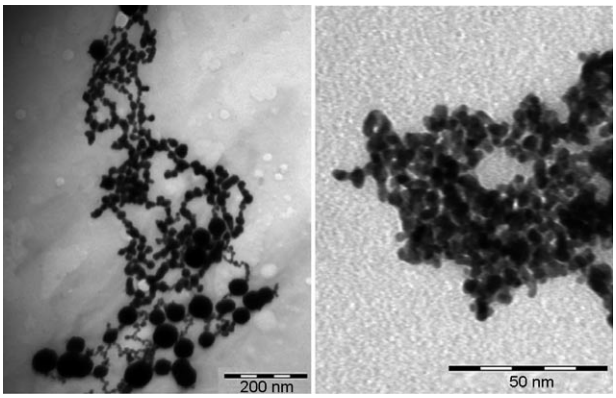


Figure 1. TEM images showing aggregated PdNPs.[15,22]

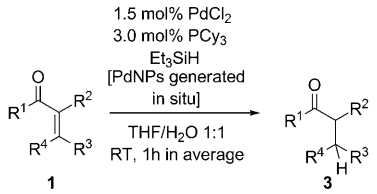
reaction is likely to proceed by a "hydride first" type mechanism and protonation of the intermediate enolate proceeds faster than its silylation. Otherwise, the enolsilanes would accumulate in the reaction mixture, since they are stable to the reaction conditions. Finally, any explanation for the selectivity must account for the result that differently prepared PdNPs (see above) display similar stereoselectivities.

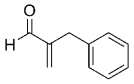
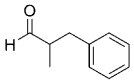
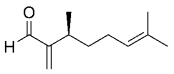
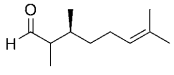
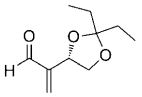
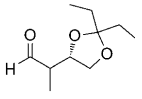
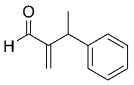
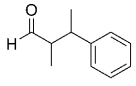
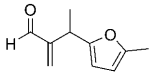
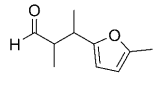
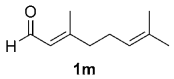
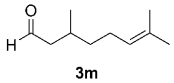
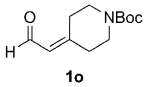
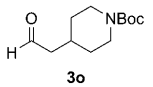
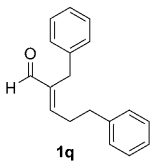
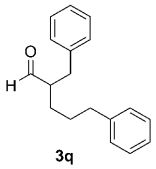
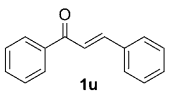
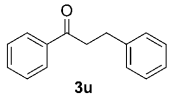
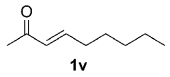
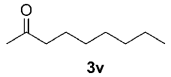
A possible rationalisation for these results consistent with these observations is presented in Scheme 2. The mechanism is believed to be initiated from a PdNP complex of the enal. In the proposed mechanism, the initial hydropalladation step is followed by irreversible O-silylation of the O-bound Pd enolate,[24] trapping the product as a (*Z*)-enolsilane (α-substituted enals) or (*E*)-enolsilane (β-substituted enals). The role of the PdNPs in this scenario is to facilitate hydropalladation in the *s-trans* conformation of the enal. This process might be difficult with a mononuclear Pd species for steric reasons, but could be readily achieved with a nanoparticle because two different Pd atoms could be involved in hydride delivery and the formation of the Pd–O bond. Under aqueous conditions, the palladium enolate species could then be readily protonated, affording the saturated products **3**.

In further support of the proposed mechanism, a competition experiment with Et_3SiD and Ph_3SiH was carried out (Scheme 2c). The differently silylated products **2a** and **2a′** were generated with good stereoselectivity and in a 1:1 ratio. However, both products were deuterated to a similar extent, indicating full and reversible cleavage of the silanes prior to the hydrosilylation event.

Finally, in the presence of alcohols, the formation of saturated acetals is likely to proceed by an acid-catalysed acetalisation. Indeed, when a 1:1 mixture of cyclohexenone **1u** and 4-methylcyclohexanone were subjected to the reaction conditions with ethylene glycol, 4-methylcyclohexanone was also acetalised at a rate comparable to the formation of **4u** (see Supporting Information).

Table 3. Reduction of unsaturated carbonyl compounds to saturated carbonyls under aqueous conditions.



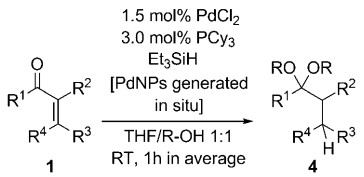
Entry	Enal/Enone	Product	Yield[a] [%]
1	 **1a**	 **3a**	93
2	 **1b**	 **3b** (1.5:1 d.r.)	84
3	 **1f**	 **3f** (1.5:1 d.r.)	78
4	 **1g**	 **3g** (1:1 d.r.)	84
5	 **1i**	 **3i** (5:4 d.r.)	87
6	 **1m**	 **3m**	92
7	 **1o**	 **3o**	93
8	 **1q**	 **3q**	87
9	 **1u**	 **3u**	91
10	 **1v**	 **3v**	94

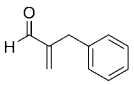
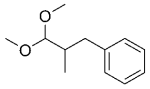
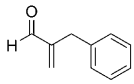
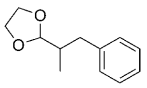
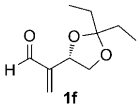
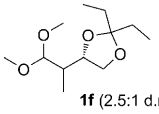
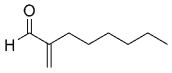
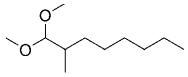
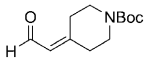
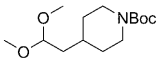
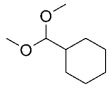
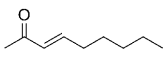
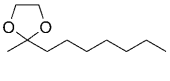
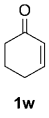
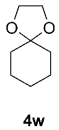
[a] Yield of isolated product.

Conclusion

We have developed a stereoselective PdNP-catalysed hydrosilylation method for enals and enones with the following useful features: 1) the reduction can be performed chemoselectively in the presence of other potentially reducing groups, such as nitro compounds or other C=C bonds; 2) conjugate reduction affords highly versatile nucleophiles,

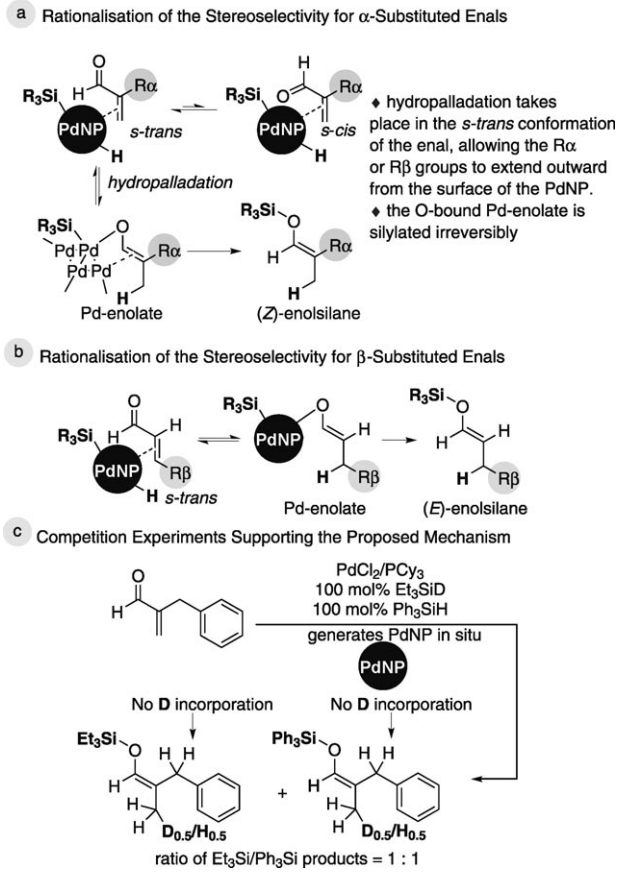
Table 4. Reduction of unsaturated carbonyl compounds to saturated acetals under mixed solvent conditions.[a]



Entry	Enal/Enone	Product	Yield[b] [%]
1	 1a	 4a	95
2	 1a	 4a'	93
3	 1f	 1f (2.5:1 d.r.)	81
4	 1h	 4h	93
5	 1o	 4o	95
6	 1r	 4r	89
7	 1v	 4v	94
8	 1w	 4w	98

[a] Boc = *tert*-butyloxycarbonyl. [b] Yield of isolated product.

such as enolsilanes or metal enolates as intermediates and 3) the conjugate reduction of the C=C bond activates the C=O bond towards nucleophilic attack, such as acetal formation. The method reported herein allows a very convenient access to enolsilanes, saturated aldehydes or ketones, or their acetals in high yields by using a single nanoparticle catalyst system. The choice of the product is determined by simply switching the solvent from THF to THF/water or THF/alcohol mixture. The products were obtained in high yields and in most cases the enolsilanes were obtained with excellent stereoselectivities. The good isomeric purity of the enolsilanes should be useful for a range of further transformations, and with the exception of cinnamaldehyde derivatives, all reduction reactions are highly chemoselective for



Scheme 2. Rationalisation for the observed stereoselectivity starting from hydrosilylated PdNPs.

the 1,4-reduction. Finally, the active catalytic species have been identified as PdNPs formed in situ, expanding the scope of PdNP catalysis to hydrosilylations of enones and enals. Further mechanistic studies, as well as studies on the scope of the transformation, are underway.

Experimental Section

General: All reactions were conducted in screw-cap glass vials. The vials were used without drying.

THF, dichloromethane, acetonitrile and toluene used were obtained by passing deoxygenated solvents through activated alumina columns (MBraun SPS-800 Series solvent purification system). Other solvents and reagents were used as supplied, unless otherwise noted.

Analytical TLC was performed by using Merck silica gel F254 (230–400 mesh) plates and analysed by UV light (254 or 366 nm) and by staining upon heating with standard vanillin, permanganate, ninhydrin or phosphomolybdic acid solutions. For silica-gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230–400 mesh) and p.a. grade solvents unless otherwise noted. GC analyses were performed with an Agilent Technologies 7890GC instrument equipped with an Agilent HP-5 capillary column ($30\times0.320\times0.25$ μm). Dibenzyl ether was used as the internal standard. IR spectra were recorded on a Bruker TENSOR27 FTIR spectrometer. Optical rotations were recorded on a Perkin–Elmer 341B polarimeter using a sodium lamp (D line). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance 250 and 500 spectrometers. The chemical shifts are reported in ppm relative to

$CHCl_3$ ($\delta = 7.26$ ppm for ^1H and $\delta = 77.2$ ppm for ^{13}C NMR spectroscopy). High-resolution mass spectrometric data were obtained with a QSTAR Elite MS/MS system by the Analytical Services of the Department of Chemistry at the University of Jyväskylä.

General procedure for catalytic system screen (Table 1, entry 1): Acrolein **1a** (50 mg, 0.34 mmol, 100 mol%) and triethylsilane (65 μL, 0.68 mmol, 200 mol%) were added to a mixture of $Pd(OAc)_2$ (3.8 mg, 0.017 mmol, 5 mol%) and PCy_3 (9.5 mg, 0.034 mmol, 10 mol%) in toluene (1.1 mL, $c_{(acrolein)} = 0.3$ M) at 0°C. The reaction mixture was stirred at RT for 14 h, then filtered through a pad of alumina and washed with hexanes. After evaporation of the solvents, the material was purified by flash chromatography (silica gel, hexanes). The desired product was isolated as a colourless oil (56 mg, 63%).

General procedure for catalytic system screen (Table 1, entries 2–4): Acrolein **1a** (50 mg, 0.34 mmol, 100 mol%) and triethylsilane (59 μL, 0.37 mmol, 110 mol%) were added to a suspension of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 1.5 mol%) or $PdCl_2$ (0.9 mg, 0.005 mmol, 1.5 mol%) and PCy_3 (2.8 mg, 0.010 mmol, 3.0 mol%) or PPh_3 (2.6 mg, 0.010 mmol, 3.0 mol%) in THF ($c_{(acrolein)} = 0.3$ M). The reaction mixture was stirred at RT for 3 h. GC analyses of the reaction mixture were performed with aliquots filtered through a short pad of alumina to remove traces of the catalyst. The alumina pad was washed with CH_2Cl_2 (1 mL).

General procedure for the preparation of enolsilanes: The acrolein (0.50 mmol, 100 mol%) and the triethylsilane (89 μL, 0.55 mmol, 110 mol%) were added to a suspension of $PdCl_2$ (1.3 mg, 0.0075 mmol, 1.5 mol%) and PCy_3 (4.2 mg, 0.015 mmol, 3.0 mol%) in dry THF ($c_{(acrolein)} = 0.3$ M). The reaction mixture was stirred at RT. After 5 min, the mixture became dark (black or brown). The reaction could be followed by TLC (eluent: hexanes/ethyl acetate 9:1) or by GC. After completion of the reaction (3 h on average), the mixture was filtered through a pad of alumina (2×2 cm), eluted with hexanes (2×10 mL) and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, hexanes or hexanes/diethyl ether 99:1) to afford the pure products.

Compound 2a: Enolsilane **2a** was obtained from acrolein **1a** (50 mg, 0.34 mmol) as the *Z* isomer as a colourless oil (75 mg, 84%). $R_f = 0.93$ (hex); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.74$ (q, $J = 8.0$ Hz, 6H; 3×CH_2), 1.06 (t, $J = 8.0$ Hz, 9H; 3×CH_3), 1.50 (d, $J = 1.5$ Hz, 3H; CH_3), 3.48 (s, 2H; CH_2), 6.25 (d, $J = 0.8$ Hz, 1H; CH), 7.18–7.34 ppm (m, 5H; 5×CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.8$, 6.8, 17.1, 35.2, 116.0, 125.7, 128.3, 129.0, 134.4, 141.3 ppm; IR (neat): 2956, 2877, 1672, 1454, 1181, 1136, 1005, 825, 727, 618 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{16}H_{26}OSiNa$: 285.1651; found: 285.1651.

Compound 2a′: Enolsilane **2a′** was obtained from acrolein **1a** (50 mg, 0.34 mmol) as the *Z* isomer as a white semi-solid (119 mg, 86%). M.p. 96.4–97.8°C; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.43$ (d, $J = 1.5$ Hz, 3H; CH_3), 3.57 (s, 2H; CH_2), 6.31 (brs, 1H; CH), 7.16–7.24 (m, 5H; 5×CH), 7.37–7.48 (m, 9H; 9×CH), 7.64–7.68 ppm (m, 6H; 6×CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 17.1$, 35.5, 117.4, 125.8, 128.2, 128.4, 129.1, 130.5, 133.6, 134.0, 135.6, 140.8 ppm; IR (neat): 3068, 3024, 2851, 695, 518 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{28}H_{26}OSiNa$: 429.1651; found: 429.1661.

Compound 2b: Enolsilane **2b** was obtained from acrolein **1b** (100 mg, 0.60 mmol) as a 20:1 mixture of *Z*/*E* isomers as a colourless oil (165 mg, 98%). $[\alpha]_D = +1.7$ ($c = 1.00$, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): $\delta =$ 0.61–0.70 (m, 6H; 3×CH_2), 0.94–1.03 (m, 12H; 4×CH_3), 1.26–1.38 (m, 2H; CH_2), 1.40 (d, $J = 1.5$ Hz, 3H; CH_3), 1.59 (s, 3H; CH_3), 1.68 (s, 3H; CH_3), 1.92 (q, $J = 7.5$ Hz, 2H; CH_2), 2.93 (sextet, $J = 7.0$ Hz, 1H; CH), 5.13–5.19 (m, 1H; CH), 6.06 ppm (s, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.8$, 6.8, 12.7, 17.7, 18.8, 25.9, 26.6, 30.6, 35.0, 120.7, 125.5, 130.9, 133.4 ppm; IR (neat): 2957, 1146, 729 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{17}H_{34}OSiNa$: 305.2277; found: 305.2265.

Compound 2c: Enolsilane **2c** was obtained from acrolein **1c** (56 mg, 0.50 mmol) as the *Z* isomer as a colourless oil (107 mg, 93%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.60$–0.69 (m, 6H; 3×CH_2), 0.95–1.01 (m, 9H; 3×CH_3), 1.13 (s, 9H; 3×CH_3), 1.47 (d, $J = 1.5$ Hz, 3H; CH_3), 5.98 ppm (d, $J = 1.5$ Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.7$, 6.9, 17.0, 29.5, 63.8, 122.0, 133.6 ppm; IR (neat): 2955, 2877, 1650, 1160, 728 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{13}H_{28}OSi$: 228.1909; found: 228.1883.

Compound 2d: Enolsilane **2d** was obtained from acrolein **1d** (100 mg, 0.62 mmol) as a 20:1 mixture of *Z*/*E* isomers as a colourless oil (140 mg, 81%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.65$–0.75 (m, 6H; 3×CH_2), 1.00–1.05 (m, 9H; 3×CH_3), 1.66 (s, 3H; CH_3), 5.01 (s, 2H; CH_2), 5.67 (brs, 1H; CH), 7.29–7.45 ppm (m, 5H; 5×CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.7$, 6.8, 16.0, 71.3, 122.9, 127.6, 127.8, 128.4, 137.1, 139.0 ppm; IR (neat): 2954, 2876, 1728, 1068, 1003, 728, 695 cm^{-1}; MS (ES+): 278 [*M*], 249 [*M*−Et], 191 [*M*−Et_3], 163 [*M*−$SiEt_3$], 115 [$SiEt_3$].

Compound 2e: Enolsilane **2e** was obtained from acrolein **1e** (100 mg, 0.58 mmol) as the *Z* isomer as a light yellow oil (142 mg, 85%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.60$–0.70 (m, 6H; 3×CH_2), 0.91–1.00 (m, 9H; 3×CH_3), 1.45 (s, 9H; 3×CH_3), 1.93 (d, $J = 2.0$ Hz, 3H; CH_3), 5.55 (brs, 1H; CH), 6.31 ppm (brs, 1H; NH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.6$, 6.7, 15.1, 28.6, 79.7, 118.1, 123.0, 153.2 ppm; IR (neat): 3347, 2955, 2877, 1697, 1367, 1150, 1065, 1004, 728 cm^{-1}; MS (ESI+): 311.2 [*M*+H+Na], 326.2 [*M*+H+K].

Compound 2f: Enolsilane **2f** was obtained from acrolein **1f** (37 mg, 0.20 mmol) as a 20:1 mixture of *Z*/*E* isomers as a colourless oil (50 mg, 84%). $[\alpha]_D = +4.3$ ($c = 0.90$ in CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): $\delta =$ 0.59–0.69 (m, 6H; 3×CH_2), 0.85–0.99 (m, 15H; 5×CH_3), 1.57 (s, 3H; CH_3), 1.61–1.73 (m, 4H; 2×CH_2), 3.55 (t, $J = 8.5$ Hz, 1H; CH(H)), 3.99 (t, $J = 7.5$ Hz, 1H; CH(H)), 5.24 (dd, $J = 6.5$, 9.0 Hz, 1H; CH), 6.20 ppm (s, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.6$, 6.7, 8.2, 8.4, 12.2, 29.8, 30.0, 67.3, 72.3, 112.3, 113.3, 137.7 ppm; IR(neat): 2941, 2880, 1722, 1075, 916, 731 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{16}H_{32}O_3SiNa$: 323.2018; found: 323.2009.

Compound 2g: Enolsilane **2g** was obtained from acrolein **1g** (50 mg, 0.31 mmol) as a colourless oil (72 mg, 84%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.73$ (q, $J = 8.0$ Hz, 6H; 3×CH_2), 1.05 (t, $J =$ 8.0 Hz, 9H; 3×CH_3), 1.38 (s, 3H; CH_3), 1.39 (d, $J = 7.4$ Hz, 3H; CH_3), 4.40 (q, $J = 7.4$ Hz, 1H; CH), 6.14 (brs, 1H; CH), 7.16 (m, 1H; CH), 7.31 ppm (d, 4H; 4×CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.8$, 6.8, 13.3, 16.9, 35.8, 120.6, 125.7, 127.6, 128.1, 133.5, 145.6 ppm; IR (neat): 2958, 2877, 1150, 697 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{17}H_{28}OSiNa$: 299.1807; found: 299.1801.

Compound 2h: Enolsilane **2h** was obtained from acrolein **1h** (42 mg, 0.30 mmol) as the *Z* isomer as a colourless oil (66 mg, 86%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.59$–0.69 (m, 6H; 3×CH_2), 0.86–0.91 (m, 3H; CH_3), 0.95–1.01 (m, 9H; 3×CH_3), 1.27–1.39 (m, 8H; 4×CH_2), 1.50 (d, $J = 1.3$ Hz, 3H; CH_3), 2.08 (t, $J = 7.0$ Hz, 2H; CH_2), 6.06 ppm (brs, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.8$, 6.8, 14.3, 17.3, 22.9, 27.5, 28.7, 29.4, 32.1, 117.5, 133.5 ppm; IR (neat): 2955, 1159, 1004, 823, 720 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{15}H_{33}OSi$: 257.2301; found: 257.2306.

Compound 2i: Enolsilane **2i** was obtained from acrolein **1i** (100 mg, 0.61 mmol) as a 13:1 mixture of *Z*/*E* isomers as an orange oil (147 mg, 86%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.70$ (q, $J = 8.0$ Hz, 6H; 3×CH_2), 1.02 (t, $J = 8.0$ Hz, 9H; 3×CH_3), 1.29 (d, $J = 7.3$ Hz, 3H; CH_3), 1.40 (d, $J = 1.5$ Hz, 3H; CH_3), 2.26 (s, 3H; CH_3), 4.29 (q, $J = 7.3$ Hz, 1H; CH), 5.84–5.88 (m, 2H; 2×CH), 6.13 ppm (brs, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.7$, 6.8, 13.3, 13.7, 16.2, 30.9, 105.0, 105.7, 118.7, 134.0, 150.2, 157.4 ppm; IR (neat): , 2877, 1716, 1458, 1005, 824, 728 cm^{-1}; HRMS (ESI+): *m/z* calcd for [$C_{16}H_{28}OSiNa$]: 303.1756; found: 303.1743.

Compound 2j: Enolsilane **2j** was obtained from acrolein **1j** (91 mg, 0.50 mmol) as a 1:50 mixture of *Z*/*E* isomers as a colourless oil (140 mg, 94%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.60$–0.70 (m, 6H; 3×CH_2), 0.92–1.01 (m, 9H; 3×CH_3), 1.25–1.51 (m, 6H; 3×CH_2), 1.84–1.93 (m, 2H; CH_2), 2.14–2.23 (m, 2H; CH_2), 3.72 (s, 3H; CH_3), 4.96 (dt, $J = 7.5$, 11.8 Hz, 1H; CH), 5.80 (dt, $J = 1.5$, 15.5 Hz, 1H; CH), 6.23 (dt, $J = 1.3$, 12.0 Hz, 1H; CH), 6.95 ppm (dt, $J = 7.0$, 15.8 Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 4.7$, 6.7, 27.2, 27.5, 30.1, 32.2, 51.6, 111.2, 121.1, 140.4, 149.8, 167.4 ppm; IR (neat): 2953, 1726, 1658, 1164, 730 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{16}H_{30}O_3SiNa$: 321.1862; found: 321.1850.

Compound 2k: Enolsilane **2k** was obtained from acrolein **1k** (110 mg, 0.50 mmol) as a 1:50 mixture of *Z*/*E* isomers as a colourless oil (146 mg, 87%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.61$–0.71 (m, 6H; 3×CH_2), 0.95–1.01 (m, 9H; 3×CH_3), 1.58–1.69 (m, 2H; CH_2), 1.94–2.03 (m, 2H; CH_2), 3.42–3.47 (m, 2H; CH_2), 3.80 (s, 3H; CH_3), 4.43 (s, 2H; CH_2) 4.98 (dt, $J = 7.5$, 12.0 Hz, 1H; CH), 6.25 (dt, $J = 1.5$, 11.8 Hz, 1H; CH), 6.86–6.90

(m, 2H; 2×CH), 7.25–7.28 ppm (m, 2H; 2×CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.6, 6.7, 14.3, 24.2, 30.7, 55.4, 69.6, 72.8, 111.0, 113.9, 129.4, 131.0, 140.5, 159.3 ppm; IR (neat): 2954, 2876, 1512, 819, 729 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{19}H_{32}O_3SiNa$: 359.2018; found: 359.2013.

Compound 2l: Enolsilane **2l** was obtained from acrolein **1l** (39 mg, 0.40 mmol) as a 1:12 mixture of *Z*/*E* isomers as a colourless oil (71 mg, 83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.61–0.71 (m, 6H; 3×CH_2), 0.85–0.91 (m, 3H; CH_3), 0.95–1.01 (m, 9H; 3×CH_3), 1.27–1.32 (m, 4H; 2×CH_2), 1.84–1.92 (m, 2H; CH_2), 4.99 (dd, *J* = 7.5, 12.0 Hz, 2H; CH_2), 6.23 ppm (d, *J* = 12.0 Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.7, 6.7, 14.1, 22.3, 27.2, 32.8, 111.9, 140.0 ppm; IR (neat): 2956, 2877, 1663, 1163, 728 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{12}H_{25}OSi$: 213.1674; found: 213.1641.

Compound 2m: Enolsilane **2m** was obtained from acrolein **1m** (46 mg, 0.30 mmol) as the isomer *E* as a colourless oil (73 mg, 90%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.62–0.68 (m, 6H; 3×CH_2), 0.96–1.02 (m, 9H; 3×CH_3), 1.21–1.35 (m, 4H; 2×CH_2), 1.60 (s, 3H; CH_3), 1.69 (s, 3H; CH_3), 1.89–2.06 (m, 3H; CH_3), 4.86 (dd, *J* = 8.8, 12.0 Hz, 1H; CH), 5.06–5.13 (m, 1H; CH), 6.21 ppm (d, *J* = 12.0 Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.7, 6.8, 17.9, 22.2, 25.9, 26.2, 32.4, 38.1, 118.1, 125.0, 131.3, 139.2 ppm; IR (neat): 2956, 2913, 2877, 1660, 1239, 729 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{16}H_{32}OSiNa$: 291.2120; found: 291.2119.

Compound 2n: Enolsilane **2n** was obtained from acrolein **1n** (102 mg, 0.50 mmol) as the isomer *E* as a colourless oil (152 mg, 95%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.66–0.75 (m, 6H; 3×CH_2), 0.99–1.05 (m, 12H; 4×CH_3), 1.45–1.66 (m, 2H; CH_2), 1.96–2.13 (m, 1H; CH), 2.46–2.65 (m, 2H; CH_2), 3.80 (s, 3H; CH_3), 4.92 (dd, *J* = 8.8, 12.0 Hz, 1H; CH), 6.26 (d, *J* = 12.0 Hz, 1H; CH), 6.84 (d, *J* = 8.5 Hz, 2H; 2×CH), 7.10 ppm (d, *J* = 8.5 Hz, 2H; 2×CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.7, 6.8, 22.3, 32.4, 33.0, 40.0, 55.4, 113.9, 117.8, 129.4, 135.2, 139.6, 157.8 ppm; IR (neat): 2951, 2912, 2870, 1661, 1456, 1410, 1375, 1238, 1157, 1009, 974, 918, 788, 725, 671 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{19}H_{32}O_2Si$: 320.2172; found: 320.2189.

Compound 2o: Enolsilane **2o** was obtained from acrolein **1o** (77 mg, 0.34 mmol) as a 1:10 mixture of *Z*/*E* isomers as a colourless oil (109 mg, 96%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.60–0.69 (m, 6H; 3×CH_2), 0.93–1.00 (m, 9H; 3×CH_3), 1.16–1.32 (m, 2H; CH_2), 1.44 (s, 9H; 3× CH_3), 1.58–1.63 (m, 2H; CH_2), 1.93–2.08 (m, 1H; CH), 2.66–2.77 (m, 2H; CH_2), 4.01–4.06 (m, 2H; CH_2), 4.94 (dd, *J* = 7.8, 12.0 Hz, 1H; CH), 6.27 ppm (dd, *J* = 1.0, 12.0 Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.7, 6.7, 28.7, 33.15, 35.2, 44.0, 79.4, 116.2, 139.8, 155.1 ppm; IR (neat): 3433, 2915, 1692, 1365, 730 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{18}H_{35}NO_3SiNa$: 364.2284; found: 364.2281.

Compound 2p: Enolsilane **2p** was obtained from acrolein **1p** (62 mg, 0.50 mmol) as a 1:10 mixture of *Z*/*E* isomers as a colourless oil (119 mg, 99%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.61–0.70 (m, 6H; 3×CH_2), 0.86–0.91 (m, 2H; CH_2), 0.98 (m, 9H; 3×CH_3), 1.26–1.27 (m, 2H; CH_2), 1.63–1.71 (m, 6H; 3×CH_2), 1.78–1.92 (m, 1H; CH), [4.31 (dd, *J* = 6.0, 9.0 Hz, 1H; CH)], 4.97 (dd, *J* = 8.0, 12.0 Hz, 1H; CH), [6.10 (dd, *J* = 1.0, 6.0 Hz, 1H; CH)], 6.24 ppm (dd, *J* = 0.8, 12.0 Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.7, 6.7, 26.4, 27.2, 34.4, 37.0, 118.5, 138.8 ppm; IR (neat): 2922, 1660, 1162, 729 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{14}H_{28}O_3SiNa$: 263.1807; found: 263.1813.

Compound 2q: Enolsilane **2q** was obtained from acrolein **1q** (75 mg, 0.30 mmol) as a 7:1 mixture of *Z*/*E* isomers as a colourless oil (90 mg, 82%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.74 (q, *J* = 7.8 Hz, 6H; 3×CH_2), 1.05 (t, *J* = 7.8 Hz, 9H; 3×CH_3), 1.63–1.76 (m, 2H; CH_2), 1.90 (t, *J* = 7.5 Hz, 2H; CH_2), 2.56 (t, *J* = 7.5 Hz, 2H; CH_2), 3.50 (s, 2H; CH_2), [3.68 (s, 2H; CH_2)], 6.27 (s, 1H; CH), [6.60 (s, 1H; CH)], 7.09–7.32 ppm (m, 10H; 10×CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.8, 6.8, 30.0, 30.9, 32.9, 35.6, 119.8, 125.7, 125.8, 128.3, 128.4, 128.6, 129.0, 135.3, 141.4, 142.9 ppm; IR (neat): 2955, 2876, 727, 696 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{24}H_{34}OSiNa$: 389.2277; found: 389.2262.

Compound 2r: Enolsilane **2r** was obtained from acrolein **1r** (57 μL, 0.05 mmol) as a Colourless oil (100 mg, 88%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.65 (q, *J* = 8.0 Hz, 6H; 3×CH_2), 0.99 (t, *J* = 8.0 Hz, 9H; 3×CH_3), 1.44–1.54 (m, 6H; 3×CH_2), 1.93 (t, *J* = 5.0 Hz, 2H; CH_2), 2.20 (t, *J* = 5.0 Hz, 2H; CH_2), 6.05 ppm (s, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 4.7, 6.8, 25.5, 27.2, 27.3, 28.7, 30.8, 122.0, 130.9 ppm; IR (neat): 2927, 1679, 1152, 727 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{13}H_{26}OSiNa$: 226.1753; found: 226.1680.

Compound 2s: Enolsilane **2s** was obtained from enone **1s** (35 mg, 0.50 mmol) as a 1:3 mixture of *Z*/*E* isomers as a colourless oil (88 mg, 95%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63–0.73 (m, 6H; 3×CH_2), 0.95–1.04 (m, 9H; 3×CH_3), 1.49–1.54 (m, 3H; CH_3), [1.74 (m, 3H; CH_3)], 1.79 (m, 3H; CH_3), 4.45 (dq, *J* = 0.8, 6.5 Hz, 1H; CH), [4.64–4.72 ppm (dq, *J* = 0.8, 6.5 Hz, 1H; CH)]; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 5.5, 6.6, 10.5, 22.6, 102.2 ppm; IR (neat): 3293, 2954, 2877, 823, 724 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{10}H_{23}OSi$: 187.1518; found: 187.1527.

Compound 2t: Enolsilane **2t** was obtained from enone **1t** (41 mg, 0.50 mmol) as a colourless oil (90 mg, 91%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.65–0.73 (m, 6H; 3×CH_2), 0.93–1.01 (m, 9H; 3×CH_3), 1.79–1.91 (m, 2H; CH_2), 2.26 (t, *J* = 7.3 Hz, 4H; 2×CH_2), 4.62 ppm (brs, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 5.0, 6.8, 21.7, 28.9, 33.7, 81.7, 102.3 ppm; IR (neat): 2956, 2913, 2877, 1660, 1457, 1414, 1377, 1239, 1159, 1005, 974, 922, 789, 729, 677 cm^{-1}; HRMS (ES+): *m/z* calcd for $C_{11}H_{22}OSi$: 198.1440; found: 198.1447.

General procedure for the preparation of aldehydes and ketones under aqueous conditions: The acrolein (0.50 mmol, 100 mol%) and the triethylsilane (89 μL, 0.55 mmol, 110 mol%) were added to a suspension of $PdCl_2$ (1.3 mg, 0.0075 mmol, 1.5 mol%) and PCy_3 (4.2 mg, 0.015 mmol, 3.0 mol%) in a mixture THF/H_2O ($c_{(acrolein)}$ = 1.0 M). The reaction mixture was stirred at RT. After 5 min, the mixture became dark (black or brown). The reaction could be followed by TLC (eluent: hexane/ethyl acetate 9:1) or GC. After completion of the reaction (1 h on average), the reaction mixture was filtered through a pad of alumina (2×2 cm) and eluted with hexanes (2×10 mL). (Note that the aqueous layer was retained by the alumina.) The filtrate was concentrated to around 1/10 of the original volume and the residue was purified by flash chromatography (silica gel, hexanes/diethyl ether 99:1) to afford the pure products.

Compound 3a: Saturated aldehyde **3a** was obtained from acrolein **1a** (1.462 g, 10.0 mmol) as an oil (1.373 g, 93%). R_f = 0.57 (hex); NMR data corresponds to that published in the literature.[25] ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 7.0 Hz, 3H; CH_3), 2.57–2.75 (m, 2H; CH_2), 3.07–3.14 (m, 1H; CH), 7.17–7.34 (m, 5H; 5×CH), 9.72 ppm (d, *J* = 1.5 Hz, 1H; CHO); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 13.4, 36.8, 48.2, 126.6, 128.7, 129.2, 139.0, 204.4 ppm, HRMS (ESI+): *m/z* calcd for $C_{10}H_{12}ONa$: 171.0786; found: 171.0789.

Compound 3b: Saturated aldehyde **3b** was obtained from acrolein **1b** (50 mg, 0.30 mmol) as a mixture of diastereoisomers as a colourless oil (42 mg, 84%). ^{1}H NMR (1.5:1 mixture of diastereomers) (250 MHz, $CDCl_3$): δ = 0.96–1.04 (m, 6H; 2×CH_3), 1.23–1.27 (m, 2H; CH_2), 1.59 (s, 3H; CH_3), 1.67 (s, 3H; CH_3), 1.85–2.07 (m, 3H; CH_2+CH), 2.22–2.38 (m, 1H; CH), 5.03–5.11 (m, 1H; CH), 9.65 ppm (dd, *J* = 1.8, 7.0 Hz, 1H; CHO); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 8.3, 10.1, 14.3, 15.6, 17.5, 17.8, 22.8, 25.5, 25.9, 27.1, 31.8, 32.4, 33.5, 33.6, 34.9, 35.0, 50.7, 51.7, 124.2, 124.3, 132.0, 205.7, 205.8 ppm; IR (neat): , 2927, 1726, 1456, 1379 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{11}H_{20}ONa+CH_3OH$: 223.1674; found: 223.1675.

Compound 3f: Saturated aldehyde **3f** was obtained from acrolein **1f** (92 mg, 0.50 mmol) as a mixture of diastereoisomers as a colourless oil (73 mg, 78%). ^{1}H NMR (1.5:1 mixture of diastereomers) (250 MHz, $CDCl_3$): 0.84–0.91 (m, 6H; 2×CH_3), 1.21 (d, *J* = 7.3 Hz, 3H; CH_3), 1.56–1.67 (m, 4H; 2×CH_2), 2.50–2.64 (m, 1H; CH), 3.57–3.67 (m, 2H; CH), 4.10–4.18 (m, 1H; CH), 4.21–4.31 (m, 1H; CH), 9.71 (d, *J* = 0.5 Hz, 1H; CHO), 9.78 ppm (d, *J* = 2.0 Hz, 1H; CHO); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 8.1, 8.4, 10.2, 29.3, 29.5, 29.7, 29.9, 49.8, 68.2, 75.8, 113.0, 203.3 ppm; IR (neat): 2941, 1710, 1460, 1057, 918, 730 cm^{-1}; HRMS (ESI+): *m/z* calcd for $C_{10}H_{18}O_3Na$: 209.1154; found: 209.1151.

Compound 3g: Saturated aldehyde **3g** was obtained from acrolein **1g** (50 mg, 0.31 mmol) as a mixture of diastereoisomers as a colourless oil (42 mg, 84%). ^{1}H NMR (1:1 mixture of diastereoisomers) (250 MHz, $CDCl_3$): δ = 0.91 and 1.09 (2×d, *J* = 7.0 Hz, 2×3H; CH_3), 1.31 (2×d, *J* = 7.0 Hz, 2×3H; CH_3), 2.29–2.69 (m, 2×1H; 2×CH), 2.96–3.08 and 3.11–3.22 (m, 2×1H; 2×CH), 7.16–7.35 (m, 2×5H; 5×CH), 9.60 (d, *J* = 2.0 Hz, 1H; CHO), 9.70 ppm (d, *J* = 3.3 Hz, 1H; CHO); ^{13}C NMR

(63 MHz, $CDCl_3$): $\delta = 10.7$, 12.7, 17.7, 20.3, 40.4, 41.1, 52.7, 53.1, 126.8, 127.7, 127.8, 128.7, 204.9, 205.0 ppm, IR (neat): 2978, 1720, 1179, 701 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{11}H_{14}O_2Na$: 201.0891; found: 201.0889.

Compound 3i: Saturated aldehyde **3i** was obtained from acrolein **1i** (82 mg, 0.50 mmol) as a mixture of diastereoisomers as a colourless oil (72 mg, 87%). ^1H NMR (5:4 mixture of diastereomers) (250 MHz, $CDCl_3$): $\delta = 0.98$ (d, $J = 7.0$ Hz, 3H; CH_3), 1.04 (d, $J = 7.0$ Hz, 3H; CH_3), 1.20 (d, $J = 7.3$ Hz, 3H; CH_3), 1.28 (d, $J = 7.3$ Hz, 3H; CH_3), 2.23 (d, $J = 3.8$ Hz, 3H; CH_3), 2.53–2.77 (m, 1H; CH), 3.19–3.33 (m, 1H; CH), 5.84–5.85 (m, 1H; CH), 5.90 (d, $J = 3.0$ Hz, 1H; CH_3), 9.70 ppm (dd, $J = 1.5$, 7.3 Hz, 1H; CHO); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 9.9$, 10.6, 13.7, 14.3, 14.9, 16.6, 22.9, 31.8, 33.5, 34.3, 50.3, 51.1, 105.9, 106.0, 106.3, 106.6, 151.0, 151.1, 155.1, 155.6, 204.7, 204.9 ppm; IR (neat): 2973, 2957, 2851, 1375, 1078 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{10}H_{14}O_2Na$: 189.0891; found: 189.0896.

Compound 3m: Saturated aldehyde **3m** was obtained from acrolein **1m** (76 mg, 0.50 mmol) as a colourless oil (71 mg, 92%). The NMR data corresponds to that published in the literature.[26] ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.97$ (d, $J = 6.8$ Hz, 3H; CH_3), 1.23–1.44 (m, 2H; CH_2), 1.60 (s, 3H; CH_3), 1.68 (s, 3H; CH_3), 1.95–2.04 (m, 2H; CH_2), 2.05–2.13 (m, 1H; CH), 2.22 (ddd, $J = 2.5$, 7.8, 15.8 Hz, 1H; CH(H)), 2.40 (ddd, $J = 2.0$, 5.5, 15.8 Hz, 1H; CH(H)), 5.05–5.12 (m, 1H; CH), 9.75 ppm (t, $J = 2.0$ Hz, 1H; CHO); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 17.9$, 20.1, 25.6, 25.9, 28.0, 37.2, 51.2, 124.3, 131.9, 203.1 ppm, HRMS (ESI+): m/z calcd for $C_{10}H_{18}O_2Na$: 193.1204; found: 193.1200.

Compound 3o: Saturated aldehyde **3o** was obtained from acrolein **1o** (34 mg, 0.15 mmol) as a colourless oil (32 mg, 93%). The NMR data corresponds to that published in the literature.[27] ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.07$–1.26 (m, 2H; CH_2), 1.43 (s, 9H; $3\times CH_3$), 1.64–1.69 (m, 2H; CH_2), 1.94–2.12 (m, 1H; CH), 2.36 (dd, $J = 1.5$, 6.8 Hz, 2H; CH_2), 2.72 (dt, $J = 2.3$, 13.3 Hz, 2H; CH_2), 4.03–4.08 (m, 2H; CH_2), 9.76 ppm (t, $J = 1.5$ Hz, 1H; CHO); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 28.6$, 30.9, 32.1, 43.9, 50.5, 79.6, 154.9, 201.6 ppm.

Compound 3q: Saturated aldehyde **3q** was obtained from acrolein **1q** (75 mg, 0.30 mmol) as a colourless oil (66 mg, 87%). ^1H NMR (250 MHz, $CDCl_3$): 1.52–1.61 (m, 2H; CH_2), 1.64–1.79 (m, 2H; CH_2), 2.55–2.69 (m, 4H; $2\times CH_2$), 2.72–2.82 (m, 1H; CH), 2.96–3.04 (m, 1H; CH), 7.14–7.36 (m, 10H; $10\times CH$), 9.67 ppm (d, $J = 2.5$ Hz, 1H; CHO); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 28.3$, 28.9, 35.2, 36.0, 53.5, 126.1, 126.6, 128.6, 128.8, 129.2, 204.6 ppm; IR (neat): 2928, 1702, 696 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{18}H_{20}ONa$: 275.1412; found: 275.1402.

Compound 3u: Saturated ketone **3u** was obtained from enone **1u** (42 mg, 0.20 mmol), as a colourless oil (38 mg, 91%). The NMR data corresponds to that published in the literature.[28] ^1H NMR (250 MHz, $CDCl_3$): $\delta = 3.08$ (t, $J = 7.6$ Hz, 2H; CH_2), 2.38 ppm (t, $J = 7.6$ Hz, 2H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$, 22.8, 24.0, 29.2, 29.3, 29.9, 31.8, 44.0, 209.4 ppm.

Compound 3v: Saturated ketone **3v** was obtained from enone **1v** (83 μL, 0.50 mmol) as a colourless oil (67 mg, 94%). The NMR data corresponds to that published in the literature.[29] ^1H NMR (250 MHz, $CDCl_3$): $\delta =$ 0.82–0.87 (m, 3H; CH_3), 1.24 (m, 8H; $4\times CH_2$), 1.48–1.60 (m, 2H; CH_2), 2.10 (s, 3H; CH_3), 2.38 ppm (t, $J = 7.5$ Hz, 2H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$, 22.8, 24.0, 29.2, 29.3, 29.9, 31.8, 44.0, 209.4 ppm.

General procedure for the preparation of acetals: The acrolein (0.50 mmol, 100 mol%) and the triethylsilane (89 μL, 0.55 mmol, 110 mol%) were added to a suspension of $PdCl_2$ (1.3 mg, 0.0075 mmol, 1.5 mol%) and PCy_3 (4.2 mg, 0.015 mmol, 3.0 mol%) in a mixture THF/MeOH or THF/ethylene glycol ($c_{(acrolein)} = 0.3$ M). The reaction mixture was stirred at RT. After 5 min, the mixture became dark (black or brown). The reaction could be followed by TLC (eluent: hexanes/ethyl acetate 9:1) or GC. After completion of the reaction (1 h on average), the reaction mixture was carefully concentrated and the residue was purified by flash chromatography (silica gel, hexanes/diethyl ether 99:1) to afford the pure products.

Compound 4a: Acetal **4a** was obtained from acrolein **1a** (30 mg, 0.20 mmol) as a colourless oil (37 mg, 95%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.88$ (d, $J = 6.8$ Hz, 3H; CH_3), 2.00–2.16 (m, 1H; CH), 2.36 (dd, $J = 9.5$, 13.5 Hz, 1H; CH(H)), 2.93 (dd, $J = 5.5$, 15.8 Hz, 1H; CH(H)), 3.40 (s, 3H; CH_3), 3.41 (s, 3H; CH_3), 4.08 (d, $J = 6.3$ Hz, 1H; CH), 7.17–7.33 ppm (m, 1H; $5\times CH$); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta =$ 14.1, 38.0, 38.3, 54.3, 54.5, 108.5, 125.9, 128.4, 129.4, 140.8 ppm; IR (neat): 2932, 1058, 745, 699 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{12}H_{18}O_2Na$: 217.1204; found: 217.1207.

Compound 4a′: Acetal **4a′** was obtained from acrolein **1a** (73 mg, 0.50 mmol) as a colourless oil (89 mg, 93%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.91$ (d, $J = 6.8$ Hz, 3H; CH_3), 1.99–2.15 (m, 1H; CH), 2.42 (dd, $J = 9.8$, 13.3 Hz, 1H; CH(H)), 2.96 (dd, $J = 5.0$, 13.3 Hz, 1H; CH(H)), 3.86–4.02 (m, 4H; $2\times CH_2$), 4.77 (d, $J = 4.0$ Hz, 1H; CH), 7.18–7.33 ppm (m, 1H; $5\times CH$); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 13.5$, 37.9, 39.1, 65.3, 107.1, 126.0, 128.4, 129.4, 140.7 ppm; IR (neat): , 1067, 944, 744, 699 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{12}H_{16}O_2Na$: 215.1048; found: 215.1039.

Compound 4f: Acetal **4f** was obtained from acrolein **1f** (92 mg, 0.50 mmol) as a 2.5:1 mixture of diastereoisomers as a colourless oil (94 mg, 81%). ^1H NMR (2.5:1 mixture of diastereomers) (250 MHz, $CDCl_3$): 0.84–0.93 (m, 9H; $3\times CH_3$), 1.55–1.68 (m, 4H; $2\times CH_2$), 1.96–2.09 (m, 1H; CH), 3.39 and 3.46 ($2\times$s, 6H; $2\times CH_3$), 3.51–3.64 (m, 1H; CH), 3.94–4.05 (m, 1H; CH), [4.15 (d, $J = 6.8$ Hz, 1H; CH), 4.34 ppm (d, $J = 3.8$ Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 8.2$, 8.5, 8.6, 29.8, 30.9, 40.2, 55.6, 56.8, 68.1, 107.1, 112.5 ppm; IR (neat): 2939, 1692, 1075, 732 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{12}H_{24}O_4Na$: 255.1572; found: 255.1572.

Compound 4h: Acetal **4h** was obtained from acrolein **1h** (70 mg, 0.50 mmol) as a colourless oil (87 mg, 93%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.87$–0.90 (m, 6H; $2\times CH_3$), 3.34 (s, 6H; $2\times CH_3$), 4.01 ppm (d, $J = 6.3$ Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.3$, 14.5, 22.9, 27.1, 29.8, 31.9, 32.1, 35.9, 54.1, 54.3, 109.2 ppm; IR (neat): 2924, 1707, 1465, 1110, 1057 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{11}H_{24}O_2Na$: 211.1674; found: 211.1672.

Compound 4o: Acetal **4o** was obtained from acrolein **1o** (34 mg, 0.15 mmol) as a colourless oil (39 mg, 95%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.26$ (m, 2H; CH_2), 1.44 (s, 9H; $3\times CH_3$), 1.52–1.54 (m, 2H; CH_2), 1.64–1.69 (m, 2H; CH_2), 2.68 (dt, $J = 2.5$, 13.3 Hz, 2H; CH_2), 3.30 (s, 6H; $2\times CH_3$), 4.02–4.08 (m, 2H; CH_2), 4.46 ppm (t, $J = 5.5$ Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.3$, 22.9, 28.7, 31.8, 32.4, 32.5, 39.2, 44.1, 52.8, 79.4, 102.7, 155.1 ppm; IR (neat): 2931, 1688, 1419, 1163, 1122 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{14}H_{27}NO_4Na$: 296.1838; found: 296.1827.

Compound 4r: Acetal **4r** was obtained from acrolein **1r** (55 mg, 0.50 mmol) as a colourless oil (70 mg, 89%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.96$–1.06 (m, 2H; CH_2), 1.15–1.21 (m, 2H; CH_2), 1.23–1.31 (m, 1H; CH), 1.52–1.67 (m, 2H; CH_2), 1.70–1.79 (m, 4H; $2\times CH_2$), 3.33 (s, 6H; $2\times CH_3$), 3.98 ppm (d, $J = 7.0$ Hz, 1H; CH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 26.0$, 26.6, 28.3, 40.3, 53.8, 108.8 ppm; IR (neat): 2954, 2927, 2877, 1716, 1679, 1458, 1448, 1414, 1379, 1237, 1213, 1152, 1089, 1068, 1004, 972, 818, 727, 685 cm^{-1}; HRMS (ESI+): m/z calcd for $C_9H_{18}O_2Na$: 181.1204; found: 181.1200.

Compound 4v: Acetal **4v** was obtained from acrolein **1v** (83 μL, 0.50 mmol) as a colourless oil (87 mg, 94%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.85$ (m, 3H; CH_3), 1.25–1.28 (m, 10H; $5\times CH_2$), 1.32–1.40 (m, 3H; CH_3), 1.56–1.63(m, 2H; CH_2), 3.87–3.92 ppm (m, 4H; $2\times CH_2$); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 14.2$, 22.8, 23.9, 24.3, 29.4, 30.0, 32.0, 39.4, 64.8, 110.4 ppm; IR (neat): 2945, 2866, 1718, 1445, 1369, 1339, 1278, 1111, 1056, 935, 825 cm^{-1}; HRMS (ESI+): m/z calcd for $C_{11}H_{22}O_2H$: 187.1698; found: 187.1710.

Compound 4w: Acetal **4w** was obtained from enone **1w** (48 μL, 0.50 mmol) as a colourless oil (70 mg, 98%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.39$–1.42 (m, 2H; CH_2), 1.60 (t, $J = 2.8$ Hz, 8H; $4\times CH_2$), 3.93 ppm (s, 4H; $2\times CH_2$); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 24.2$, 25.4, 35.4, 64.4, 109.3 ppm; IR (neat): 2933, 2862, 1099, 1037, 924 cm^{-1}; HRMS (ESI+): m/z calcd for $C_8H_{15}O_2$: 143.1072; found: 143.1069.

Recycling of the catalyst: Acrolein **1a** (44 mg, 0.30 mmol, 100 mol%), the triethylsilane (53 μL, 0.33 mmol, 110 mol%) and the internal stan-

dard dibenzyl ether (11 μL, 0.06 mmol, 20 mol%) were added to a suspension of $PdCl_2$ (1.6 mg, 0.009 mmol, 3.0 mol%) and PCy_3 (5.0 mg, 0.018 mmol, 6.0 mol%) in dry THF (1.0 mL, $c_{(acrolein)}=0.3$ M). The reaction was followed by GC. After full conversion was observed the reaction mixture was centrifuged 5 min (5200 rpm). The solution phase was removed and the solid material was rinsed with THF (1.0 mL) and centrifuged 2 min (5200 rpm). Rinsing was repeated twice. The solid material was mixed with THF (1.0 mL) and the acrolein **1a** (44 mg, 0.30 mmol, 100 mol%), the triethylsilane (53 μL, 0.33 mmol, 110 mol%) and the internal standard dibenzyl ether (11 μL, 0.06 mmol, 20 mol%) were added to the suspension. The reaction was followed by GC. After full conversion of **1a**, the recycling procedure was repeated.

Catalytic activity of the supernatant: According to our general procedure, the PdNP catalyst suspension was prepared as follows: A suspension of $PdCl_2$ (1.6 mg, 0.009 mmol, 3.0 mol%) and PCy_3 (5.0 mg, 0.018 mmol, 6.0 mol%) in dry THF (1.0 mL, $c_{(acrolein)}=0.3$ M) was stirred for 5 min and Et_3SiH (1.0 μL, 0.0063 mmol, 2,1%) was added to the mixture. After stirring for another 5 min, the mixture was centrifuged for 5 min (5200 rpm). The solution phase was separated by filtration through a 0.2 μm filter and the acrolein **1a** (44 mg, 0.30 mmol, 100 mol%), the triethylsilane (53 μL, 0.33 mmol, 110 mol%) and the internal standard: dibenzyl ether (11 μL, 0.06 mmol, 20 mol%) were added to the supernatant solution. The reaction was followed by GC and after 12 h only the acrolein and the internal standard were observed.

A sample of the supernatant was diluted with 65% HNO_3 (1:10 dilution) and subjected to inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. The concentration of palladium in the supernatant was determined by three independent measurements, affording a concentration of 35 mg L^{-1}.

Competition experiments: Et_3SiD/Ph_3SiH: Acrolein **1a** (50 mg, 0.34 mmol, 100 mol%) and a mixture of deuterated triethylsilane (55 μL, 0.34 mmol, 100 mol%) and triphenylsilane (89 mg, 0.34 mmol, 100 mol%) in dry THF (0.1 mL) were added to a suspension of $Pd(OAc)_2$ (0.9 mg, 0.005 mmol, 1.5 mol%) or $PdCl_2$ (0.9 mg, 0.005 mmol, 1.5 mol%) and PCy_3 (2.8 mg, 0.010 mmol, 3.0 mol%) in dry THF (1.0 mL, $c_{(acrolein)}=0.3$ M). The reaction mixture was stirred at RT for 3 h. The material was filtered through a pad of alumina, eluted with hexane and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, hexanes or hexanes/diethyl ether 99:1) to afford the pure products **2a** and **2a′.** ^{1}H NMR spectroscopic analysis (250 MHz, $CDCl_3$) indicated that the CH_3 signal at $\delta=1.5$ ppm had reduced in intensity by 0.5 H (see the Supporting Information).

No hydrolysis of the enolsilane 2a under aqueous conditions: Acrolein **1a** (44 mg, 0.30 mmol, 100 mol%) and the triethylsilane (53 μL, 0.33 mmol, 110 mol%) were added to a suspension of $PdCl_2$ (0.8 mg, 0.0045 mmol, 1.5 mol%) and PCy_3 (2.5 mg, 0.009 mmol, 3.0 mol%) in a mixture THF/H_2O ($c_{(acrolein)}=1.0$ M). The reaction mixture was stirred at RT. The reaction was monitored by GC (aliquot of reaction mixture diluted in CH_2Cl_2) or by ^{1}H NMR spectroscopy (reaction in an NMR tube using [D_8]THF/H_2O 10:1) and no enolsilane was formed, only acrolein (starting material) and saturated aldehyde (final product) were observed.

When enolsilane **2a** (66 mg, 0.25 mmol, 100 mol%) was added to a reaction mixture containing acrolein **1a** (37 mg, 0.25 mmol, 100 mol), $PdCl_2$ (0.7 mg, 0.004 mmol, 1.5 mol%), PCy_3 (2.1 mg, 0.0075 mmol, 3.0 mol%) and Et_3SiH (45 μL, 0.28 mmol, 110 mol%) in dry THF (0.8 mL, $c_{(acrolein)}=0.3$ M) and stirred at RT overnight, no degradation of the enolsilane was observed (as determined by GC by using dibenzyl ether as the internal standard).

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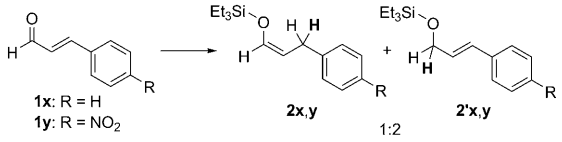

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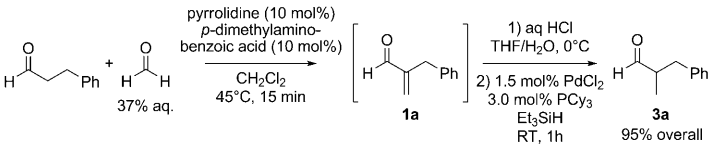
[22] We also briefly examined the possibility of combining the α-methylenation process and the subsequent hydrosilylation process into a one-pot aldehyde α-methylation procedure. For example, α-methylenation of 3-phenylpropionaldehyde, followed by acidification of the reaction mixture and subsequent hydrosilylation, afforded the α-methylated product **3a** in 95% overall yield.



[23] The pH of the aqueous reaction mixture drops below two during the course of the reaction (see the Supporting Information).
[24] Both O- and C-bound Pd enolates have been characterised in the literature (for examples, see: D. A. Culkin, J. F. Hartwig, *Organometallics* **2004**, *23*, 3398–3416). In a C-bound enolate, the selectivity might be compromised by free rotation of around the C–CHO bond, and as such, we suggest that the O-bound Pd enolate is formed. Importantly, this mechanism requires, for geometric reasons, that hydride delivery and binding of the enolate to palladium take place at different Pd atoms. This can be readily achieved by PdNPs, but is difficult to achieve in solution with mononuclear Pd species.
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