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Article

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Pd-Boron Catalyzed One Carbon Isomerization of Olefins: Water Assisted Process at Room Temperature

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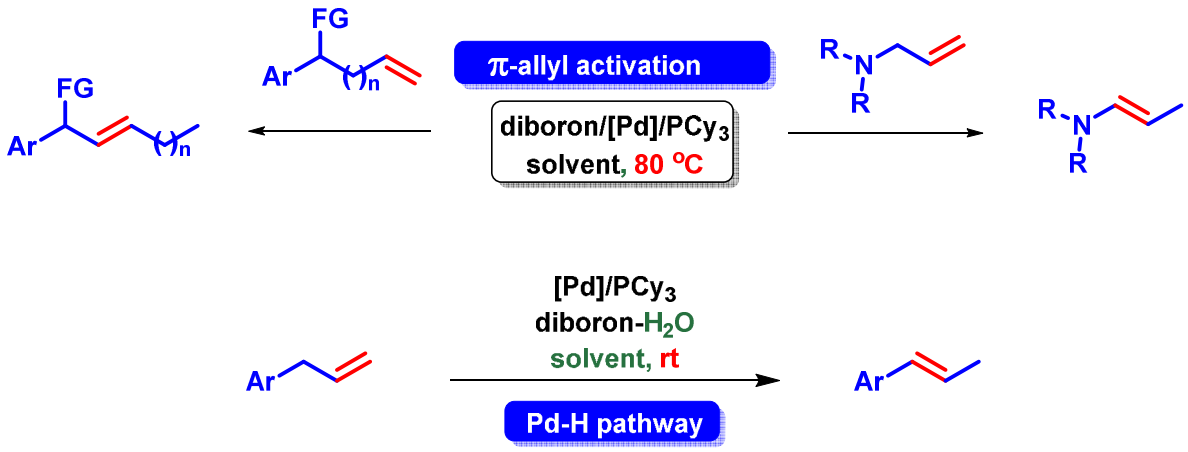
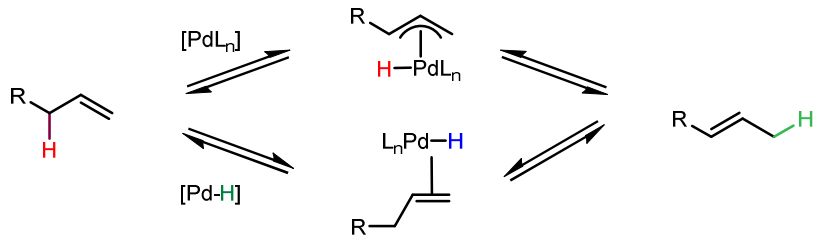
ABSTRACT

A palladium-boronate/borane-system catalyzed isomerization of olefins has been uncovered. An efficient catalytic combination of $[Pd(OAc)_2]_3$-boronate-PCy_3,enabled olefin isomerization at 80 °C has been investigated. Addition of water to the reaction showed a remarkable improvement and the isomerization occurred at ambient temperature. These catalytic systems function efficiently for the isomerization of functionalized as well as unfunctionalized olefins. The catalytic conditions demonstrate the involvement of both non-hydride and metal-hydride medium and can be switchable with water as an additive.



Introduction

Alkenes are highly useful precursors for a variety of organic transformations that are present in a number of organic compounds.[1,2] Transition metal catalyzed isomerization of alkenes, for obtaining highly substituted olefins, is a highly atom-, redox-, and step-economical process.[3-5] Isomerization of terminal olefins to internal olefins is an important process that leads to more complex molecular scaffolds.[6] Isomerization of functionalized olefins, to obtain heterofunctionalized olefins, with a defined stereoselectivity, has been achieved using transition metal catalysts such as, Pd, Rh, Ru, Ir, Fe, Co etc.[7] Palladium complexes have been known as excellent catalysts for isomerization of allyl groups and there are number of reports on the palladium catalyzed isomerization of olefin that involve movement of double bond over one position. Pd-Catalyzed isomerization of double bonds can be broadly classified into two categories *viz.,* isomerization by pre-made or *in situ*-generated palladium-hydride complexes[8] and isomerization by non-hydride palladium complexes (Scheme 1).[4a,9,10] The scope of the isomerization reaction catalyzed by palladium-hydride complexes is limited, which demonstrates the transformation of (i) allyl alcohols to the corresponding carbonyl compounds,[7a,10] (ii) allyl ethers to their enol ethers,[11](iii) allyl amines to their enamines.[12] The isomerization of olefins, using palladium hydride complexes, has been extensively studied, whereas the isomerization using non-hydride palladium catalytic systems have been underexplored.[13] To date, to the best of our knowledge, there is only one report, on non-hydride based palladium catalyst for the isomerization of terminal alkenes to 2-alkenes by RajanBabu and coworkers.[13]



Scheme 1. General mechanism

π-Acceptor ligands such as boranes or boronates have emerged as efficient ancillary ligands with metal catalysts for activation of olefins, carbon monoxide, hydrogen, etc.[14] This characteristic property of boranes or boronates can be attributed to their potential to engage in Lewis acid-coligand-metal-substrate bridging interaction. In light of this, we report isomerization of olefins over one position using a palladium-boronate/borane catalytic system. Addition of water into the reaction, surprisingly, showed a remarkable improvement and isomerization occurs at ambient temperature. Catalytic systems, palladium-boronate and palladium-borane, function efficiently for the isomerization of functionalized as well as unfunctionalized olefins. The catalytic composition of B_2Pin_2 (10 mol%), $[Pd(OAc)_2]_3$ (1.6 mol%), and PCy_3 is expected to form a $(phosphine)_n$-Pd-Boronate transient complex, which is evident from literature reports.[15] These isomerization reactions catalyzed by Pd-borane or Pd-borate systems illustrate the olefin activation concept by coordination of olefins with Pd-borane complex. These complexes facilitate a facile 1,n-hydride shifts at 80 °C. Moreover, a single catalytic combination with simple variation of conditions, in this case addition of water, provides access to both non-hydride as well as hydride pathways for olefin isomerization.

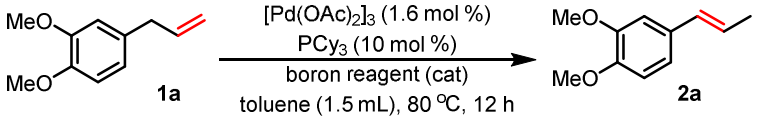
Results and Discussion

Optimization of reaction conditions

In light of the literature precedent,[4] and continuation of our work,[16] we commenced the screening studies using 4-allyl-1,2-dimethoxybenzene (**1a**) as the model substrate and performed the reactions with different boron sources in toluene at 80 °C (Table 1). The initial quantitative amount of B_2Pin_2 (100 mol %) was screened with respect to the palladium catalyst source. The four-fold decrease in the boronate amount (~12.5 mol %, catalytic) furnished the corresponding product in 92% yield. Further, when the reactions were carried out in lesser amounts (10 mol %) the reactions outcome was unaffected (entries 1-4). These preliminary studies revealed that B_2Pin_2 (10mol %), $[Pd(OAc)_2]_3$ (1.6 mol %), and PCy_3(10

mol %), are necessary for the olefin isomerization. The reaction of **1a** with B_2Pin_2 (10 mol %), $[Pd(OAc)_2]_3$ (1.6 mol %), and PCy_3 (10 mol %) at 80 °C furnished the corresponding isomerized product (*E*)-1,2-dimethoxy-4-(prop-1-en-1-yl)benzene (**2a**)in 92% yield (entry 4, Table 1). This isomerization of alkene was not efficient at lower temperature (10% at 60 °C, entry 5). The isomerization of **1a** using other ligands such, Segphos, Xphos, and rac-BINAP were found to be less effective and provided the isomerized product **2a** in low yields (29, 35, and 30%, respectively, entries 6-8). The reaction of **1a** with other Pd-catalysts such as Pd_2dba_3, and $Pd(PPh_3)_4$ furnished the isomerized product **2a**, albeit, in low yields (50, and 31%, respectively, entries 9-10), whereas the similar reaction of **1a** with $Pd(dppf)Cl_2$ was futile (entry 11). Next, it was noticed that the boron

Table 1. Screening Studies for Optimization[a]



entry	boron reagent (mol %)	Pd- source (1.6 mol %)	ligand (10 mol %)	**2** yield (%)
1	none	$[Pd(OAc)_2]_3$	PCy_3	trace
2	B_2Pin_2 (100)	none	PCy_3	nd
3	B_2Pin_2 (100)	$[Pd(OAc)_2]_3$	none	nd
4	**B_2Pin_2 (10)**	**$[Pd(OAc)_2]_3$**	**PCy_3**	**92**
5	B_2Pin_2 (10)	$[Pd(OAc)_2]_3$	PCy_3	10[b]
6	B_2Pin_2 (10)	$[Pd(OAc)_2]_3$	Segphos	29
7	B_2Pin_2 (10)	$[Pd(OAc)_2]_3$	Xphos	35
8	B_2Pin_2 (10)	$[Pd(OAc)_2]_3$	*rac*-BINAP	30
9	B_2Pin_2 (10)	$Pd_2(dba)_3$	PCy_3	50[c]
10	B_2Pin_2 (10)	$Pd(PPh_3)_4$	PCy_3	31[c]
11	B_2Pin_2 (10)	$Pd(dppf)Cl_2$	PCy_3	nd[c]

12	$B(OPh)_3$ (10)	$[Pd(OAc)_2]_3$	PCy_3	nd
13	$B(OMe)_3$ (10)	$[Pd(OAc)_2]_3$	PCy_3	nd
14	Ph-BPin (10)	$[Pd(OAc)_2]_3$	PCy_3	30
15	Ph-vinyl-Bpin (10)	$[Pd(OAc)_2]_3$	PCy_3	41
16	**BEt_3 (10)**	**$[Pd(OAc)_2]_3$**	**PCy_3**	**90**
17	**BPh_3 (10)**	**$[Pd(OAc)_2]_3$**	**PCy_3**	**99**

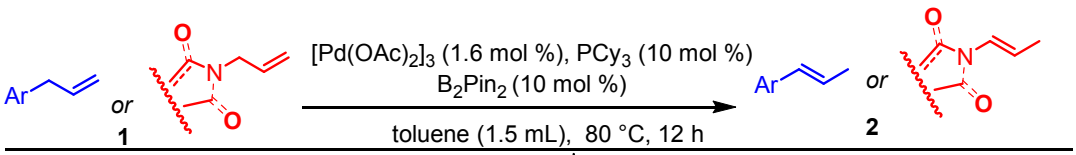
[a] Reaction conditions: **1a** (0.5 mmol), B_2Pin_2 (0.1 mmol), [Pd](1.6 mol%), PCy_3 (10 mol %), toluene (1 mL), at 80 °C, 12 h. [b] at 60 °C, [c] [Pd] 5 mol %, *nd* = not detected.

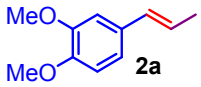
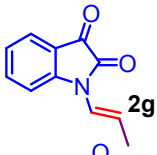
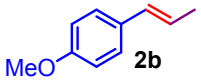
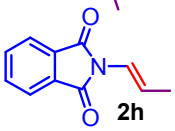
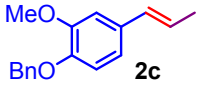
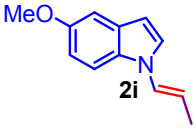
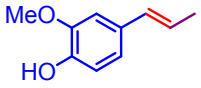
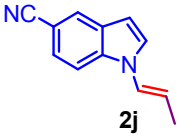
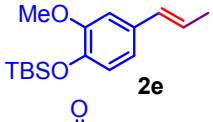
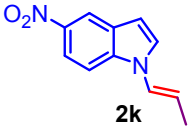
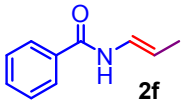
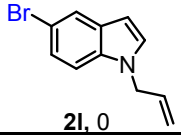
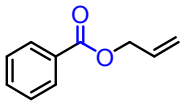
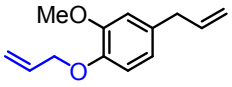
reagents such as $B(OPh)_3$ and $B(OMe)_3$ were not useful in promoting the isomerization (entries 12-13). Interestingly, the use of phenyl boronic acid pinacol ester (Ph-BPin) and phenylvinylboronic acid pinacol ester (Ph-vinyl-BPin) under the reaction conditions furnished the product **2** in 30, and 41% yields, respectively (entries 14 and 15). The isomerization also proceeded well with boranes such as BEt_3 and BPh_3 furnishing the product **2a** in excellent yields (90 and 99%, respectively, entries 16-17). The use of BPh_3 was restricted as it is highly moisture sensitive. Additionally, the room temperature reactions with water as additive did not proceed well with BPh_3. Therefore, further reactions for exploring the scope of the reactions have been carried out using B_2Pin_2.

With the optimal conditions in hand, we explored the scope and limitations of the palladium-catalyzed isomerization reaction. Subjecting a variety of allylbenzene derivatives for isomerization, the corresponding isoeugenol derivatives **2a-2e** were obtained in good to excellent yields (92, 92, 98, 50 and 97%, respectively) with excellent selectivity (94:6, 96:4, 95:5, 97:3, and 95:5 *E/Z* ratios, respectively, entries 1-5, Table 2). Notably, 4-allyl-2-methoxyphenol, which contains a phenolic OH group, showed a good compatibility with the metal catalyst and furnished the isomerized product **2d**, in moderate yield (entry 4, Table 2). Further, we tested the efficacy of isomerization by subjecting a few *N*-allyl derivatives for isomerization, which provided the corresponding enamines and enamides. As enamines and enamides are important frameworks for a number of organic transformations, we hope this method could be an easy alternative for synthesizing these precursors. As expected, the reaction of *N*-

allylbenzamide, under the optimal conditions furnished the expected isomerized product (*E*)-*N*-(prop-1-en-1-yl)benzamide (**2f**) in 69% yield with moderate selectivity (60:40; *E:Z* ratios, entry 6). Further, the same isomerization reaction of *N*-allylbenzamide was also carried out on a gram scale, affording the isomerized product **2f** in 67% yield (entry 6, Table 2). Interesting molecules such as *N*-allylisatin and *N*-allyl phthalimide derivatives formed the corresponding *E*-isomers **2g** and **2h,** exclusively, in excellent yields (86 and 96%, respectively, entries 7 and 8). Similarly, the isomerization of *N*-allyl indole derivatives was also facile and afforded the corresponding enamines **2i**, **2j**, and **2k** in excellent yields (89, 93, and 99%, respectively, entries 9-11) with good *E*-selectivity (82:18, 81:19 and 89:11 ratios, respectively).

Table 2. Isomerization for linear allyl substrates[a,b,c,d]



entry	product	*E/Z*	yield (%)[b]	entry	product	*E/Z*	yield (%)
1	 **2a**	94:6	92 90 (BEt_3)	7	 **2g**	100:0	86
2	 **2b**	96:4	92	8	 **2h**	100:0	96
3	 **2c**	95:5	98	9	 **2i**	82:18	89
4	 **2d**	97:3	50	10	 **2j**	81:19	93
5	 **2e**	95:5	97	11	 **2k**	89:11	99
6	 **2f**	60:40	69 67 (gram scale)				
unsuccessful substrates	 **2l**, 0				 **2m**, 0		
	 **2n**, 0						

[a] Reaction conditions: **1a** (0.5 mmol), B_2Pin_2 (0.1 mmol), $[Pd(OAc)_2]_3$ (1.6 mol %), PCy_3 (10 mol %), toluene (1.5 mL), at 80 °C, 12 h. [b] E/Z ratio are determined from ^{1}H-NMR (J_{trans} vs J_{cis}).[17]

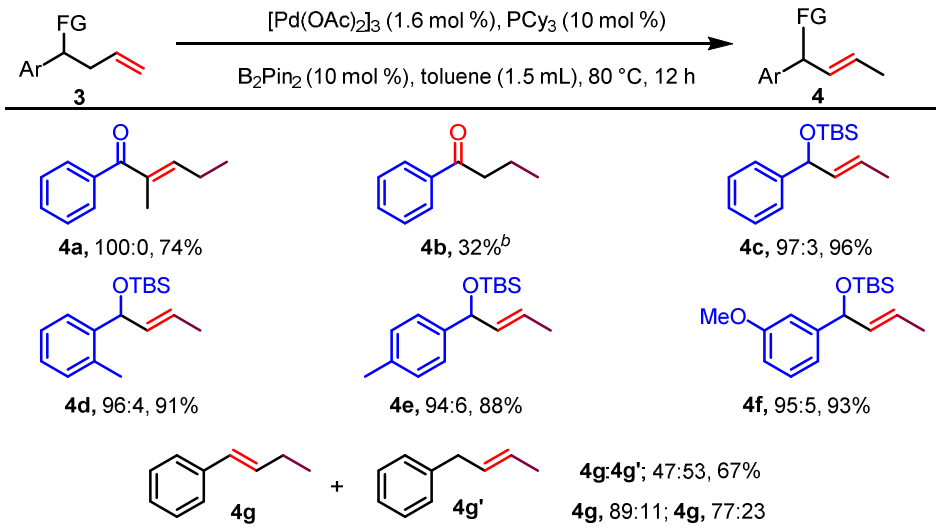
As can be seen in Table 2, the isomerization of olefins that contain nitrile and nitro functional groups proceeded well furnishing the isomerized products **2j** and **2k**, indicating that these functional groups are well tolerated under the reaction conditions. We noticed that bromo substitution on the indole derivative was detrimental for the reaction as the reaction of 1-allyl-5-bromo-1H-indole did not furnish the isomerized product **2l**. This outcome can be rationalized on basis of the possibility of oxidative insertion of Pd-

catalyst at the C_{sp2}-Br center resulting in poisoning of the catalyst. Similarly, allyl benzoate and 4-allyl-1-(allyloxy)-2-methoxybenzene that contain O-allyl group did not undergo isomerization reaction and failed to furnish isomerized products **2m** and **2n**. The isomerization of *O*-allyl of ethers and esters are considered to be unreactive and hence requires more efficient catalytic systems.

To expand the substrate scope, olefins with extended and functionalized chains were employed for the palladium catalyzed isomerization reaction. Thus, the reaction of 2- methyl-1-phenylpent-4-en-1-one **3a** under the isomerization conditions was successful and furnished the corresponding thermodynamically stable *E*-isomer **4a**, exclusively**,** in good yield (74%, Table 3). The smooth isomerization of 2-methyl-1-phenylpent-4-en-1-one **3a** over two positions to obtain **4a** supported the idea that the heteroatom coordination of the keto group. Therefore, we expected the transformation would also be consistent with the homoallylic alcohols to produce the corresponding ketone. Hence, employing 1-phenylbut-3-en-1-ol (**3b)** under the standard reaction conditions proved successful, affording the product **4b** in moderate yield (32%, Table 3). In the reaction of **3b,** a smooth isomerization of homoallylic alcohol (**3b**) furnished corresponding enol, which formed thermodynamically more favored butyrophenone **4b**. The corresponding allylic alcohol ((E)-1-phenylbut-2-en-1-ol), which forms after one carbon isomerization was the only byproduct observed in this reaction. To test the generality of this observation, we subjected the O-protected homoallylic alcohol, *tert*-butyldimethyl((1-phenylbut-3-en-1-yl)oxy)silane, under optimal isomerization reaction conditions to obtain the isomerized product **4c** in excellent yield (96%) and excellent selectivity (97:3 ratio, Table 3). Further, *tert*-butyldimethyl((1-(o-tolyl)but-3-en-1-yl)oxy)silane, a substrate with methyl substitution at the *ortho*–position, underwent a smooth isomerization to form the product **4d** in excellent yield (91%) with good selectivity (96:4 ratio, Table 3). Other substrates such as **3e**, and **3f** with *p*-methyl and *m*-methoxy substitution on the phenyl ring, formed the corresponding isomerized products **4e** and **4f** in 88 and 93%, respectively, with good selectivity (94:6, and 95:5 ratios, respectively, Table 3). In these examples, the reaction outcome was independent of the presence of sub-

stitutions at *ortho*- or *para*-positions for the aryl ring. Interestingly, the reaction of but-3-en-1-ylbenzene (**3g**), without any extra activating group, furnished a mixture of isomerized products **4g** and **4g′** in good yields (67%, and 47:53 ratios, Table 3).

Table 3. Substrate scope for functionalized olefins[a]

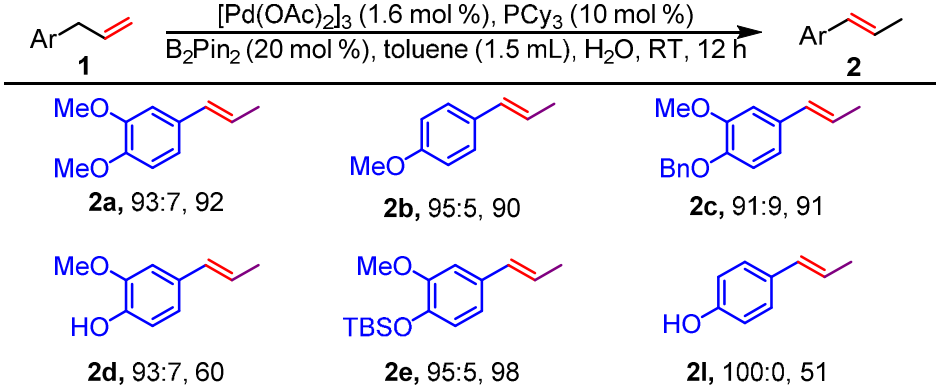


[a] Reaction conditions: **3** (0.5 mmol), B_2Pin_2 (0.1 mmol), $Pd(OAc)_2]_3$ (1.6 mol %), PCy_3 (10 mol%), toluene (1 mL), at 80 °C, 12 h. . [b] E/Z ratio are determined from ^{1}H-NMR (J_{trans} vs J_{cis})[17] [c] 1-phenylbut-3-en-1-ol was used as the starting material.

In light of our earlier studies[16] to generate hydrogen using Pd-H (generated *in situ*) with water, we performed isomerization reaction using water (5 equiv) as an additive. Our primary concept involved the array of metal-hydride catalyzed olefin isomerization reactions to be feasible with the Pd-H species that is generated from the reaction of diboron-H_2O with palladium. The process is advantageous in many aspects as it provides advantages such as site selective metal-hydride insertion, functional group tolerance etc. This idea led to a remarkable result and the isomerization proceeded very efficiently at room temperature (Table 4). Thus, the reaction of 4-allyl-1,2-dimethoxybenzene **1a** at ambient temperature under the optimal conditions, in the presence of water at room temperature, furnished the isomerized product **2a** in excellent yield and selectivity (92% yield, and selectivity, 93:7 ratio). With this interesting

outcome, we carried out a few more isomerization reactions, and as can be seen, various allyl benzene derivatives were isomerized at ambient temperature to furnish the corresponding isomerized olefins in good yields and good selectivity. Thus, the isomerization of 1-methoxy-4-vinylbenzene (**1b**), 1-(benzyloxy)-2- methoxy-4-vinylbenzene (**1c**), 2-methoxy-4-vinylphenol (**1d**), and *tert*-butyl(2-methoxy-4-vinylphenoxy) dimthylsilane (**1e**), in the presence of water, proceeded very well at room temperature furnishing the corresponding isomerized products **2b**, **2c**, **2d** and **2e** in good yields (90, 91, 60, and 98%, respectively) and good selectivity (95:5, 91:9, 93:7, and 95:5 ratios, respectively). The isomerization reaction of **1d** and **1l**, allylbenzene systems containing phenolic OH group, proceeded well furnishing the corresponding *E*-isomers, **2d** and (*E*)-4-(prop-1-en-1-yl)phenol (**2l**), exclusively, in moderate yields 60 and 51%, respectively (Table 4). Importantly, the palladium-hydride mediated olefin isomerization at room temperature is rare.[10c] In this regard, our method demonstrated a process which is feasibility at room temperature. The isomerization reactions with bromo- substituent and O-allyl substrates were ineffective under this catalytic condition as well, nevertheless the subject is under study on improving the catalyst efficiency.

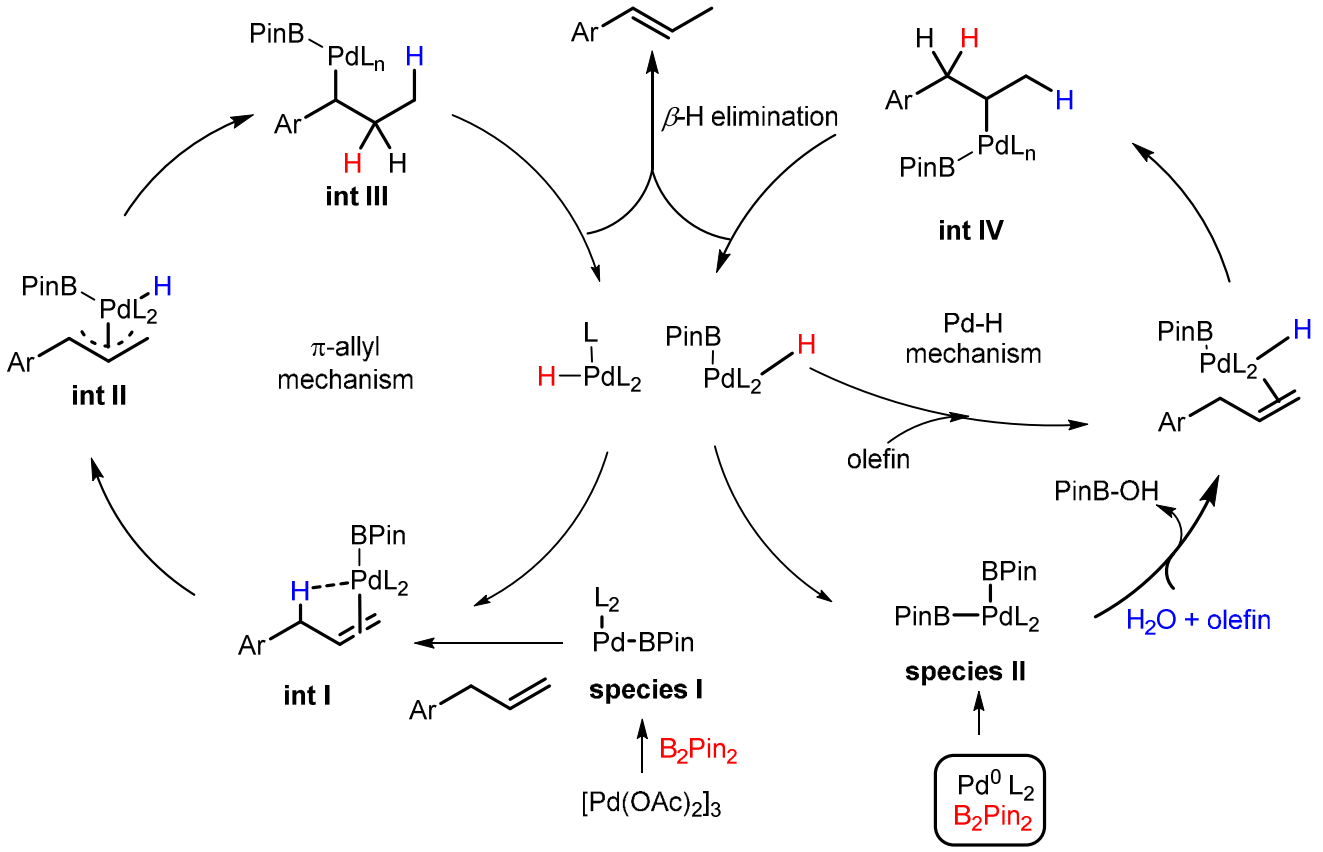
Table 4. Isomerization at ambient temperature[a]



[a] Reaction conditions: **1a** (0.5 mmol), B_2Pin_2 (0.2 mmol), $Pd(OAc)_2]_3$ (1.6 mol %), PCy_3 (10 mol %), H_2O (1 mmol), toluene (1 mL), at RT, 12 h. . [b] E/Z ratio are determined from ^{1}H-NMR (J_{trans} vs J_{cis}).[17]

The isomerization reaction is expected to follow two different pathways under variable conditions (Scheme 2). In the first case, wherein Pd/B_2Pin_2 is employed, the catalytic cycle possibly involves a non-hydride activation for the isomerization of olefins. The process commences with the formation of **species I** from the reaction of Lewis acidic B_2Pin_2, $Pd(OAc)_2]_3$ and ligand PCy_3 (Scheme 2a).[15,18] Similarly, the reaction of Lewis acidic B_2Pin_2, $Pd(OAc)_2]_3$ and ligand PCy_3 in H_2O generates the Pd- **I** with olefin facilitate the formation of π-allylic intermediate **int II** which forms **int III** with a hydride migration, followed by β-H elimination results in the formation of the corresponding isomerized product. On the other hand, the use of water as an additive completely changes the mechanistic pathway. As evident from our previous study,[16b] and concurrent reports[18] on the formation of the Pd-H (**species II**) from $Pd/B_2Pin_2/H_2O$ combination,[16] we hypothesize that the reaction has a possibility of involving a metal hydride intermediate for the isomerization of olefins. Thus, the reaction of olefin with species **II**, initiates hydride migration forming the intermediate **int IV** which upon β-hydride elimination forms the isomerized product.

Scheme 2. Plausible mechanism



In conclusion, a simple and mild catalytic system has been developed for a facile isomerization of unactivated as well as activated olefins. This method provides a simple method for synthesizing highly functionalized olefinic frameworks. This strategy has been used for synthesizing a variety of enamines, enamides and O-protected allylic alcohol derivatives. The investigation to drive the isomerization at room temperature using a Pd-Hydride, generated *in-situ,* was successful which is performed using water as an additive. Further mechanistic studies to obtain insights into the reaction mechanism are underway in our laboratory.

EXPERIMENTAL SECTION

General Information. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$or DMSO-d_6.Tetramethylsilane (TMS; δ = 0.00 ppm) for ^{1}H NMR in $CDCl_3$, and residual non-deuterated solvent

peak (δ = 2.50 ppm) in DMSO-d_6, served as an internal standard. The solvent signal ($CDCl_3$, δ = 77.00 ppm; and DMSO-d_6, δ = 39.5 ppm) was used as internal standard for ^{13}C NMR. IR spectra were measured using an FT-IR spectrometer. Mass spectra were obtained with a Q-TOF Mass Spectrometer (HRMS). Flash column chromatography was carried out by packing glass columns with commercial silica gel 230-400 mesh (commercial suppliers) and thin-layer chromatography was carried out using silica gel GF-254. All catalysts, reagents and reactants were procured from commercial suppliers. All solvents were distilled under nitrogen atmosphere prior to use. Toluene was dried over Na. Unless otherwise noted, commercially available chemicals were distilled and degassed before use. Palladium acetate (II) trimer (CAS: 3375-31-3) was used for the reaction.

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I. General procedures for isomerizationof olefins at 80 ^{o}C

To an oven-dried Teflon capped vial equipped with a magnetic stirring bar were added sequentially bis(pinacolato)diboron (12 mg, 0.1 mmol), PCy_3 (14 mg, 10 mol%), $[Pd(OAc)_2]_3$ (5 mg, 1.6 mol %) and alkene (0.5 mmol) in toluene (1.5 mL) under argon. The mixture was stirred at 80 °C for 12 h (monitored by TLC). Upon completion of the reaction, the resulting mixture was filtered through a short column of silica gel (eluted with EtOAc) and concentrated. This crude mixture was further purified on a silica gel column chromatography to obtain the pure product.

II. General procedures for isomerisation of olefins at RT

To an oven-dried Teflon capped vial equipped with a magnetic stirring bar were added sequentially bis(pinacolato)diboron (24 mg, 0.2 mmol), PCy_3 (14 mg, 10 mol %), $[Pd(OAc)_2]_3$ (5 mg, 1.6 mol %), water (1 mmol), and alkene (0.5 mmol) in toluene (1.5 mL) under argon. The mixture was stirred at

room temperature for 12 h (monitored by TLC). Upon completion of the reaction, the resulting mixture was filtered through a short column of silica gel (eluted with EtOAc) and concentrated. This crude mixture was further purified on a silica gel column chromatography to obtain the pure product.

Characterization data for products

(*E*)-1,2-Dimethoxy-4-(prop-1-en-1-yl)benzene (2a):[18] Prepared as described in the general experimental procedure. colourless liquid; yield:92% (82 mg); R_f (5% EtOAc/hexane): 0.6; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.89 (s, 1H), 6.87-6.78 (m, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.15-6.06 (m, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.87 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.9, 148.1, 131.1, 130.5, 123.7, 118.6, 111.1, 108.3, 55.9, 55.7, 18.3; **HRESI-MS** (*m/z*): Calculated for $C_{11}H_{14}O_2$ (M + Na): 201.0891, found (M + Na): 201.0889.

(*E*)-1-Methoxy-4-(prop-1-en-1-yl)benzene (2b):[4c] Prepared as described in the general experimental procedure. colourless liquid; yield: 92% (68 mg); R_f (5% EtOAc/hexane): 0.9; **IR** (Neat, cm^{-1}): 1510, 1460, 1282, 1247, 1176, 1112, 1036, 964; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.13-6.04 (m, 1H), 3.79 (s, 3H), 1.85 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 158.6, 130.8, 130.3, 126.9, 123.4, 113.9, 55.2, 18.4.

(*E*)-1-(Benzyloxy)-2-methoxy-4-(prop-1-en-1-yl)benzene (2c):[19]Prepared as described in the general experimental procedure. colourless liquid; yield:98% (124 mg); R_f (5% EtOAc/hexane): 0.7; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42-7.41 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 6.89 (s, 1H), 6.78 (s, 2H), 6.31 (d, *J* = 15.6 Hz, 1H), 6.13-6.04 (m, 1H), 3.87 (s, 3H), 1.84 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 149.6, 147.2, 137.2, 131.6, 130.5, 128.4, 127.7, 127.2, 123.9, 118.5, 114.1, 109.1, 55.9, 18.3; **HRESI-MS** (*m/z*): Calculated for $C_{17}H_{18}O_2$ (M + Na): 277.1204, found (M + Na): 277.1202.

(*E*)-2-Methoxy-4-(prop-1-en-1-yl)phenol (2d):[21] Prepared as described in the general experimental procedure. colourless liquid; yield:50% (41 mg); R_f (5% EtOAc/hexane): 0.1; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.89 (s, 1H), 6.87-6.78 (m, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.15-6.06 (m, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.87 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.9, 148.1, 131.1, 130.5, 123.7, 118.6, 111.1, 108.3, 55.9, 55.7, 18.3.

(*E*)-*tert*-Butyl(2-methoxy-4-(prop-1-en-1-yl)phenoxy)dimethylsilane (2e):[20] Prepared as described in the general experimental procedure. colourless liquid; yield:97% (135 mg); R_f (5% EtOAc/hexane): 0.9; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.84 (s, 1H), 6.76 (s, 2H), 6.32 (d, *J* = 15.6 Hz, 1H), 6.13-6.04 (m, 1H), 3.80 (s, 3H), 1.85 (d, *J* = 6.4 Hz, 3H), 0.98 (s, 9H), 0.1 (s, 6H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 150.9, 144.2, 131.9, 130.7, 123.7, 120.8, 118.6, 109.4, 55.4, 25.7, 18.4, 18,3; **HRESI-MS** (*m/z*): Calculated for $C_{16}H_{26}O_2Si$ (M + Na): 301.1600, found (M + Na): 301.1601.

(*E*)-*N*-(Prop-1-en-1-yl)benzamide (2f):[22] Prepared as described in the general experimental procedure. colourless liquid; yield: 69% (56 mg), for gram scale 67 % (675 mg); R_f (10% EtOAc/hexane): 0.2; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (br s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.49-7.38 (m, 3H), 6.97-6.91 (m, 1H), 5.38-5.29 (m, 1H), 1.71 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 164.3, 133.8, 131.6, 128.5, 127.0, 123.6, 108.9, 14.9; **HRESI-MS** (*m/z*): Calculated for $C_{10}H_{11}O$ (M + Na): 184.0738, found (M + Na): 184.0739.

(*E*)-*N*-(Prop-1-en-1-yl)benzamide (2f′):[22] Prepared as described in the general experimental procedure. colourless liquid; yield: 55%; R_f (10% EtOAc/hexane): 0.3; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (br s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.49-7.38 (m, 3H), 6.97-6.91 (m, 1H), 5.38-5.29 (m, 1H), 1.71 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz,

$CDCl_3$): δ 164.3, 133.8, 131.6, 128.5, 127.0, 123.6, 108.9, 14.9; **HRESI-MS** (*m/z*): Calculated for $C_{10}H_{11}O$ (M + Na): 184.0738, found (M + Na): 184.0739.

(*E*)-1-(Prop-1-en-1-yl)indoline-2,3-dione (2g): Prepared as described in the general experimental procedure. colourless liquid; yield: 96% (90 mg); R_f(5% EtOAc/hexane): 0.8; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64-7.60 (m, 2H), 7.16-7.10 (m, 2H), 6.44-6.31 (m, 2H), 1.9 (d, *J* = 6 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.9, 148.1, 131.1, 130.5, 123.7, 118.6, 111.1, 108.3, 55.9, 55.7, 18.3; **HRESI-MS** (*m/z*): Calculated for $C_{11}H_9NO_2$ (M + Na): 210.0531, found (M + Na): 210.0535.

(*E*)-2-(Prop-1-en-1-yl)isoindoline-1,3-dione (2h): Prepared as described in the general experimental procedure. yellow solid; yield:86% (80 mg); R_f(10% EtOAc/hexane): 0.4; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86-7.83 (m, 2H), 7.74-7.71 (m, 2H), 6.59-6.54 (m, 2H), 1.84 (d, *J* = 8.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 166.6, 134.2, 131.6, 123.4, 118.3, 118.0, 16.2; **HRESI-MS** (*m/z*): Calculated for $C_{11}H_9NO_2$ (M + H): 188.0712, found (M + Na): 188.0712.

(*E*)-5-Methoxy-1-(prop-1-en-1-yl)-1H-indole (2i): Prepared as described in the general experimental procedure. pale yellow liquid; yield:89% (84 mg); R_f(10% EtOAc/hexane): 0.7; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.21 (m, 2H), 7.06 (s, 1H), 6.92-6.86 (m, 2H), 6.47 (m, 1H), 5.76-5.70 (m, 1H), 3.83 (s, 3H), 1.85 (d, *J* = 6.7 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 136.4, 129.8, 128.3, 127.7, 126.7, 126.3, 126.3, 126.2, 125.0, 124.8, 123.8, 123.7, 121.8, 154.5, 154.4, 131.5, 130.5, 129.1, 128.4, 127.9, 124.9, 124.8, 117.5, 112.2, 112.1, 110.7, 110.4, 103.2, 102.8, 102.4, 55.8, 15.2, 12.9; **HRESI-MS** (*m/z*): Calculated for $C_{12}H_{13}NO$ (M + H): 188.1075, found (M + Na): 188.1077.

(*E*)-1-(Prop-1-en-1-yl)-1H-indole-5-carbonitrile (2j): Prepared as described in the general experimental procedure. colourless liquid; yield:93% (85 mg); R_f (10% EtOAc/hexane): 0.4; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 8.12 (d, 2.4 Hz, 1H), 7.45-7.41 (m, 3H), 6.91 (d, *J* = 13.6 Hz, 1H), 6.62 (dd, *J* = 6.7, 1.4 Hz, 1H), 5.88-5.80 (m, 1H), 1.90 (d, *J* = 6.7, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 136.4, 129.8, 128.3, 127.7, 126.7, 126.3, 126.3, 126.2, 125.0, 124.8, 123.8, 123.7, 121.8, 120.5, 120.4, 114.1, 110.9, 110.3, 104.2, 103.3, 103.1, 15.1, 12.8; **HRESI-MS** (*m/z*): Calculated for $C_{12}H_{10}N_2$ (M + Na): 205.0745, found (M + Na): 205.0742.

(*E*)-5-Nitro-1-(prop-1-en-1-yl)-1H-indole (2k): Prepared as described in the general experimental procedure. pale yellow liquid; yield:98% (99 mg); R_f (10% EtOAc/hexane): 0.5; **IR** (Neat, cm^{-1}): 1579, 1505, 1451, 1395, 1332, 1221, 1064, 926; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.5 (s, 1H), 8.12 (d, *J* = 2.4 Hz, 1H), 7.46-7.42 (m, 2H), 6.95 (d, *J* = 16 Hz, 1H), 6.73 (dd, *J* = 6.7 Hz, 1.4 Hz, 1H), 5.93-5.85 (m, 1H), 1.92 (dd, *J* = 6.7, 1.4 Hz, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 142.0, 137.7, 130.7, 127.9, 127.7, 124.0, 122.5, 118.0, 117.9, 117.8, 117.6, 114.8, 110.1, 109.4, 105.7, 104.9, 15.2, 12.9;**HRESI-MS** (*m/z*): Calculated for $C_{11}H_{10}N_2O_2$ (M + H): 203.0821, found (M + Na): 203.0821.

(*E*)-2-Methyl-1-phenylpent-2-en-1-one & (E)-2-methyl-1-phenylpent-3-en-1-one (4a & 4a′): Prepared as described in the general experimental procedure. colourless liquid; yield:74% (64 mg); R_f (10% EtOAc/hexane): 0.55; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856;(**3a**) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39-7.66 (m, 5H), 6.27-6.32 (m, 1H), 2.25-2.35 (m, 2H), 1.97-1.98 (m, 3H), 1.05 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 199.1, 148.2, 138.8, 135.9, 132.9, 131.3, 129.3, 128.0, 31.8, 22.4, 13.0. (**3a′**) **^{1}H NMR** (500 MHz, CDCl3) δ 7.99 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 5.61 – 5.58 (m, *J* = 5.6, 3.3 Hz, 2H), 4.14 – 4.09 (m, 1H), 1.66 (dd, *J* = 3.6, 1.1 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 201.91, 136.78,

133.04, 131.19, 128.80, 128.77, 127.64, 44.75, 18.29, 17.73. **HRESI-MS** (*m/z*): Calculated for $C_{12}H_{14}O$ (M + Na): 197.0942, found (M + Na): 197.0947.

1-Phenylbutan-1-one (4b):[23] Prepared as described in the general experimental procedure. pale yellow liquid; yield:32% (24 mg); R_f (5% EtOAc/hexane): 0.8; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39-7.36 (m, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 1.74–1.66 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ: 200.5, 137.2, 132.9, 128.6, 128.0, 40.5, 17.8, 13.9.

(*E*)-*tert*-Butyldimethyl((1-phenylbut-2-en-1-yl)oxy)silane (4c):[18] Prepared as described in the general experimental procedure. colourless liquid; yield:96% (126 mg); R_f (5% EtOAc/hexane): 0.9; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856;**^{1}H NMR** (400 MHz, $CHCl_3$) δ(ppm) 7.35 (m ,5H), 5.65 (m, 1H), 5.60 (m, 1H), 5.15 (, d, 1H, *J* = 6.4 Hz), 1.83 (d, 1/10 of 3H, *J* = 5.4 Hz), 1.71 (d, 9/10 of 3H, *J* = 6.1 Hz), 0.94 (s, 9H), 0.09 (s, 3H), 0.03 (s, 3H);); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ (ppm) 144.1, 134.6, 127.7, 126.4, 125.4, 125.1, 124.7, 75.2, 69.4(min), 25.5, 17.9, 17.2, -4.8, -5.1; **HRESI-MS** (*m/z*): Calculated for $C_{16}H_{26}O_{Si}$ (M + Na): 285.1650, found (M + Na): 285.1651.

(*E*)-*tert*-Butyldimethyl((1-(o-tolyl)but-2-en-1-yl)oxy)silane (4d): Prepared as described in the general experimental procedure. colourless liquid; yield:91% (126 mg); R_f (5% EtOAc/hexane): 0.9; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 5.60-5.49 (m, 2H), 5.27 (d, *J* = 5.6 Hz, 1H), 2.29 (s, 3H), 1.60 (d, *J* = 5.6 Hz, 3H), 0.9 (s, 9H), 0.05 (s, 3H), 0.01 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 142.3, 134.0, 133.6, 126.7, 126.1, 125.9, 125.0, 25.9, 19.1, 18.3, 17.5, -4.6, -4.8; **HRESI-MS** (*m/z*): Calculated for $C_{17}H_{28}OSi$ (M + Na): 299.1807, found (M + Na): 299.1811.

(*E*)-*tert*-Butyldimethyl((1-(p-tolyl)but-2-en-1-yl)oxy)silane (4e): Prepared as described in the general experimental procedure. colourless liquid; yield:88% (122 mg); R_f (5% EtOAc/hexane): 0.9; **IR** (Neat,

cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24-7.20 (m, 1H), 6.93-6.89 (m, 2H), 6.78-6.75 (m, 1H), 5.7-5.61 (m, 1H), 5.57-5.51 (m, 1H), 5.10 (d, *J* = 2 Hz, 1H), 3.8 (s, 3H), 1.70 (d, *J* = 5.6 Hz, 3H), 0.9 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 159.5, 146.3, 134.8, 129.0, 125.1, 118.2, 112.2, 111.2, 55.12, 25.9, 25.8, 18.3, 17.5, -4.5, -4.8; **HRESI-MS** (*m/z*): Calculated for $C_{17}H_{28}OSi$ (M + Na): 299.1807, found (M + Na): 299.1810.

(*E*)-*tert*-Butyl((1-(3-methoxyphenyl)but-2-en-1-yl)oxy) dimethylsilane (4f): Prepared as described in the general experimental procedure. colourless liquid; yield:93% (136 mg); R_f (5% EtOAc/hexane): 0.8; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.89 (s, 1H), 6.87-6.78 (m, 2H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.15-6.06 (m, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.87 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.9, 148.1, 131.1, 130.5, 123.7, 118.6, 111.1, 108.3, 55.9, 55.7, 18.3; **HRESI-MS** (*m/z*): Calculated for $C_{17}H_{28}O_2Si$ (M + Na): 315.1756, found (M + Na): 315.1753.

(*E*)-But-1-en-1-ylbenzene & (E)-but-2-en-1-ylbenzene (4g & 4g′):[24] Prepared as described in the general experimental procedure. colourless liquid; yield:67% (45 mg); R_f (10% EtOAc/hexane): 0.4; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.3-7.25 (m, 6H), 7.19-7.15 (m, 4H), 6.37 (d, *J* = 16 Hz, 0.8 H), 6.29-6.22 (m, 0.8 H), 5.6-5.47 (m, 2 H), 3.31 (d, *J* = 6.3 Hz, 2H), 2.2 (m, 1.6 H), 1.68 (m, 3H), 1.08 (t, *J* = 7.5 Hx, 2.6 H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 141.0, 137.9, 132.6, 130.8, 128.9, 128.7, 128.4,128.38, 128.32, 126.7, 126.3, 125.88, 125.85, 125.79,124.8, 39.0, 33.1, 29.7, 26.0, 17.8, 14.11, 13.6, 12.8.

(*E*)-4-(Prop-1-en-1-yl)phenol (2l):[25] Prepared as described in the general experimental procedure. colourless liquid; yield:51% (34 mg); R_f (20% ethyl acetate/hexane): 0.46; **IR** (Neat, cm^{-1}): 1513, 1413, 1263, 1232, 1191, 1027, 963, 856; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.85 (d, J = 7.2 Hz, 3H), 4.9 (s, 1H)

6.09 (dq, J = 18.0, 7.2 Hz, 1H), 6.34 (d, J = 18.0 Hz,1H), 6.74 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8, 2H); **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100 MHz) δ 18.3, 115.3, 123.5, 127.0, 130.2, 132.9, 154.4.

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION: The optimization data**,** ^1H, and ^{13}C NMR spectral data of all compounds.

REFERENCES AND NOTES

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