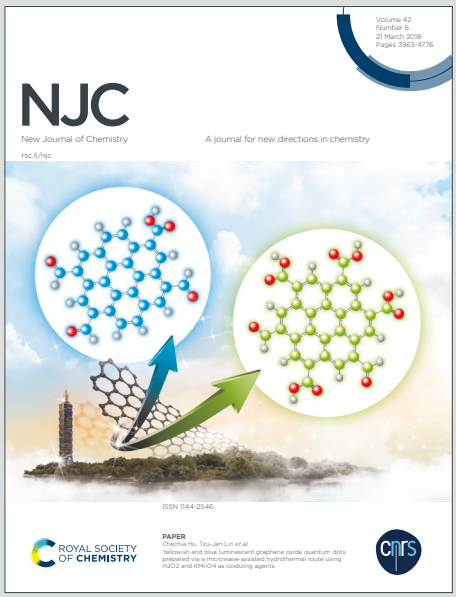
NJC

New Journal of Chemistry

A journal for new directions in chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Sakuramoto, Y. Donaka, M. Tobisu and T. Moriuchi, *New J. Chem.*, 2019, DOI: 10.1039/C9NJ01905G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

View Article Online
DOI: 10.1039/C9NJ01905G

ARTICLE

Oxovanadium(V)-Catalyzed Deoxygenative Homocoupling Reaction of Alcohols†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Takashi Sakuramoto,[a] Yosuke Donaka,[b] Mamoru Tobisu [a] and Toshiyuki Moriuchi *[a,b]

Oxovanadium(V)-catalysed transformation of alcohols in the presence of hydrazine derivatives was demostrated. Direct hydrazination reaction of 1,3-diphenylprop-2-en-1-ol with 1,1-diphenylhydrazine in the presence of $VO(OSiPh_3)_3$ as a catalyst and MS3A as a dehydrating reagent proceeded to afford the corresponding hydrazination product. On the contrary, the utilization of 1,1-dimethylhydrazine instead of 1,1-diphenylhydrazine was found to induce the deoxygenative homocoupling reaction of the allyl alcohol to give the corresponding 1,5-diene as a major product. In addition to the deoxygenative homocoupling product, the allyl amine into which aniline was introduced was also obtained by using 1,2-diphenylhydrazine in the reaction of 1,3-diphenyl-2-methylprop-2-en-1-ol. Oxovanadium(V)-catalyzed deoxygenative homocoupling reaction of benzyl alcohols could be also performed in the presence of 1,1-dimethylhydrazine.

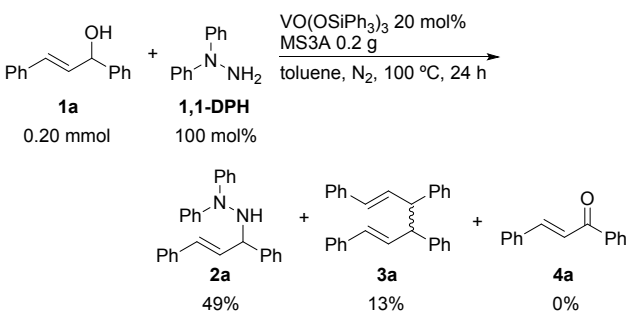
Introduction

Development of synthetic methods for compounds containing 1,5-diene structure is an important research topic[1] because compounds containing 1,5-diene structure serve as precursors for the synthesis of natural products.[2] The utilization of allyl alcohols, which are provided in bulk and obtained cheaply, is regarded as one of a reliable strategy for synthesis of 1,5-diene structures. Formation of 1,5-diene structures from allylic acetates have been reported,[1c-e] wherein two steps are needed to synthesize 1,5-diene structures from allyl alcohols and undesired by-products are given. From the view point of biomass conversion, deoxygenative reaction is focused on. For example, deoxygenative coupling of 2-arylethanols catalyzed by Ir, Ru, or Mn catalyst has been reported.[3] Synthesis of 1,5-diene structure through deoxygenative homocoupling reaction of allyl alcohols have been also demonstrated by using $TiCl_3$,[1a] $NbCl_5$[1b] or La[1f]. However, addition of metal salts is necessary in these reactions.

The utilization of oxophilicity of vanadium compounds is regarded as one of useful methods for deoxygenation of alcohols.[4] Actually, Kataoka and Tani reported vanadium(II)-induced reductive coupling reaction of ketones.[5] Also, Nicholas group demonstrated the deoxygenative homocoupling reaction of alcohols by using oxovanadium(V) complexes.[6] In this reaction, however, ketones were produced as by-products through oxidation of alcohols used as substrates. Selective synthesis of coupling products through vanadium-catalysed deoxygenative homocoupling reaction of alcohols has not been achieved. Generally, a reducing reagent is required to promote the catalytic deoxygenative coupling reaction.[1] The deoxygenative homocoupling reaction of alcohols utilizing organic reductants has not been performed. We have already reported oxovanadium(V)-catalysed direct amination of allyl alcohols.[7] During the development of the vanadium-catalyzed transformation of allyl alcohols, hydrazine derivatives were found to serve as reductants to induce the deoxygenative homocoupling reaction of allyl alcohols. From these points of view, we herein report oxovanadium(V)-catalysed direct hydrazination of allyl alcohol and deoxygenative homocoupling reaction of alcohols depending on hydrazine derivatives.

Results and discussion

Our study began by evaluating the effect of hydrazine derivatives in oxovanadium(V)-catalysed direct hydrazination of allyl alcohols. The reaction of 1,3-diphenylprop-2-en-1-ol (**1a**) with 1,1-diphenylhydrazine (**1,1-DPH**) in the presence of $VO(OSiPh_3)_3$ (20 mol%) as a catalyst and MS3A (0.2 g) as a

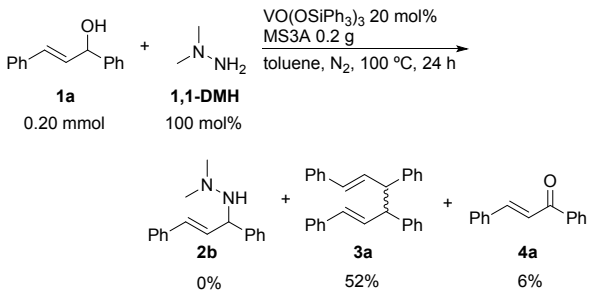


Scheme 1 Direct hydrazination reaction of allyl alcohol **1a** with **1,1-DPH**.

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan.
[b] Present address: Division of Molecular Materials Science, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

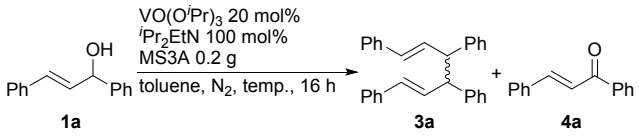
View Article Online
DOI: 10.1039/C9NJ01905G



Scheme 2 Deoxygenative homocoupling reaction of allyl alcohol **1a** in the presence of **1,1-DMH**.

dehydrating reagent at 100 °C was found to afford the corresponding allyl hydrazine **2a** in 49% yield as a major product with the deoxygenative homocoupling product 1,5-diene **3a** in 13% yield (Scheme 1). On the contrary, the deoxygenative homocoupling reaction of allyl alcohol was occurred instead of the hydrazination reaction in the case of 1,1-dimethylhydrazine (**1,1-DMH**), resulting in the formation of 1,5-diene **3a** in 52% yield (*dl*/*meso* = 1:1) as a major product, wherein a small amount of *E*-chalcone (**4a**), the oxidized product of allyl alcohol **1a**, was obtained as a by-product (Scheme 2).

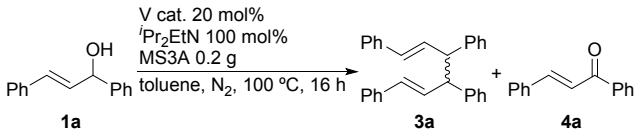
Table 1 The vanadium-catalyzed deoxygenative homocoupling reaction of 1,3-diphenylprop-2-en-1-ol (**1a**).[a,b]



Entry	Reaction conditions	Yield of **3a**[c] (%)	Yield of **4a** (%)
1	at 100 ºC	45	30
2	without $VO(O^iPr)_3$ at 100 ºC	0	0
3	without $^iPr_2EtN$ at 100 ºC	12	trace
4	without MS3A at 100 ºC	16	13
5	at 80 ºC	46	28
6	at 50 ºC	5	5

[a] Reaction conditions: 0.20 mmol of 1,3-diphenylprop-2-en-1-ol (**1a**), 20 mol% of $VO(O^iPr)_3$, 100 mol% of $^iPr_2EtN$, 0.2 g MS3A, 1.0 mL toluene, under nitrogen atmosphere. [b] The yield was determined by ^1H NMR. [c] NMR yield (%) = [product (mmol) x 2 / substrate (mmol)] x 100.

Table 2 The effect of vanadium catalyst for deoxygenative homocoupling reaction of 1,3-diphenylprop-2-en-1-ol (**1a**).[a,b]



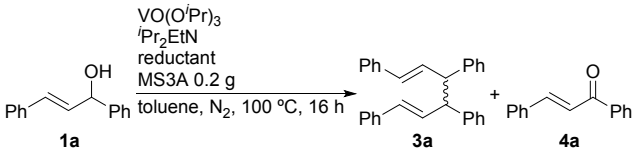
Entry	V cat.	Yield of **3a**[c] (%)	Yield of **4a** (%)
1	$VO(O^iPr)_3$	45	30
2	$VO(OSiPh_3)_3$	13	7
3	$VO(acac)_2$	46	25
4	VCl_3	44	17

[a] Reaction conditions: 0.20 mmol of 1,3-diphenylprop-2-en-1-ol (**1a**), 20 mol% of $VO(O^iPr)_3$, 100 mol% of $^iPr_2EtN$, 0.2 g MS3A, 1.0 mL toluene, under nitrogen atmosphere. [b] The yield was determined by ^1H NMR. [c] NMR yield (%) = [product (mmol) x 2 / substrate (mmol)] x 100.

The effect of oxovanadium compounds was examined in the deoxygenative homocoupling reaction of allyl alcohol (Tables 1 and 2). Allyl alcohol **1a** was converted to 1,5-diene **3a** and ketone **4a** in the presence of $VO(O^iPr)_3$ as a catalyst, *N*,*N*-diisopropylethylamine ($^iPr_2EtN$) as a base and MS3A as a dehydrating reagent at 100 °C (entry 1). The deoxygenative homocoupling reaction was not performed in the absence of $VO(O^iPr)_3$ (entry 2), indicating that the oxovanadium(V) compound plays an important role in the deoxygenative homocoupling reaction of allyl alcohol. The catalytic reaction without $^iPr_2EtN$ resulted in a lower yield (entry 3). MS3A was found to serve as a key role as dehydrating reagent to remove generated water (entry 4). The deoxygenative homocoupling reaction of **1a** proceeded successfully even at 80 °C (entry 5). Reducing the reaction temperature to 50 °C caused a decrease in the yield of **3a** (entry 6). The utilization of $VO(OSiPh_3)_3$ instead of $VO(O^iPr)_3$ led to lower yield than $VO(O^iPr)_3$, (Table 2, entries 1 and 2). Oxovanadium(IV) compound $VO(acac)_2$ also showed similar reactivity (entry 3). By using low-valent VCl_3, the formation of the oxidized product **4a** could be suppressed a little (entry 4).

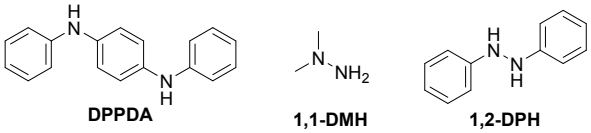
To improve the yield of 1,5-diene **3a**, organic reductants for the deoxygenative homocoupling reaction of allyl alcohol **1a** was investigated. Although the use of *N*,*N'*-diphenyl-*p*-phenylenediamine (**DPPDA**) or ascorbic acid did not show an enhanced yield of **3a** (Table 3, entries 1-3) hydrazine derivatives

Table 3 The vanadium-catalyzed deoxygenative homocoupling reaction of 1,3-diphenylprop-2-en-1-ol (**1a**) in the presence of reductants.[a,b]

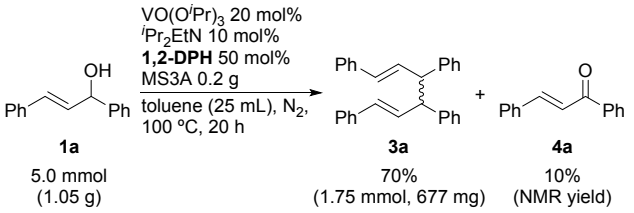


Entry	reductant (mol%)	$VO(O^iPr)_3$ (mol %)	$^iPr_2EtN$ (mol %)	Yield of **3a**[c] (%)	Yield of **4a** (%)
1	none	20	100	45	31
2	**DPPDA** (50 mol%)	20	100	38	24
3	ascorbic acid (50 mol%)	20	100	42	29
4	**1,1-DMH** (50 mol%)	20	100	54	15
5	**1,1-DMH** (50 mol%)	20	0	62	7
6	**1,1-DMH** (100 mol%)	20	0	49	11
7	**1,1-DMH** (50 mol%)	10	0	53	10
8	**1,1-DMH** (50 mol%)	5	0	50	10
9	**1,1-DMH** (50 mol%)	3	0	45	12
10	**1,2-DPH** (50 mol%)	20	100	65	14
11	**1,2-DPH** (50 mol%)	20	50	65	12
12	**1,2-DPH** (50 mol%)	20	20	69	11
13	**1,2-DPH** (50 mol%)	20	10	73	11
14	**1,2-DPH** (50 mol%)	20	0	31	trace

[a] Reaction conditions: 0.20 mmol of 1,3-diphenylprop-2-en-1-ol (**1a**), $VO(O^iPr)_3$, $^iPr_2EtN$, 0.2 g MS3A, 1.0 mL toluene, under nitrogen atmosphere. [b] The yield was determined by ^1H NMR. [c] NMR yield (%) = [product (mmol) x 2 / substrate (mmol)] x 100.

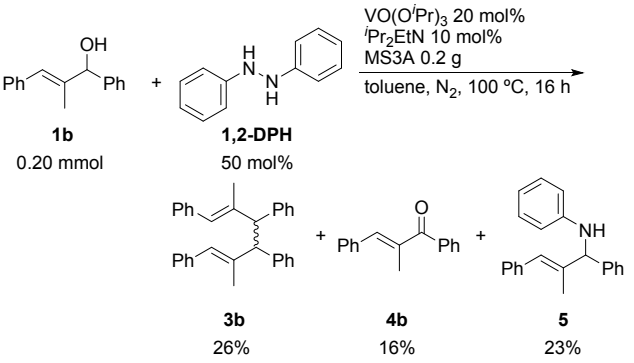


were disclosed to be effective for the deoxygenative homocoupling reaction. When the deoxygenative homocoupling reaction of **1a** was performed with 50 mol% of **1,1-DMH**, 1,5-diene **3a** was obtained in 54% yield and the yield of **4a** got lower than the condition without **1,1-DMH** (entry 4). The reaction without $^{i}Pr_2EtN$ proceeded well to afford 1,5-diene **3a** in 62% yield as shown in entry 5. However, increasing the amount of **1,1-DMH** to 100 mol% resulted in lower yield (entry 6). A decrease in the catalyst loading of $VO(O^{i}Pr)_3$ resulted in a decrease in the yield of **3a** (entries 7-9). The utilization of 1,2-diphenylhydrazine (**1,2-DPH**) instead of **1,1-DMH** was found to be efficacious to the deoxygenative homocoupling reaction in the condition with 100 mol% of $^{i}Pr_2EtN$ (entry 10). The yield of **3a** was improved by reducing the amount of $^{i}Pr_2EtN$ in the case of **1,2-DPH** (entries 11 and 12). Eventually, 1,5-Diene **3a** was obtained in 73 % yield in the condition with 10 mol% of $^{i}Pr_2EtN$ (entry 13). However, the reaction without $^{i}Pr_2EtN$ showed a significant decrease in the yield of **3a** (entry 14). It is worth mentioning that gram-scale oxovanadium(V)-catalysed deoxygenative homocoupling reaction of **1a** with **1,2-DPH** as a reductant could be performed to afford the 1,5-diene **3a** in 70% isolated yield (Scheme 3).



Scheme 3 Gram-scale oxovanadium(V)-catalyzed deoxygenative homocoupling reaction of allyl alcohol **1a** in the presence of **1,2-DPH**.

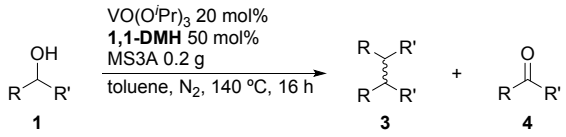
To explore the validity of this catalytic system, the substrate scope of allyl alcohols was examined under the optimized reaction conditions as shown in entry 13 of Table 3. When 1,3-diphenyl-2-methylprop-2-en-1-ol (**1b**) was used as allyl alcohol, 1,5-diene **3b** (*dl*/*meso* = 1:1) was given in 26% yield (Scheme 4). In addition to the deoxygenative homocoupling product, allyl amine **5** into which aniline was introduced was also detected as a by-product in 23% yield. In this reaction, **1,2-DPH** appears to serve as an aniline source.

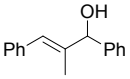
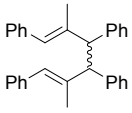
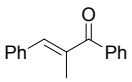
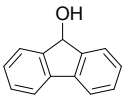
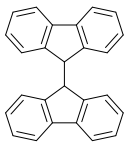
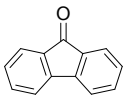


Scheme 4 Deoxygenative homocoupling reaction of allyl alcohol **1b** in the presence of **1,2-DPH**.

The applicability for the deoxygenative homocoupling reaction was investigated by using **1,1-DMH** as a reductant (Table 4). Starting from the α-methylated alcohol **1b**, 1,5-diene **3b** (*dl*/*meso* = 1:1) was obtained in 46% yield (entry 1). This catalytic system could be applied to the deoxygenative homocoupling reaction of diphenylmethanol (**1c**) to give the desired coupling product **3c** in 65% yield (entry 2). The catalytic deoxygenative homocoupling reaction of 1-phenylethan-1-ol (**1d**) proceeded moderately to yield the corresponding coupling product **3d** (*dl*/*meso* = 1:1) as shown in entry 3. 9*H*,9'*H*-9,9'-Bifluorene (**3e**) could be obtained in 36% yield from 9*H*-fluoren-9-ol (**1e**) by using this catalytic system.

Table 4 Substrate scope in the vanadium-catalyzed deoxygenative homocoupling reaction of alcohols.[a,b]

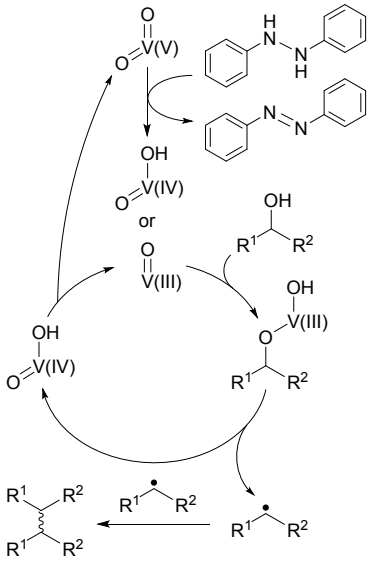


Entry	Substrate	Products	
1	 **1b**	 **3b** 46%[c] (*dl*/*meso* = 1:1)	 **4b** 13%
2	 **1c**	 **3c** 65%[c]	 **4c** 26%
3	 **1d**	 **3d** 42%[c] (*dl*/*meso* = 1:1)	 **4d** 5%
4	 **1e**	 **3e** 36%[c]	 **4e** trace

[a] Reaction conditions: 0.20 mmol of alcohols, 20 mmol% of $VO(O^{i}Pr)_3$, 50 mmol% of **1,1-DMH**, 0.2 g MS3A, 1.0 mL toluene, under nitrogen atmosphere. [b] The yield was determined by ^{1}H NMR. [c] NMR yield (%) = [product (mmol) x 2 / substrate (mmol)] x 100.

To gain insight into the reaction mechanism, ^{51}V NMR measurement was examined (Fig. S1, ESI). The ^{51}V chemical shift of $VO(O^{i}Pr)_3$ in the presence of **1,2-DPH**, $^{i}Pr_2NEt$ and MS3A in toluene-d_8 was detected at -630 ppm. Increasing the temperature to 100 °C, the peak intensity of $VO(O^{i}Pr)_3$ decreased, indicating that V(V) species was reduced to a low-valent vanadium species, such as V(IV) or V(III). Proposed catalytic cycle for deoxygenative homocoupling reaction of

View Article Online
DOI: 10.1039/C9NJ02757A



Scheme 5 Proposed catalytic cycle for deoxygenative homocoupling reaction of alcohols.

alcohols based on the above-mentioned results is illustrated in Scheme 5. The reaction of the reduced V(III) species, which is likely to be generated by the reaction of the V(V) species with **1,2-DPH**, with the alcohol produces the V(IV) species and the radical intermediate, affording the deoxygenative homocoupling product. The V(IV) species disproportionates to give the V(V) and V(III) species. The regenerated V(III) species begins a new catalytic cycle.

Conclusions

Catalytic direct hydrazination of allyl alcohol and deoxygenative homocoupling reaction of alcohols depending on hydrazine derivatives were performed by utilizing oxovanadium(V) catalysts. The oxovanadium(V)-catalysed reaction of 1,3-diphenylprop-2-en-1-ol with 1,1-diphenylhydrazine was found to afford the corresponding allyl hydrazine as a major product whereas the utilization of 1,1-dimethylhydrazine instead of 1,1-diphenylhydrazine induced the deoxygenative homocoupling reaction of the allyl alcohol to give the corresponding 1,5-diene as a major product. Furthermore, gram-scale oxovanadium(V)-catalysed deoxygenative homocoupling reaction proceeded successfully. Oxovanadium(V)-catalyzed deoxygenative homocoupling reaction of benzyl alcohols could be also performed in the presence of 1,1-dimethylhydrazine. Studies on the reaction mechanism and synthetic versatility are now in progress.

Experimental

General

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-ECS 400 (400 and 100 MHz, respectively) spectrometer. Chemical shifts are given in δ (ppm) relative to the residual solvent signal as an internal standard. High resolution mass spectra (HRMS) were measured on a JEOL JMS-700 spectrometer using electron impact (EI) or fast atom bombardment (FAB) mode. Column chromatography was performed with SiO_2 (Wakogel C-200 or Silica Gel 60 (spherical) NH_2).

Materials

Allyl alcohol **1b** (65564-83-2)[7] and $VO(OSiPh_3)_3$[8] were prepared according to the literature method. The other reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary.

Procedure for direct hydrazination of allyl alcohol 1a with 1,1-diphenylhydrazine.

In a 5 mL screw-capped vial, 1,3-diphenylprop-2-ene-1-ol (**1a**) (42 mg, 0.20 mmol), 1,1-diphenylhydrazine (**1,1-DPH**) (33 μL, 0.20 mmol), $VO(OSiPh_3)_3$ (36 mg, 0.040 mmol), MS3A (0.2 g) and toluene (2.0 mL) were placed at a glove box filled with nitrogen. The mixture was stirred at 100 °C for 24 h, followed by treatment with water, and extraction with ether. The organic layer was dried over Na_2SO_4, filtrated, and evaporated. Triphenyl methane was added as an internal standard, and ^{1}H NMR analysis was performed to determine an NMR yield.

(*E*)-2-(1,3-Diphenylallyl)-1,1-diphenylhydrazine (2a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-6.99 (m, 20H), 6.47-6.38 (m, 2H), 4.67 (d, J = 5.9 Hz, 1H), 4.40 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 147.8, 141.1, 137.0, 131.9, 130.9, 129.2, 128.7, 128.6, 128.1, 127.9, 127.7, 126.6, 122.4, 120.7, 64.9 ppm; HRMS (FAB) *m/z* Calcd. for $C_{27}H_{24}N_2$ (M^+), 376.1934; Found, 376.1944.

Procedure for deoxygenative homocoupling reaction of alcohols.

In a 5 mL screw-capped vial, alcohol (**1**) (0.20 mmol), 1,1-dimethylhydrazine (**1,1-DMH**) (7.6 μL, 0.10 mmol), $VO(O^iPr)_3$ (9.2 μL, 0.040 mmol), MS3A (0.2 g) and toluene (1.0 mL) were placed at a glove box filled with nitrogen. The mixture was stirred at 100 or 140 °C for 24 h, followed by filtration through Celite® with ethyl acetate. The solvent was removed. Triphenyl methane was added as an internal standard, and ^{1}H NMR analysis was performed to determine an NMR yield.

1,3,4,6-Tetraphenyl-1,5-hexadiene [CAS Registry No. 204578-86-9] (3a). Mixture of stereoisomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.07 (m, 20H), 6.57-6.51 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.34-6.28 (m, 1H), 6.20 (d, J = 15.8 Hz, 1H), 3.92-3.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.6, 142.4, 137.5, 137.4, 132.1, 131.9, 131.3, 131.1, 128.6, 128.42, 128.37, 128.35, 128.32, 128.2, 127.1, 127.0, 126.5, 126.2, 126.14, 126.09, 55.3, 55.2 ppm; HRMS (EI) *m/z* Calcd. for $C_{30}H_{26}$ (M^+), 386.2029; Found, 386.2025.

2,5-Dimethyl-1,3,4,6-tetraphenyl-1,5-hexadiene (3b). Mixture of stereoisomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.05 (m, 18H), 6.91-6.89 (m, 2H), 6.72 (s, 1H), 6.35 (s, 1H), 4.29 (s, 1H), 4.16 (s, 1H), 1.78 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 142.0, 141.0, 140.2, 139.0, 138.28, 138.26, 129.0, 128.8,

View Article Online
DOI: 10.1039/C9NJ01905G

128.7, 128.5, 128.1, 127.99, 127.95, 127.8, 127.5, 126.7, 126.2, 126.1, 126.0, 125.9, 56.7, 56.0, 16.1, 14.5 ppm; HRMS (EI) *m/z* Calcd. for $C_{32}H_{30}$ (M^+), 414.2348; Found, 414.2340.

1,1,2,2-Tetraphenyl-ethane [CAS Registry No. 632-50-8] (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.3 Hz, 8H), 7.11 (t, J = 7.3 Hz, 8H), 7.01 (t, J = 7.3 Hz, 4H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.4, 128.5, 128.1, 125.8, 56.3 ppm; HRMS (EI) *m/z* Calcd. for $C_{26}H_{22}$ (M^+), 334.1716; Found, 334.1718.

2,3-Diphenyl-buthane [CAS Registry No. 5789-35-5] (3d). Mixture of stereoisomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.00 (m, 20H), 2.98-2.90 (m, 1H), 2.84-2.76 (m, 1H), 1.28 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.5, 145.8, 128.3, 127.8, 127.7, 127.6, 126.0, 125.7, 47.2, 46.4, 21.0, 17.9 ppm; HRMS (EI) *m/z* Calcd. for $C_{16}H_{18}$ (M^+), 210.1403; Found, 210.1406.

9*H*,9'*H*-9,9'-Bifluorene [CAS Registry No. 1530-12-7] (3e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-6.97 (m, 16H), 4.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 144.7, 141,7, 127.4, 126.9, 124.2, 119.8, 49.9 ppm; HRMS (FAB) *m/z* Calcd. for $C_{26}H_{18}$ (M^+), 330.1409; Found, 330.1410.

Procedure for a gram scale deoxygenative homocoupling reaction of allyl alcohol 1a

In a 100 mL three-necked flask with a reflux condenser, 1,3-diphenylprop-2-ene-1-ol (**1a**) (1.1 g, 5.0 mmol), 1,2-diphenylhydrazine (**1,2-DPH**) (0.46 g, 2.5 mmol), $VO(O^iPr)_3$ (0.23 mL, 1.0 mmol), $^iPr_2EtN$ (87 µL, 0.50 mmol), MS3A (5.0 g) and toluene (25 mL) were placed at a glove box filled with nitrogen. The mixture was stirred at 100 °C for 20 h, followed by filtration through Celite® with ethyl acetate. The solvent was removed. The residue was heated under a reduced pressure to remove azobenzene and 1,2-diphenylhydrazine. The residue chromatographed on a silica gel column eluting with hexane and chloroform (7/3, v/v) to give 677 mg (70% yield) of **3a**

Procedure for synthesis of allyl amine from allyl alcohol 1b and 1,2-diphenylhydrazine.

In a 5 mL screw-capped vial, 1,3-diphenyl-2-methylprop-2-ene-1-ol (**1b**) (45 mg, 0.20 mmol), 1,2-diphenylhydrazine (**1,2-DPH**) (18 mg, 0.10 mmol), $VO(O^iPr)_3$ (9.2 µL, 0.040 mmol), $^iPr_2EtN$ (3.5 µL, 0.020 mmol), MS3A (0.2 g) and toluene (1.0 mL) were placed at a glove box filled with nitrogen. The mixture was stirred at 100 °C for 16 h, followed by filtration through Celite® with ethyl acetate. Triphenyl methane was added as an internal standard, and ^{1}H NMR analysis was performed to determine an NMR yield.

(*E*)-*N*-(1,3-Diphenyl-2-methylallyl)aniline (5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.15 (m, 12H), 6.78 (s, 1H), 6.72 (t, J = 7.8 Hz, 1H), 6.63 (d, J = 7.8 Hz, 2H), 4.87 (s, 1H), 4.10 (s, 1H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 147.4, 141.4, 137.7, 137.3, 129.1, 129.0, 128.7, 128.1, 127.60, 127.59, 126.5, 126.4, 117.6, 113.4, 66.3, 15.8 ppm; HRMS (FAB) *m/z* Calcd. for $C_{22}H_{21}N$ (M^+), 299.1669; Found,299.1672.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Thanks are due to the Analytical Center, Graduate School of Engineering, Osaka University.

Notes and references

1 (*a*) J. E. McMurry and M. Silvestri, *J. Org. Chem.*, 1975, **40**, 2687-2688; (*b*) M. Sato and K. Oshima, *Chem. Lett.*, 1982, **11**, 157-160; (*c*) S. Sasaoka, T. Yamamoto, H. Kinoshita, K. Inomata and H. Kotake, *Chem. Lett.*, 1985, **14**, 315-318; (*d*) J. Yoshida, H. Funahashi, H. Iwasaki and N. Kawabata, *Tetrahedron Lett.*, 1986, **27**, 4469-4472; (*e*) Y. Masuyama, K. Maekawa, T. Kurihara and Y. Kurusu, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2311-2313; (*f*) T. Nishino, Y. Nishiyama and N. Sonoda, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 635-641.

2 For reviews see: (*a*) J. A. Marshall, *Synthesis*, 1971, **1971**, 229-235; (*b*) N. S. Sheikh, *Org. Biomol. Chem.*, 2014, **12**, 9492-9504; (*c*) J. Adrian, L. J. Gross and C. B. W. Stark, *Beilstein J. Org. Chem.*, 2016, **12**, 2104-2123; (*d*) S. Katayama, T. Koge, S. Katsuragi, S. Akai and T. Oishi, *Chem. Lett.*, 2018, **47**, 1116-1118.

3 (*a*) Y. Obora, Y. Anno, R. Okamoto, T. Matsu-ura and Y. Ishii, *Angew. Chem. Int. Ed.*, 2011, **50**, 8618-8622; (*b*) S. Manojveer, S. J. K. Forrest and M. T. Johnson, *Chem. Eur. J.*, 2018, **24**, 803-807; (*c*) Y. Wang, Z. Shao, K. Zhang and Q. Liu, *Angew. Chem. Int. Ed.*, 2018, **57**, 15143-15147.

4 For reviews see: (*a*) T. Hirao, *Chem. Rev.*, 1997, **97**, 2707-2724; (*b*) P. P. Reddy, C. Y. Chu, D. R. Hwang, S. K. Wang and B. J. Uang, *Coord. Chem. Rev.*, 2003, **237**, 257-269; (*c*) J. A. L. da Silva, J. J. R. F. da Silva and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2011, **255**, 2232-2248; (*d*) D. Wischang, O. Brücher and J. Hartung, *Coord. Chem. Rev.*, 2011, **255**, 2204-2217; (*e*) S. Takizawa, H. Groger and H. Sasai, *Chem. Eur. J.*, 2015, **21**, 8992-8997.

5 (*a*) Y. Kataoka, I. Makihira, H. Akiyama and K. Tani, *Tetrahedron Lett.*, 1995, **36**, 6495-6498; (*b*) Y. Kataoka, H. Akiyama, I. Makihira and K. Tani, *J. Org. Chem.*, 1996, **61**, 6094-6095; (*c*) Y. Kataoka, H. Akiyama, I. Makihira and K. Tani, *J. Org. Chem.*, 1997, **62**, 8109-8113.

6 (*a*) E. Steffensmeier and K. M. Nicholas, *Chem. Commun.*, 2018, **54**, 790-793; (*b*) E. Steffensmeier, M. T. Swann and K. M. Nicholas, *Inorg. Chem.*, 2019, **58**, 844-854.

7 T. Sakuramoto, T. Hirao, M. Tobisu and T. Moriuchi, *ChemCatChem*, 2019, **11**, 1175-1178.

8 F. Preuss and H. Noichl, *Z. Naturforsch., B: Chem. Sci.*, 1987, **42**, 121-129.

Catalytic direct hydrazination of allyl alcohol and deoxygenative homocoupling reaction of alcohols depending on hydrazine derivatives were performed by utilizing oxovanadium(V) catalysts.