RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2021, **11**, 35342

Chemo- and regioselective cross-dehydrogenative coupling reaction of 3-hydroxycarbazoles with arenols catalyzed by a mesoporous silica-supported oxovanadium†

Kengo Kasama, [a] Kyohei Kanomata, [a] Yuya Hinami,[a] Karin Mizuno,[a] Yuta Uetake,[bc] Toru Amaya, [bd] Makoto Sako, [e] Shinobu Takizawa, [e] Hiroaki Sasai[e] and Shuji Akai *[a]

Received 19th October 2021
Accepted 25th October 2021

DOI: 10.1039/d1ra07723f

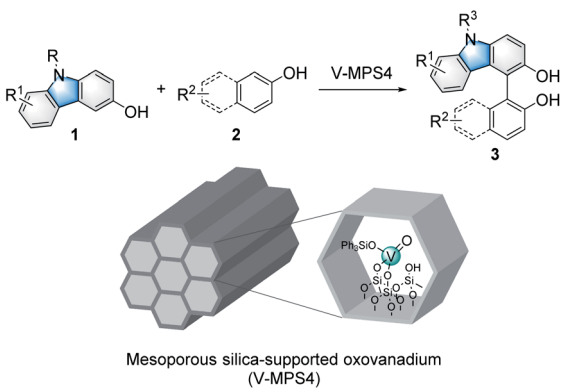
rsc.li/rsc-advances

Cross-dehydrogenative coupling between 3-hydroxycarbazoles and 2-naphthols has been achieved by using a mesoporous silica-supported oxovanadium catalyst.

Introduction

Immobilized catalysts have inherent advantages in the chemical and pharmaceutical industries because they are easy to reuse and handle in practical applications.[1] However, they are often less active than the corresponding homogeneous catalysts because their support materials have negative impacts on the chemical microenvironment around their active centers.[2] On the other hand, we recently developed a highly active heterogeneous oxovanadium catalyst, V-MPS4, in which pentavalent oxovanadium is covalently bound to the inner surfaces (diameter of 4 nm) of mesoporous silica.[3] V-MPS4 has served as a catalyst for racemization[4a,b] and the direct nucleophilic substitution[4c] of alcohols in a redox-neutral fashion. Considering the rapid development of vanadium-catalyzed oxidative couplings of arenols in recent years,[5] we envisioned that V-MPS4 could also be used as a redox catalyst for the oxidative couplings of biaryls *via* an oxovanadium(V/IV) cycle.

Among a range of oxidative biaryl couplings, those of carbazoles have recently drawn significant attention owing to the unique reactivity of the products and their potentials as biologically active compounds[6] and functional molecules.[7] Catalytic homo-coupling reactions of hydroxycarbazoles and enantioselective variants have been performed using $VO(acac)_2$ (ref. 8) and Schiff base–derived optically active oxovanadium complexes,[9] respectively. On the other hand, intermolecular oxidative couplings of hydroxycarbazoles with other arenols, namely cross-dehydrogenative coupling (CDC) reactions, have not yet been fully developed. The known reactions reportedly suffered from issues related to homocoupling and low regioselectivity; thus, they required excess amounts of coupling partners to obtain satisfactory yields for the cross-coupling products. Over-oxidation of products is another critical problem these couplings face.[10] Moreover, no CDC reaction of hydroxycarbazoles mediated by heterogeneous oxovanadium catalysts has been reported so far.[11] The use of heterogeneous catalysts for this reaction would be advantageous in terms of reuse and handling. In addition, that would also be effective in avoiding unnecessary contact between the product and the catalyst to address its over-oxidation issue. Herein, we report V-MPS4-catalyzed chemo- and regioselective CDC reactions of 3-hydroxycarbazoles with arenols using molecular oxygen as the



Scheme 1 Heterogeneous oxovanadium-catalyzed cross-dehydrogenative couplings of hydroxycarbazoles **1** with arenols **2**.

[a]*Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan. E-mail: akai@phs.osaka-u.ac.jp*

[b]*Division of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

[c]*Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI) Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

[d]*Graduate School of Science, Nagoya City University, Nagoya, Aichi 467-8501, Japan*

[e]*SANKEN (The Institute of Scientific and Industrial Research), Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ra07723f

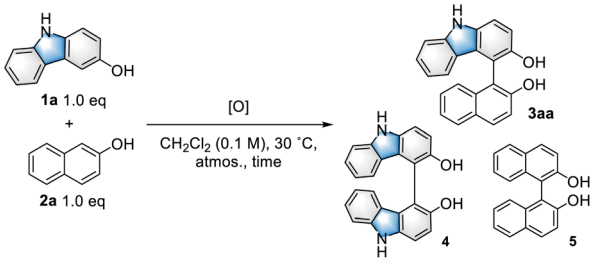
terminal oxidant (Scheme 1), with a finding that the heterogeneous catalysts are superior to the corresponding homogeneous ones for this reaction.

Results and discussion

Optimization of the reaction conditions

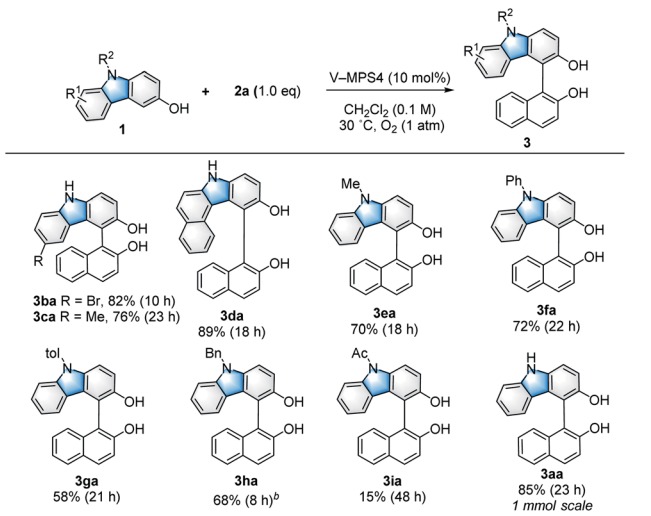
Initially, the CDC reaction conditions were screened using unprotected 3-hydroxycarbazole (**1a**) and one equivalent of 2-naphthol (**2a**) (Table 1). The reaction using the V-MPS4 catalyst (10 mol% vanadium) in CH_2Cl_2 under an oxygen atmosphere at 30 °C afforded cross-coupling product **3aa** in 87% NMR yield after 12 h, at which point the substrates were completely consumed (entry 1). Only a trace amount of homo-dimer **4** was obtained (<5% yield), and neither regioisomers of **3aa** nor homo-dimer **5** were observed. The reaction performed using air instead of molecular oxygen as the reoxidant also proceeded smoothly to afford **3aa** in 86% yield, although a prolonged reaction time was required (entry 2). The use of a stoichiometric amount of (diacetoxyiodo)benzene ($PhI(OAc)_2$) afforded **3aa** in only 46% yield with significant decomposition of the starting materials (entry 3). The use of reoxidants other than molecular oxygen with V-MPS4 was not effective for this reaction (Table S1 in ESI†). For comparison, other homogeneous catalysts often used in CDC reactions were also investigated. The reaction using $Fe(acac)_3$ (ref. 12) did not proceed at all, while those employing $Mn(acac)_3$ (ref. 13) and CuCl(OH)·TMEDA[14] gave complex mixtures (entries 4–6). Without a catalyst, the reaction under an oxygen atmosphere did not proceed at all (entry 7). Under a nitrogen atmosphere without any oxidants, V-MPS4 gave a trace amount of **3aa** (entry 8). An organic solvent-soluble oxovanadium(v) catalyst, $VO(OSiPh_3)_3$, which is the starting material for the preparation of V-MPS4, afforded **3aa** in low yield (entry 9). The vanadium atom of V-MPS4 is covalently bound to two silanol groups on the inner surface of mesoporous silica and has one $OSiPh_3$ group,[3,4b] while that of $VO(OSiPh_3)_3$ has three bulky $OSiPh_3$ groups. Thus, we deduce that steric effects are the most responsible for the difference of catalytic activity. On the other hand, the oxovanadium(iv) homogeneous catalyst $VO(acac)_2$ (ref. 8) afforded **3aa** in a lower yield (77%, entry 10). Further screening of vanadium catalysts and reaction conditions revealed that V-MPS4 with molecular oxygen as the reoxidant (entry 1) were the optimal conditions (Table S2 in ESI†). During condition screening, the over-oxidation and decomposition of **3aa** were often observed. For example, the reaction using $VO(acac)_2$ (10 mol%) resulted in the complete decomposition of **3aa** after 96 h (entry 11). In contrast, **3aa** was obtained in 53% yield even after 96 h with V-MPS4 (10 mol%) (entry 12). These results also indicated that V-MPS4 has a higher substrate selectivity than that of $VO(acac)_2$. Although the precise reaction mechanism using V-MPS4 is still under investigation, its superior catalytic performance and substrate selectivity may be attributable to its mesoporous structure, on which the oxovanadium catalyst is immobilized.[4b] The coupling reaction of **1a** with **2a** on a larger scale was then performed to show the scalability of this reaction. The reaction on a 1 mmol scale proceeded smoothly to give **3aa** in 85% yield (entry 13).

Table 1 Optimization of reaction conditions[a]



Entry	[O] (mol%)	Time	Yield of **3aa**[b]
1	V-MPS4 (10)	12 h	87% (93%)[c]c
2[d]	V-MPS4 (10)	84 h	86%
3[d]	$PhI(OAc)_2$ (100)	2 h	46%
4	$Fe(acac)_3$ (10)	18 h	No reaction
5	$Mn(acac)_3$ (100)	12 h	Complex mixture
6[d]	CuCl(OH) TMEDA (1)	12 h	Complex mixture
7	None	18 h	No reaction
8[e]	V-MPS4 (10)	18 h	<5%
9	$VO(OSiPh_3)_3$ (10)	18 h	33%
10	$VO(acac)_2$ (10)	12 h	77%
11	$VO(acac)_2$ (10)	96 h	Decomposed
12	V-MPS4 (10)	96 h	53%
13[f]	V-MPS4 (10)	23 h	85%[c]

[a] Unless otherwise noted, the reaction was conducted using **1a** (0.10 mmol) and **2a** (0.10 mmol) with the indicated catalyst and solvent (0.1 M) at 30 °C under an oxygen atmosphere. [b] Determined by ^{1}H NMR analysis of the crude product using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield. [d] Under air. [e] Under N_2. [f] The reaction was conducted in a 1 mmol scale.



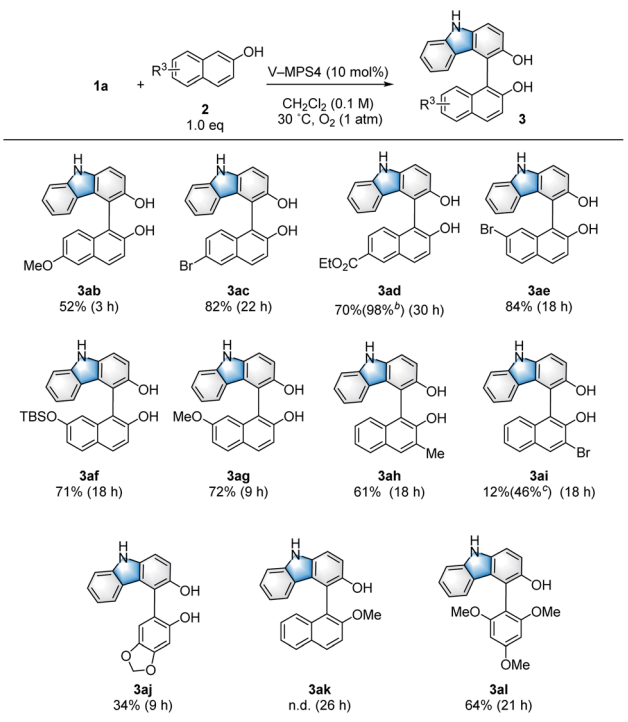
Scheme 2 Substrate scope of 3-hydroxycarbazoles. [a]Unless otherwise noted, the reaction was conducted using **1** (0.10 mmol), **2a** (0.10 mmol), and V-MPS4 (10 mol% based on vanadium) in CH_2Cl_2 (0.1 M) at 30 °C under an oxygen atmosphere. The isolated yield of the product **3** is shown, and the reaction time is given in the parentheses. [b]Two equivalents of **2a** were used.

Scope and limitations of 3-hydroxycarbazoles

With the optimized reaction conditions in hand (Table 1, entry 1), the scope and limitations of the 3-hydroxycarbazoles (**1**) were investigated (Scheme 2). 3-Hydroxycarbazoles bearing either a 6-Br or 6-Me substituent smoothly reacted with **2a** (1.0 equiv.) to afford the corresponding products (**3ba** and **3ca**, respectively). A π-expanded carbazole was also applicable to this reaction, giving cross-coupled product **3da** in 89% yield. *N*-Substituted carbazoles were then investigated. 3-Hydroxycarbazoles bearing Me, Ph, or *p*-tolyl (4-Me-C_6H_4) groups on their nitrogen atoms reacted smoothly to give the corresponding products (**3ea**, **3fa**, and **3ga**, respectively) in 58–72% yield. Additionally, *N*-Bn-substituted 3-hydroxycarbazole **1h** also gave product **3ha** in 68% yield, although two equivalents of **2a** were necessary because of the low reactivity of **1h**. It is noteworthy that the reaction of electron-withdrawing *N*-Ac-substituted 3-hydroxycarbazole **1i** could afford product **3ia**, because it hardly proceeded with previously reported optically active oxovanadium complexes;[9a] this is likely because of the high oxidation potential of **1i**.

Scope and limitations of 2-naphthols

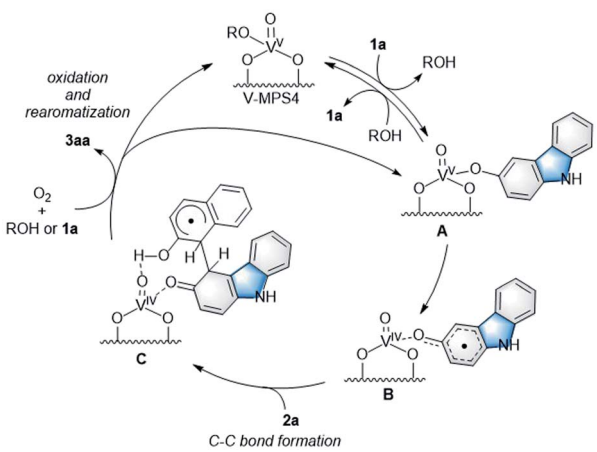
The scope and limitations of the 2-naphthols (**2**) were investigated (Scheme 3). 2-Naphthols with either an electron-donating or electron-withdrawing group at the 6-position gave the corresponding products (**3ab–3ad**) in 52–82% yield. In addition, **3ad** was obtained almost quantitatively by using two equivalents of the corresponding naphthol (**2d**). The use of naphthols substituted at the 7-position also afforded the target compounds (**3ae–3ag**) in good yields (71–84%). The reaction was tolerant to the introduction of a Me group at the 3-position of 2-naphthol, affording **3ah** in 61% yield. Although the introduction of an electron-withdrawing Br substituent at the 3-position resulted in only a 12% yield for product **3ai**, this yield was improved to 46% in the presence of Na_2CO_3 (1.5 equiv.); this is likely because of the increased nucleophilicity of **2i** under basic conditions.[15] In addition to 2-naphthols, sesamol also afforded coupling product **3aj**. However, methyl protection of the phenolic hydroxy group of **2a** completely suppressed the formation of cross-coupling product **3ak** to give only a trace amount of the dimer **4**. On the other hand, 1,3,5-trimethoxybenzene (**2l**) reacted smoothly to give the product **3al** (64% yield). In some cases, the coupling products (**3**) of the present CDC reaction gradually decomposed due to over-oxidation (Table 1, entries 11 and 12). Thus, to ensure high yields, the reaction mixtures were filtered immediately after **1** was consumed to remove the catalyst; this was confirmed by TLC analysis. Furthermore, the reaction rate was strongly dependent on the electron density of **2**, where those bearing electron-donating groups reacted faster than those bearing electron-withdrawing groups.



Scheme 3 Substrate scope of 2-naphthols. [a]Unless otherwise noted, the reaction was conducted using **1a** (0.10 mmol), **2** (0.10 mmol), and V-MPS4 (10 mol% based on vanadium) in CH_2Cl_2 (0.1 M) at 30 °C under an oxygen atmosphere. The isolated yield of the product **3** is shown, and the reaction time is given in the parentheses. [b]Two equivalents of **2c** were used. [c]Anhydrous Na_2CO_3 (1.5 equiv.) was added.

Mechanism investigation

To investigate the reaction mechanism, reactions of **1a** and **2a** were conducted under typical conditions with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), a radical scavenger, which significantly suppressed the reaction to form **3aa** in 21% NMR yield after 12 h (Scheme S1 in ESI†). Based on this, a plausible mechanism for the CDC reaction between **1a** and **2a** was proposed (Scheme 4). Initially, V-MPS4 is in a substituent exchange equilibrium with either **1a** or **2a**, where its preferential reaction with **1a** gives intermediate **A**. The intermediate can convert into radical intermediate **B**, which contains



Scheme 4 Plausible reaction mechanism.

vanadium(IV), *via* one-electron oxidation; this is because the oxidation potential of **1a** is lower than that of **2a** (based on cyclic voltammogram in MeCN with Bu_4NPF_6: $E_{\mathbf{1a}(ox)} = 0.45$ V (*vs.* Fc/Fc^+) and $E_{\mathbf{2a}(ox)} = 0.93$ V (*vs.* Fc/Fc^+)).[11] Subsequently, its C–C bond formation[16] with **2a** gives **C**. Finally, oxidation by molecular oxygen and rearomatization complete the catalytic cycle with the regeneration of V-MPS4 and/or **A**, releasing **3aa** as the product. The formation of a vanadium(IV) species was confirmed by electron spin resonance (ESR) analysis of V-MPS4 after performing the CDC reaction under a nitrogen atmosphere (Fig. 1a and S1 in ESI†). A clear octet signal that is characteristic of vanadium(IV) was observed, which indicated that a vanadium(IV) species was formed as a result of the CDC reaction. Meanwhile, the ESR spectrum of the original V-MPS4 structure, with vanadium(V), did not show any detectable signals.

Characterization of V-MPS4 catalyst

The characterization was previously reported, including pore size, surface area measurement, elemental analysis, and solid-state ^{13}C NMR.[4b] The local structure and oxidation state of the vanadium center of V-MPS4 were further investigated by X-ray absorption spectroscopy (XAS) to support the proposed mechanism. The V-K edge X-ray absorption near-edge structure (XANES) spectrum of freshly prepared V-MPS4 showed that the absorption edge energy

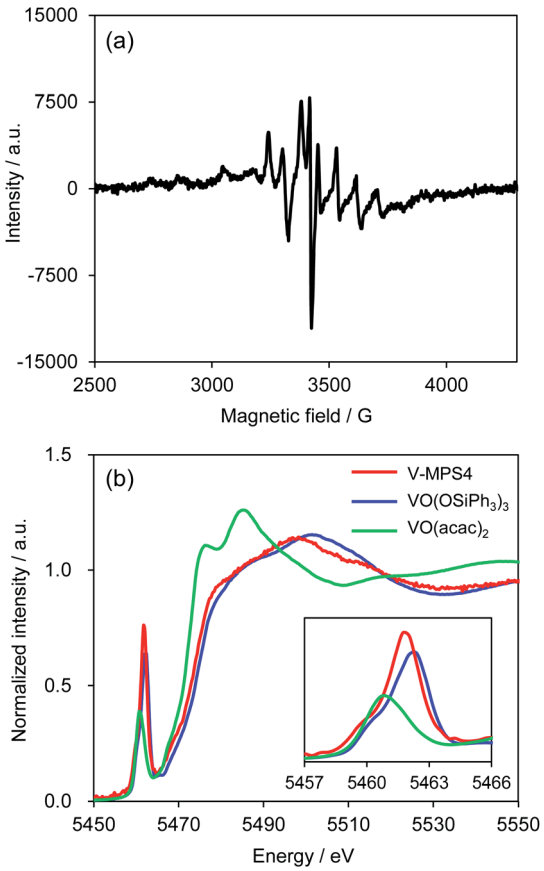
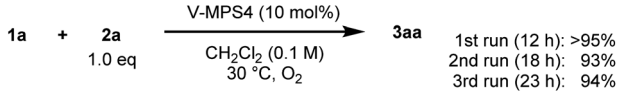


Fig. 1 ESR and XANES spectra. (a) ESR spectrum of V-MPS4 after the reaction; (b) V-K edge XANES spectra of V-MPS4 (red), $VO(OSiPh_3)_3$ (blue), and $VO(acac)_2$ (green). The insert shows a magnified view of the pre-edge peaks.



Scheme 5 Reusability of V-MPS4 catalyst.

was closer to that of $V^{(V)}O(OSiPh_3)_3$ than to that of $V^{(IV)}O(acac)_2$, suggesting that the oxidation state did not change during the immobilization process (Fig. 1b). In addition, the shape of the XANES spectrum of V-MPS4, including the pre-edge peak, was similar to that of $VO(OSiPh_3)_3$. This indicated that the tetrahedral (T_d) geometry around the vanadium center was retained, as shown in Scheme 1.

Reusability and leaching examinations of V-MPS4

The reusability and metal leaching of V-MPS4 were investigated (Scheme 5). Although the reaction rate decreased slightly with the repeated use of V-MPS4, product **3aa** was still obtained in high yield (≥93%) during the third reuse of the catalyst by extending the reaction time until **1a** was consumed. The leaching of vanadium from V-MPS4 in CH_2Cl_2 was evaluated using inductively coupled plasma atomic emission spectrometry. Less than 1% of vanadium was released from V-MPS4 into the solvent during 12 h of stirring. In addition, performing the same CDC reaction in the supernatant after removing V-MPS4 afforded only a trace amount of **3aa** (<5% yield, Scheme S2 in ESI†). These results strongly indicate that the catalytic process is heterogeneous. The observed decrease in the reaction rate in the recycling experiment is probably attributable to the formation of insoluble polymer byproducts on V-MPS4.

Conclusions

In conclusion, CDC reactions between 3-hydroxycarbazoles **1** and 2-naphthols **2** were achieved using mesoporous silica-supported oxovanadium (V-MPS4) as a heterogeneous catalyst. The reaction proceeded smoothly under ambient pressure using molecular oxygen as the terminal oxidant. The two coupling partners, **1** and **2**, were used in a 1 : 1 molar ratio to obtain the desired cross-coupling products **3** in high yields and with excellent chemo- and regioselectivities, resulting in excellent atom efficiency. In addition, the reaction showed a wide substrate scope, including *N*-substituted 3-hydroxycarbazoles. Particularly noteworthy is the fact that the heterogeneous V-MPS4 catalyst has a much higher activity than $VO(OSiPh_3)_3$, even though the oxovanadium structures of both reagents are almost identical. Furthermore, V-MPS4 was reused three times without a significant decrease in product yield. Further expansion of the present CDC strategy, as well as mechanistic studies and detailed analyses of V-MPS4, are ongoing in our laboratory.

Experimental

Substrate synthesis

Compounds **2a–2c**, **2e**, **2g**, **2h**, **2j**, and **2k** were purchased from commercial suppliers. Compounds **1e–1i**, and **2f** were prepared

according to the literature procedure.[9a,b,17,18] Compounds **1a–1d**, **2d**, and **2h** were synthesized as described in ESI.†

Preparation of $VO(OSiPh_3)_3$

Ph_3SiOH (6.74 g, 24.4 mmol, 3.05 eq.) was placed in a round-bottom flask (200 mL) and toluene (80 mL) was added to the flask, followed by $VO(Oi\text{-}Pr)_3$ (1.9 mL, 8.0 mmol). The mixture was refluxed for 2 h under argon atmosphere using a Dean–Stark apparatus. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was washed with hexane (200 mL × 1) and then dried *in vacuo* to afford $VO(OSiPh_3)_3$ (7.22 g, >99% yield). Its ^1H NMR spectrum was in good agreement with the literature data.[19]

Preparation of V-MPS4

V-MPS4 was prepared according to the literature procedure[4b] with a modification. In brief, mesoporous silica TMPS-4R (3.33 g, Taiyo Kagaku Co., Ltd., Tokyo, Japan) was placed in a three-neck flask (500 mL) and dried overnight at 150 °C *in vacuo*. After cooling to 80 °C, dry toluene (250 mL) was added (suspension A). In another round-bottom flask (100 mL), Ph_3SiOH (3.32 g, 12 mmol, 3.0 eq.) was placed and toluene (50 mL) was added to the flask, followed by $VO(Oi\text{-}Pr)_3$ (0.94 mL, 4.0 mmol). Then, the resultant mixture was refluxed for 2 h using a Dean–Stark apparatus under argon atmosphere to form $VO(OSiPh_3)_3$. After cooling to 80 °C, the as-prepared solution of $VO(OSiPh_3)_3$ was cannulated to the suspension A and the resultant mixture was heated at 80 °C for 8 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residue was transferred into a 50 mL glass centrifuging tube in a plastic bag under nitrogen flow. The centrifuging tube was sealed with a rubber septum and the residue was suspended in dry hexane/CH_2Cl_2 (6 mL/24 mL). The suspension was sonicated for 3 min and then centrifuged (3000 rpm, 10 min). After removing the supernatant by cannulation, the suspending/centrifuging process was repeated four more times. After that, precipitate was dried in the same centrifuging tube overnight *in vacuo* at room temperature to afford V-MPS4 (3.16 g). The vanadium content of the as-prepared V-MPS4 was 0.19–0.22 mmol g^{-1}, which was determined by ICP-AES analysis using calibration curve method. As-prepared V-MPS4 was stored in a refrigerator under argon atmosphere.

General procedure for the cross-dehydrogenative coupling (CDC) reaction

A 15 mL screw-cap test tube was charged with 3-hydroxycarbazole (**1a**) (18.3 mg, 0.10 mmol), 2-naphthol (**2a**) (14.4 mg, 0.10 mmol), V-MPS4 (47 mg, 10 mol% based on vanadium content), and CH_2Cl_2 (1.0 mL, 0.1 M). After oxygen was purged to the tube, the reaction mixture was stirred at 30 °C in a sealed condition. After complete consumption of **1a** was confirmed by TLC analysis, V-MPS4 was filtered through a short pad of silica gel (hexane/EtOAc = 1 : 1, 100 mL) and the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 4 : 1 to 2 : 1) to afford **3aa** as a pale brown solid (30.3 mg, 93% yield).

A large scale CDC reaction

A 30 mL round-bottom flask was charged with **1a** (183 mg, 1.0 mmol), **2a** (144 mg, 1.0 mmol), V-MPS4 (0.47 g, 10 mol% based on vanadium content), and evacuated and back-filled with oxygen three times. After CH_2Cl_2 (10 mL, 0.1 M) was added to the flask, the reaction mixture was stirred at 30 °C under an oxygen atmosphere (balloon). After complete consumption of **1a** was confirmed by TLC analysis, V-MPS4 was filtered through a short pad of silica gel (hexane/EtOAc = 1 : 1, 200 mL) and the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 4 : 1 to 2 : 1) to afford **3aa** (275 mg, 85% yield).

4-(2-Hydroxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3aa). ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.03 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 9.2 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.39–7.36 (m, 2H), 7.34–7.25 (m, 4H), 6.77 (t, J = 7.4 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.26 (s, 1H), 4.71 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 148.2, 140.3, 134.6, 132.8, 131.4, 129.4, 128.4, 127.5, 126.0, 124.1, 124.0, 122.6, 122.4, 121.4, 119.3, 117.8, 115.0, 112.6, 111.7, 110.6, 110.5. Its NMR data were in good agreement with those in the previous report.[11]

6-Bromo-4-(2-hydroxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3ba). A pale brown solid **3ba** (33.3 mg, 82% yield) was obtained from **1b** (26.2 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.06 (d, J = 9.2 Hz, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.44 (d, J = 9.2 Hz, 1H), 7.40 (ddd, J = 8.0, 6.3, 1.7 Hz, 1H), 7.36–7.24 (m, 6H), 6.72 (d, J = 1.7 Hz, 1H), 5.23 (s, 1H), 4.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 148.5, 138.8, 134.9, 132.5, 131.7, 129.4, 128.8, 128.6, 127.7, 124.2, 124.1, 124.0, 123.8, 121.6, 117.7, 116.0, 112.9, 112.0, 111.9, 111.1, 110.8. Its NMR data were in good agreement with those in the previous report.[11]

4-(2-Hydroxynaphthalen-1-yl)-6-methyl-9*H*-carbazol-3-ol (3ca). A white solid **3ca** (26.0 mg, 76% yield) was obtained from **1c** (19.7 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 9.2 Hz, 1H), 7.96 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.44–7.22 (m, 7H), 7.09 (d, J = 8.0 Hz, 1H), 6.44 (s, 1H), 5.32 (s, 1H), 4.69 (s, 1H), 2.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 148.0, 138.6, 134.9, 132.8, 131.3, 129.3, 128.42, 128.35, 127.5, 127.4, 124.1, 124.0, 122.5, 122.3, 121.1, 117.7, 114.8, 112.5, 111.9, 110.6, 110.2, 21.3. mp: 210–213 °C. IR (neat) ν 3400, 1643 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{23}H_{17}NO_2$ $[M^{+\cdot}]$: 339.1254, found: 339.1248.

11-(2-Hydroxynaphthalen-1-yl)-7*H*-benzo[*c*]carbazol-10-ol (3da). A white solid **3da** (28.8 mg, 89% yield) was obtained from **1d** (23.3 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). ^1H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 8.9 Hz, 2H), 7.69 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.39–7.30 (m, 4H), 7.11 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 6.63 (ddd, J = 8.6, 6.9, 1.7 Hz, 1H), 6.56 (d, J = 8.6 Hz, 1H), 5.25 (s, 1H), 4.84 (s, 1H). ^1H NMR (500 MHz, acetone-d_6) δ 10.83 (brs, 1H), 8.07 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.73–7.66 (m, 5H), 7.40 (d, J =

9.2 Hz, 1H), 7.26 (d, J = 8.6 Hz, 2H), 7.21 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.11 (brs, 1H), 7.11 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.01 (ddd, J = 8.6, 6.9, 1.7 Hz, 1H), 6.73 (d, J = 8.6 Hz, 1H), 7.11 (ddd, J = 8.6, 6.9, 1.7 Hz, 1H). ^{13}C NMR (125 MHz, acetone-d_6) δ 154.7, 150.4, 139.8, 136.2, 135.2, 130.73, 130.70, 130.0, 129.9, 129.3, 128.8, 128.3, 127.0, 126.1, 126.0, 125.93, 125.88, 123.8, 122.5, 119.52, 119.47, 117.0, 115.2, 114.2, 114.0, 113.1. mp: 268–270 °C. IR (neat) ν 3408, 1620, 1532, 1516 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{26}H_{17}NO_2$ [M$^{+\bullet}$]: 375.1252, found: 375.1254.

4-(2-Hydroxynaphthalen-1-yl)-9-methyl-9*H*-carbazol-3-ol (3ea). A white solid **3ea** (20.7 mg, 61% yield) was obtained from **1e** (19.7 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.6 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.51 (d, J = 8.6 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.39–7.27 (m, 6H), 6.77 (ddd, J = 8.0, 6.2, 1.8 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 5.25 (s, 1H), 4.71 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 147.9, 141.5, 136.3, 132.8, 131.3, 129.4, 128.4, 127.5, 125.8, 124.1, 124.0, 121.8, 121.6, 121.4, 118.7, 117.8, 114.8, 111.9, 110.8, 110.4, 108.3, 29.2. Its NMR data were in good agreement with those in the previous report.[11]

4-(2-Hydroxynaphthalen-1-yl)-9-phenyl-9*H*-carbazol-3-ol (3fa). A white solid **3fa** (29.0 mg, 72% yield) was obtained from **1f** (25.9 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 9.2 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.66–7.60 (m, 4H), 7.52–7.48 (m, 2H), 7.45 (d, J = 8.6 Hz, 1H), 7.41–7.31 (m, 4H), 7.27–7.23 (m, 2H), 6.81 (ddd, J = 8.0, 6.8, 1.2, 1H), 6.72 (d, J = 8.0 Hz, 1H), 5.33 (s, 1H), 4.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 148.6, 141.5, 137.5, 136.2, 132.8, 131.4, 129.9, 129.4, 128.4, 127.6, 127.2, 126.1, 124.2, 124.1, 122.4, 122.2, 121.4, 119.8, 117.8, 115.0, 111.8, 111.7, 110.6, 109.6 (one carbon overlapped). mp: 257–260 °C. IR (neat) ν 3505, 3417 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{28}H_{19}NO_2$ [M$^{+\bullet}$]: 401.1410, found: 401.1411.

4-(2-Hydroxynaphthalen-1-yl)-9-(*p*-tolyl)-9*H*-carbazol-3-ol (3ga). A white solid **3ga** (24.5 mg, 59% yield) was obtained from **1g** (27.3 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.6 Hz, 1H), 7.94 (dd, J = 7.7, 2.0 Hz, 1H), 7.49–7.37 (m, 8H), 7.34–7.31 (m, 2H), 7.26–7.23 (m, 2H), 6.82–6.78 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 5.35 (s, 1H), 4.77 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 148.4, 141.6, 137.5, 136.3, 134.8, 132.8, 131.4, 130.5, 129.4, 128.4, 127.6, 127.1, 126.0, 124.2, 124.1, 122.3, 122.1, 121.3, 119.6, 117.8, 114.9, 111.83, 111.81, 110.6, 109.6, 21.3. mp: 147–155 °C. IR (neat) ν 3422 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{29}H_{21}NO_2$ [M$^{+\bullet}$]: 415.1567, found: 415.1570.

9-Benzyl-4-(2-hydroxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3ha). A white solid **3ha** (28.3 mg, 68% yield) was obtained from **1h** (27.3 mg, 0.10 mmol) and **2a** (28.8 mg, 0.20 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 9.2 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.47–7.43 (m, 2H), 7.38 (ddd, J = 8.0, 6.3, 1.7 Hz, 1H), 7.36–7.27 (m, 8H), 7.24–7.22 (m, 2H), 6.78 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 5.56 (s, 2H), 5.29 (s, 1H), 4.72 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 148.1, 141.3, 137.1, 135.9, 132.8, 131.4, 129.4, 128.8, 128.4, 127.6, 127.5, 126.5, 126.0, 124.1, 124.0, 122.1, 121.9, 121.5, 119.0, 117.8, 114.9, 111.8, 110.91, 110.88, 108.7, 46.7. mp: 200–205 °C. IR (neat) ν 3529, 3483, 3422, 1618, 1596 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{29}H_{21}NO_2$ [M$^{+\bullet}$]: 415.1567, found: 415.1571.

1-(3-Hydroxy-4-(2-hydroxynaphthalen-1-yl)-9*H*-carbazol-9-yl) ethan-1-one (3ia). A white solid **3ia** (5.4 mg, 15% yield) was obtained from **1i** (22.5 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). ^{1}H NMR (500 MHz, acetone-d_6) δ 8.33 (d, J = 9.2 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 7.99 (d, J = 8.6 Hz, 1H), 8.06 (br, 2H), 7.92 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.6 Hz, 1H), 7.31–7.27 (m, 2H), 7.24–7.21 (m, 3H), 6.82 (t, J = 8.0 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 2.92 (s, 3H). ^{13}C NMR (125 MHz, acetone-d_6) δ 170.5, 154.1, 153.3, 140.1, 134.8, 133.9, 130.9, 129.9, 129.0, 127.4, 127.32, 127.26, 125.0, 123.9, 123.7, 122.2, 119.5, 117.7, 116.6, 116.4, 116.1, 115.2, 27.9 (one carbon overlapped). mp: >300 °C. IR (neat) ν 3380, 1657, 1509 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{24}H_{17}NO_3$ [M$^{+\bullet}$]: 367.1203, found: 367.1203.

4-(2-Hydroxy-6-methoxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3ab). A pale brown solid **3ab** (18.8 mg, 52% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2b** (17.4 mg, 0.10 mmol). ^{1}H NMR (500 MHz, acetone-d_6) δ 10.16 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.54 (s, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 2.7 Hz, 1H), 7.24 (s, 1H), 7.18 (d, J = 8.6 Hz, 1H), 7.17–7.13 (m, 2H), 6.86 (dd, J = 9.2, 2.7 Hz, 1H), 6.66 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, acetone-d_6) δ 156.7, 152.2, 149.8, 141.8, 135.6, 130.8, 130.1, 129.2, 127.0, 125.7, 124.0, 122.3, 119.8, 119.4, 118.6, 116.5, 116.1, 115.0, 112.1, 111.3, 107.3, 55.5 (one carbon overlapped). mp: 108–112 °C. IR (neat) ν 3326, 2921, 2850, 1599, 1501 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{23}H_{17}NO_3$ [M$^{+\bullet}$]: 355.1203, found: 355.1204.

4-(6-Bromo-2-hydroxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3ac). A white solid **3ac** (33.0 mg, 82% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2c** (22.3 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.07 (d, J = 2.3 Hz, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 8.6, 2.0 Hz, 1H), 7.29–7.26 (m, 1H), 7.19 (d, J = 9.2 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 5.30 (s, 1H), 4.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 148.1, 140.3, 134.6, 131.4, 130.7, 130.4, 130.33, 130.32, 126.11, 126.06, 122.5, 122.2, 121.2, 119.4, 119.0, 117.8, 115.1, 112.8, 112.3, 110.6, 110.1. Its NMR data were in good agreement with those in the previous report.[11]

Ethyl 6-hydroxy-5-(3-hydroxy-9*H*-carbazol-4-yl)-2-naphthoate (3ad). A white solid **3ad** (39.0. mg, 98% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2d** (43.2 mg, 0.20 mmol), and **3ad** (28.0 mg, 70% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2d** (21.6 mg, 0.10 mmol). ^{1}H NMR (500 MHz, acetone-d_6) δ 10.21 (s, 1H), 8.65 (s, 1H), 8.25 (s, 1H), 8.17 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.51–7.47 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 9.2 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.60 (t, J = 7.4 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 4.35 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, acetone-d_6) δ 167.0, 156.2, 149.9, 141.8, 137.5, 135.6, 132.0, 131.7, 128.8, 126.2, 125.77, 125.75, 123.95, 123.91, 122.0, 120.5, 118.7, 116.9, 116.2, 114.2, 112.4, 111.4, 61.2, 14.7 (one carbon overlapped). mp: 157–160 °C. IR (neat) ν 3404, 1702, 1620 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{25}H_{19}NO_4$ [M$^{+\bullet}$]: 397.1309, found: 397.1309.

4-(7-Bromo-2-hydroxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3ae). A pale brown solid **3ae** (34.0 mg, 84% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2e** (22.3 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.99 (d, J = 9.2 Hz, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.46–7.42 (m, 3H), 7.39 (d, J = 8.6 Hz, 1H), 7.30–7.26 (m, 2H), 6.79 (dd, J = 8.0, 6.8, 1.2 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 5.31 (s, 1H), 4.63 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 148.1, 140.4, 134.6, 134.2, 131.2, 130.0, 127.8, 127.5, 126.2, 126.1, 122.5, 122.2, 122.1, 121.1, 119.4, 118.2, 115.2, 112.9, 111.5, 110.6, 109.9. Its NMR data were in good agreement with those in the previous report.[11]

4-(7-((*Tert*-butyldimethylsilyl)oxy)-2-hydroxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3af). A pale violet solid **3af** (32.3 mg, 71% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2f** (27.4 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.28 (s, 1H), 7.25 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 6.95 (dd, J = 8.8, 2.4 Hz, 1H), 6.77 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 5.27 (s, 1H), 4.76 (s, 1H), 0.77 (s, 9H), −0.14 (s, 3H), −0.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 152.6, 148.1, 140.3, 134.5, 134.2, 131.0, 129.8, 125.9, 125.0, 122.6, 122.4, 121.6, 119.9, 119.3, 115.4, 114.9, 112.5, 111.7, 110.7, 110.6, 110.4, 25.6, 18.1, −4.81, −4.85. mp: 145–150 °C. IR (neat) ν 3421, 2955, 2930, 2859, 1620, 1510 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{28}H_{29}NO_3Si$ [M$^{+\bullet}$]: 455.1911, found: 455.1911.

4-(2-Hydroxy-7-methoxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3ag). A white solid **3ag** (25.5 mg, 72% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2g** (17.4 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.29–7.26 (m, 3H), 7.03 (dd, J = 8.9, 2.6 Hz, 1H), 6.80 (t, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 2.3 Hz, 1H), 5.25 (s, 1H), 4.77 (s, 1H), 3.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 153.0, 148.2, 140.3, 134.6, 134.2, 131.1, 130.0, 126.0, 124.7, 122.4, 121.4, 119.4, 116.1, 115.1, 115.0, 112.6, 110.9, 110.7, 110.5, 103.0, 55.1. Its NMR data were in good agreement with those in the previous report.[11]

4-(2-Hydroxy-3-methylnaphthalen-1-yl)-9*H*-carbazol-3-ol (3ah). A brown solid **3ah** (20.6 mg, 61% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2h** (15.8 mg, 0.10 mmol). ^{1}H NMR (500 MHz, acetone-d_6) δ 10.22 (s, 1H), 7.83–7.82 (m, 2H), 7.50 (d, J = 8.6 Hz, 1H), 7.43 (s, 1H), 7.40 (dt, J = 8.0, 0.7 Hz, 1H), 7.33 (d, J = 1.0 Hz, 1H), 7.24 (ddd, J = 8.0, 6.7, 1.3 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 7.17–7.14 (m, 2H), 7.10 (ddd, J = 8.0, 6.7, 1.3 Hz, 1H), 6.59 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.49 (dt, J = 8.0, 0.7 Hz, 1H), 2.50 (d, J = 1.0 Hz, 3H). ^{13}C NMR (125 MHz, acetone-d_6) δ 152.8, 150.2, 141.8, 135.6, 133.6, 130.0, 129.9, 128.2, 128.0, 126.0, 125.8, 125.2, 124.1, 123.9, 123.7, 122.2, 118.7, 116.3, 115.5, 114.0, 112.6, 111.3, 17.6. mp: 217–220 °C. IR (neat) ν 3503, 3421, 1622, 1508 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{23}H_{17}NO_2$ [M$^{+\bullet}$]: 339.1254, found: 339.1251.

4-(3-Bromo-2-hydroxynaphthalen-1-yl)-9*H*-carbazol-3-ol (3ai). A brown solid **3ai** (4.9 mg, 12% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2i** (22.3 mg, 0.10 mmol). The same **3ai** (18.7 mg, 46% yield) was also obtained from **1a** (18.3 mg, 0.10 mmol) and **2i** (22.3 mg, 0.10 mmol) in the presence of Na_2CO_3 (15.9 mg, 0.15 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.11 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.6 Hz, 1H), 7.41–7.36 (m, 2H), 7.32–7. 24 (m, 4H), 6.77 (t, J = 8.0, 1H), 6.55 (d, J = 8.0 Hz, 1H), 5.72 (s, 1H), 4.63 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 147.7, 140.4, 134.6, 133.3, 132.3, 129.8, 127.8, 127.4, 125.9, 125.1, 124.5, 122.4, 122.3, 121.3, 119.3, 115.1, 114.2, 112.6, 112.0, 111.6, 110.6. mp: 165–170 °C. IR (neat) ν 3421, 1619 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{22}H_{14}NO_2{}^{79}Br$ [M$^{+\bullet}$]: 403.0202, found: 403.0207.

4-(6-Hydroxybenzo[*d*][1,3]dioxol-5-yl)-9*H*-carbazol-3-ol (3aj). A brown solid **3aj** (11.0 mg, 34% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2j** (13.8 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C) δ 7.90 (br s, 1H), 7.41–7.38 (m, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 9.2 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H), 6.82 (s, 1H), 6.76 (s, 1H), 6.07 (s, 1H), 6.03 (s, 1H), 4.89 (brs, 1H), 4.81 (brs, 1H). Two singlet signals (6.07 and 6.03 ppm) were observed by ^{1}H NMR analysis at 60 °C, while at room temperature these signals were observed like as two sets of doublets. These signals were attributed to OCH_2O by ^{13}C DEPT135, 2D-HMQC, 2D-HMBC NMR spectra (see ESI†). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 149.2, 147.7, 142.3, 140.3, 134.4, 126.1, 122.4, 122.3, 121.6, 119.3, 114.9, 113.5, 112.1, 110.6, 110.5, 109.5, 101.6, 98.8. mp: 110 °C. IR (neat) ν 3393, 1622 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{19}H_{13}NO_4$ [M$^{+\bullet}$]: 319.0839, found: 319.0838.

4-(2,4,6-Trimethoxyphenyl)-9*H*-carbazol-3-ol (3al). A brown solid **3al** (20.0 mg, 64% yield) was obtained from **1a** (18.3 mg, 0.10 mmol) and **2l** (16.8 mg, 0.10 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (brs, 1H), 7.31–7.27 (m, 3H), 7.15 (d, J = 8.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.93–6.89 (ddd, J = 8.0, 6.3, 1.7 Hz, 1H), 6.37 (s, 2H), 4.95 (brs, 1H), 3.96 (s, 3H), 3.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 159.6, 147.3, 140.3, 134.3, 125.1, 123.8, 122.9, 121.2, 118.5, 114.5, 113.6, 110.6, 110.3, 103.5, 91.3, 56.0, 55.5. mp: 238 °C. IR (neat) ν 3393, 1622 cm^{-1}. HRMS (MALDI) m/z calcd for $C_{21}H_{19}NO_4$ [M$^{+\bullet}$]: 319.0839, found: 319.0838.

Catalyst reuse experiment

To a 15 mL centrifuging tube, **1a** (18.3 mg, 0.10 mmol), **2a** (14.4 mg, 0.10 mmol), V-MPS4 (47 mg, 10 mol% based on vanadium content), and CH_2Cl_2 (1.0 mL, 0.1 M) were added. After the tube was purged with oxygen, the reaction mixture was stirred at 30 °C. After complete consumption of **1a** was confirmed by TLC analysis, EtOAc (4 mL) was added and the mixture was centrifuged (3000 rpm, 10 min), and the supernatant was removed by cannulation. The precipitate was resuspended in EtOAc (5 mL), sonicated for 1 min, centrifuged (3000 rpm, 10 min), and the supernatant was removed by cannulation. After this process was repeated twice, the precipitate was dried *in vacuo* (<1.0 torr) overnight at room temperature. The resultant precipitate was used for the next reaction by adding **1a**, **2a** and CH_2Cl_2 followed by purging with oxygen. The combined supernatant obtained from each reaction was concentrated *in vacuo* and the yield of **3aa** was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard.

Leaching examination of V-MPS4

Sample preparation for ICP-AES analysis. To a screw-cap test tube, V-MPS4 (47 mg, 0.010 mmol based on vanadium content) and CH_2Cl_2 (1.0 mL) were added. The suspension was stirred for 12 h at 30 °C. After that, the suspension was centrifuged (3000 rpm, 10 min) and the precipitated V-MPS4 was filtered off on a membrane filter (0.2 μm). The filtrate was evaporated *in vacuo*. To the residue was added 60% nitric acid (1.0 mL), and the resultant solution was stirred for 5 h at room temperature. Then, the solution was diluted with distilled water in a 25 mL volumetric flask. After passing through a membrane filter (0.2 μm pore), the solution was analyzed by ICP-AES to determine the vanadium content. The result (0.11 mg L^{-1}) corresponds to 0.55% (0.0028 mg, 0.055 μmol) of vanadium in V-MPS4.

Reaction using a supernatant. To a 15 mL centrifuged tube, V-MPS4 (47 mg, 0.010 mmol based on vanadium content) and CH_2Cl_2 (1.0 mL) were added. The suspension was stirred for 12 h at 30 °C. After that, the suspension was centrifuged (3000 rpm, 10 min) and the precipitated V-MPS4 was filtered off on a membrane filter (0.2 μm pore). The filtrate was added to another 15 mL centrifuging tube containing **1a** (18.3 mg, 0.10 mmol) and **2a** (14.4 mg, 0.10 mmol). After the tube was purged with oxygen, the mixture was stirred at 30 °C for 12 h. After the reaction, the mixture was filtered off through a short pad of silica gel (hexane/EtOAc = 1 : 1, 100 mL) and the filtrate was evaporated under reduced pressure. A trace amount of coupling product **3aa** (<5% yield) was detected by ^{1}H NMR analysis of the crude mixture. A blank experiment using CH_2Cl_2 was also conducted and **3aa** was not detected by the ^{1}H NMR analysis (Scheme S2, ESI†).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

XAS measurements were performed at the BL14B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Number 2021A1630). We thank Dr Tetsuo Honma (JASRI) for supporting the XAS experiments. This work was financially supported in part by the JSPS KAKENHI (Grant Numbers 18H02556, 21H02605, 20K22542, and 20K15279), the Mitsubishi Gas Chemical Award in Synthetic Organic Chemistry (Japan), the RIKEN-Osaka University Science and Technology Hub Collaborative Research Program from RIKEN and Osaka University, the Platform Project for Supporting Drug Discovery and Life Science Research (Basis for Supporting Innovative Drug Discovery and Life Science Research (BINDS)) from AMED (Grant Number 21am0101084), and the Sasagawa Scientific Research Grant from the Japan Science Society. K. Kasama would like to thank Nagai Memorial Research Scholarship from the Pharmaceutical Society of Japan and the Tokyo Biochemical Research Foundation for financial support. We acknowledge Taiyo Kagaku Co., Ltd. (Tokyo, Japan) for kindly supplying mesoporous silica (TMPS-4R).

Notes and references

1 (*a*) W. Wang, L. Cui, P. Sun, L. Shi, C. Yue and F. Li, *Chem. Rev.*, 2018, **118**, 9843; (*b*) S. Kramer, N. R. Bennedsen and S. Kegnæs, *ACS Catal.*, 2018, **8**, 6961.
2 M. Tada and Y. Iwasawa, *Chem. Commun.*, 2006, 2833.
3 M. Egi, K. Sugiyama, M. Saneto, R. Hanada, K. Kato and S. Akai, *Angew. Chem., Int. Ed.*, 2013, **52**, 3654.
4 (*a*) S. Akai, *Chem. Lett.*, 2014, **43**, 746; (*b*) K. Sugiyama, Y. Oki, S. Kawanishi, K. Kato, T. Ikawa, M. Egi and S. Akai, *Catal. Sci. Technol.*, 2016, **6**, 5023; (*c*) T. Nishio, S. Yoshioka, K. Hasegawa, K. Yahata, K. Kanomata and S. Akai, *Eur. J. Org. Chem.*, 2021, 4417.
5 (*a*) H. Pellissier, *Coord. Chem. Rev.*, 2020, **418**, 213395; (*b*) M. Sako, S. Takizawa and H. Sasai, *Tetrahedron*, 2020, **76**, 131645; (*c*) R. R. Langeslay, D. M. Kaphan, C. L. Marshall, P. C. Stair, A. P. Sattelberger and M. Delferro, *Chem. Rev.*, 2019, **119**, 2128.
6 (*a*) G. Bringmann, T. Gulder, T. A. M. Gulder and M. Breuning, *Chem. Rev.*, 2011, **111**, 563; (*b*) Z. Xie, X. Yang, Y. Duan, J. Han and C. Liao, *J. Med. Chem.*, 2021, **64**, 1283; (*c*) S. Issa, A. Prandina, N. Bedel, P. Rongved, S. Yous, M. Le Borgne and Z. Bouaziz, *J. Enzyme Inhib. Med. Chem.*, 2019, **34**, 1321.
7 (*a*) P. N. M. Botman, M. Postma, J. Fraanje, K. Goubitz, H. Schenk, J. H. V. Maarseveen and H. Hiemstra, *Eur. J. Org. Chem.*, 2002, 1952; (*b*) D. Devadiga, M. Selvakumar, P. Shetty, M. S. Santosh, R. S. Chandrabose and S. Karazhanov, *Int. J. Energy Res.*, 2021, **45**, 6584.
8 C. Brütting, R. F. Fritsche, S. K. Kutz, C. Börger, A. W. Schmidt, O. Kataeva and H. J. Knölker, *Chem.–Eur. J.*, 2018, **24**, 458.
9 (*a*) M. Sako, A. Sugizaki and S. Takizawa, *Bioorg. Med. Chem.*, 2018, **28**, 2751; (*b*) H. Kang, Y. E. Lee, P. V. G. Reddy, S. Dey, S. E. Allen, K. A. Niederer, P. Sung, K. Hewitt, C. Torruellas, M. R. Herling and M. C. Kozlowski, *Org. Lett.*, 2017, **19**, 5505; (*c*) M. Sako, K. Ichinose, S. Takizawa and H. Sasai, *Chem.–Asian J.*, 2017, **12**, 1305; (*d*) L. Liu, P. J. Carroll and M. C. Kozlowski, *Org. Lett.*, 2015, **17**, 508.
10 (*a*) J. L. Avila-Melo, A. Benavides, A. F. Gutiérrez, J. Tamariz and H. A. J. Vázquez, *Synthesis*, 2021, **53**, 2201; (*b*) Y.-S. Wang, H. P. He, Y. M. Shen, X. Hong and X. J. Hao, *J. Nat. Prod.*, 2003, **66**, 416.
11 In recent, the first CDC reaction between 3-hydroxycarbazoles and 2-naphthols catalyzed by an optically active oxovanadium complex was reported, see: M. Sako, K. Higashida, G. T. Kamble, K. Kaut, A. Kumar, Y. Hirose, D. Zhou, T. Suzuki, M. Rueping, T. Maegawa, S. Takizawa and H. Sasai, *Org. Chem. Front.*, 2021, **8**, 4878.
12 M. J. S. Dewar and T. Nakaya, *J. Am. Chem. Soc.*, 1968, **90**, 7134.
13 M. Nakajima, I. Miyoshi, K. Kanayama, S. Hashimoto, M. Noji and K. Koga, *J. Org. Chem.*, 1999, **64**, 2264.
14 S. Kasemthaveechok, L. Abella, M. Jean, M. Cordier, T. Roisnel, N. Vanthuyne, T. Guizouarn, O. Cador,

J. Autschbach, J. Crassous and L. Favereau, *J. Am. Chem. Soc.*, 2020, **142**, 20409.

15 (*a*) K. Kasama, H. Aoyama and S. Akai, *Eur. J. Org. Chem.*, 2020, 654; (*b*) G. A. I. Moustafa, K. Kasama, K. Higashio and S. Akai, *RSC Adv.*, 2019, **9**, 1165.

16 (*a*) A. Libmasn, H. Shalit, Y. Vainer, S. Narute, S. Kozuch and D. Pappo, *J. Am. Chem. Soc.*, 2015, **137**, 11453; (*b*) H. Egami, K. Matsumoto, T. Oguma, T. Kunisu and T. Katsuki, *J. Am. Chem. Soc.*, 2010, **132**, 13633.

17 S. Xia, L. Gan, K. Wang, Z. Li and D. Ma, *J. Am. Chem. Soc.*, 2016, **138**, 13493.

18 Y. F. Wong, Z. Wang and J. Sun, *Org. Biomol. Chem.*, 2016, **14**, 5751.

19 B. M. Trost and J. S. Tracy, *Chem.–Eur. J.*, 2015, **21**, 15108.