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Vanadium-Catalyzed Sulfenylation of Indoles and 2-Naphthols with Thiols under Molecular Oxygen

Yasunari Maeda, Motonori Koyabu, Takahiro Nishimura,* and Sakae Uemura*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

takahiro@scl.kyoto-u.ac.jp; uemura@scl.kyoto-u.ac.jp

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Vanadium oxyacetylacetonate [$VO(acac)_2$] works as a catalyst for the direct synthesis of 3-sulfanylindoles from indoles and thiols under an atmospheric pressure of molecular oxygen as a reoxidant. For example, the reaction of 2-phenylindole with benzenethiol in the presence of a catalytic amount of $VO(acac)_2$, potassium iodide, and 2,6-di-*tert*-butyl-*p*-cresol in chlorobenzene under molecular oxygen proceeds to afford 2-phenyl-3-(phenylsulfanyl)indole in 86% yield. This catalytic system can also be applied to 2-naphthols instead of indoles to give the corresponding 1-sulfanyl-2-naphthols in up to 57% yield.

Introduction

Indole derivatives have been well-known as important compounds such as biologically active substances and intermediates of many pharmaceuticals. Especially, 3-sufanylindoles are of interest as the precursors of anti-HIV active compounds,[1] antinociceptive active compounds,[2] 5-lipoxygenase inhibitors,[3] organic nonlinear optical materials,[4] etc. Although many useful methods of sulfenylation at the 3-position of indoles have been reported using a variety of reagents such as succinimide-sulfonium salt, sulfenic acid chloride, acyloxysulfonium salt, sulfide, disulfide, mono-*O*,*S*-acetal, etc., most of them need stoichiometric amounts of the reagents.[5] On the other hand, direct synthetic methods of 3-sulfanylindoles from indoles and thiols have been known, but they also need stoichiometric amounts of organic or inorganic reagents such as I_2,[6a,b] *N*-chlorosuccinimide,[6c] and phenyliodine(III)bis-(trifluoroacetate).[6d] One catalytic method for substitution by sulfur moiety at the 3-position of indole with disulfide using $AlCl_3$ as a catalyst has been reported, but severe reaction conditions were required and the yield of 3-sulfanylindole was relatively low.[7]

Vanadium compounds have been known as important oxidation catalysts for the synthesis of acids such as phthalic acid,[8] and unique organic reactions using them as catalysts have appeared in recent years.[9] Recently, we have reported the vanadium-complex-catalyzed oxidation of propargylic alcohols under an atmospheric pressure of molecular oxygen.[10] During the course of our further studies on this subject, we found that some vanadium complexes worked as efficient catalysts for the direct synthesis of 3-sulfanylindoles from thiols and indoles in the presence of an atmospheric pressure of molecular oxygen. Moreover, the use of 2-naphthols as substrates instead of indoles resulted in a formation of the corresponding 1-sulfanyl-2-naphthols, which could be used as agricultural chemicals for powdery mildew.[11] We report herein the direct catalytic synthesis of 3-sulfanylindoles

* To whom correspondence should be addressed. Tel/Fax: +81-75-383-2517.

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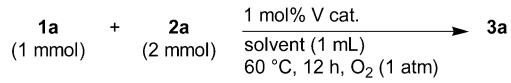
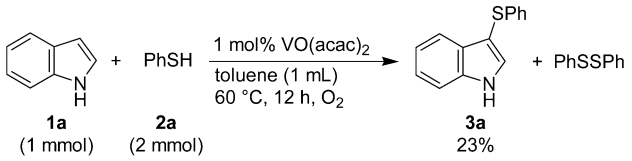
TABLE 1. Vanadium-Catalyzed Synthesis of 3-(Phenylsulfanyl)indole (3a) under Various Conditions



entry	solvent	catalyst	conversion of **1a** (%)	isolated yield of **3a** (%)[a]
1	toluene	$VO(acac)_2$	43	23
2	acetonitrile	$VO(acac)_2$	20	2
3	$ClCH_2CH_2Cl$	$VO(acac)_2$	59	16
4	**chlorobenzene**	**$VO(acac)_2$**	**60**	**38**
5	DMF	$VO(acac)_2$	1	0
6	ethanol	$VO(acac)_2$	2	tr
7	chlorobenzene	$V(acac)_3$	60	32
8	chlorobenzene	$VO(hfac)_2$	44	26
9	chlorobenzene	$VOCl_3$	44	28
10	chlorobenzene	$VOSO_4 \cdot nH_2O$	1	tr
11	chlorobenzene	V_2O_5	1	tr

[a] Based on **1a** employed.

SCHEME 1



and 1-sulfanyl-2-naphthols by reactions of indoles and 2-naphthols with thiols, respectively.

Results and Discussion

Vanadium-Catalyzed Synthesis of 3-Sulfanylindoles from Indoles and Thiols under Molecular Oxygen. First, indole (**1a**) and benzenethiol (**2a**) were chosen as substrates, and their reaction was examined under various reaction conditions (Table 1). Treatment of **1a** (1 mmol) and **2a** (2 mmol) in toluene (1 mL) in the presence of a catalytic amount of $VO(acac)_2$ (0.01 mmol) at 60 °C for 12 h under an atmospheric pressure of molecular oxygen gave 3-(phenylsulfanyl)indole (**3a**) in 23% yield together with diphenyl disulfide (1.38 mmol, 69% yield) and some unidentified compounds (Scheme 1 and Table 1, entry 1). Among solvents examined such as acetone, 1,2-dichloroethane, chlorobenzene, *N*,*N*-dimethylformamide, and ethanol (entries 2−6), chlorobenzene was revealed to be the solvent of choice, and **3a** was obtained in 38% yield (entry 4). Next, we examined the reaction in chlorobenzene using other vanadium compounds as catalysts in which $V(acac)_3$, $VO(hfac)_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate), and $VOCl_3$ were slightly less effective than $VO(acac)_2$ (entries 7−9). The use of $VOSO_4 \cdot nH_2O$ and V_2O_5 did not give any **3a** (entries 10 and 11). Some other transition metal compounds such as $(NH_4)_2Ce(NO_3)_6$, $Ti(O^iPr)_4$, $ZrCl_4$, $MoO_2(acac)_2$, $Mn(OAc)_2 \cdot 4H_2O$, $Fe(OAc)_2$, $Co(OAc)_2 \cdot 4H_2O$, $Ni(acac)_2$, $Pd(acac)_2$, and CuCl were found to be completely ineffective for this reaction.

TABLE 2. Optimization of the Reaction

entry	**2a** (mmol)	$VO(acac)_2$ (mmol)	PhCl (mL)	time (h)	conversion of **1a** (%)	isolated yield of **3a** (%)[a]
1	2	0.01	1	12	60	38
2	2	0.01	0.5	12	56	32
3	1	0.01	1	12	51	16
4	5	0.01	1	12	85	33
5[b]	2	0.01	1	12	9	tr
6	**2**	**0.01**	**1**	**48**	**65**	**44**
7	2	0.01	1	72	90	42
8	2	0.05	1	48	30	6
9[c]	2	0.01	1	48	0	−

[a] Based on **1a** employed. [b] MS3Å (250 mg) was added. [c] Under N_2 (1 atm).

Next, the effect of the amount of a catalyst and a solvent was investigated (Table 2). The reaction in a higher concentration of substrates did not improve the yield of **3a** (entry 2). Increasing or reducing of the amount of **2a** decreased the yield of **3a** (entries 3 and 4). When MS3Å was added as a dehydrating agent in this reaction mixture, **3a** was not obtained at all and diphenyl disulfide was formed selectively (1.9 mmol, 95% yield) (entry 5). Although a higher yield of **3a** was attained after 48 h (entry 6), the yield of **3a** was not improved by prolonging the reaction time further irrespective of higher conversion of **1a** (entry 7). When the amount of catalyst was increased, the yield of **3a** diminished due to the preferential formation of diphenyl disulfide (entry 8). The reaction under nitrogen atmosphere did not afford **2a** at all, suggesting that the presence of molecular oxygen is essential for this reaction (entry 9).

Further, the effect of additives was examined in order to improve the yield of **3a** (Table 3). When the reaction was carried out in the presence of 10 mol % KI under the same reaction conditions of entry 6 of Table 2, the yield of **3a** increased up to 66% yield (entry 2).[12] Other additives such as NaI, CsI, KBr, LiCl, and *n*-Bu_4NI were not effective (entries 3−6). Any appreciable improvement of the yield of **3a** was not observed by increasing or decreasing the amount of KI (entries 7 and 8).

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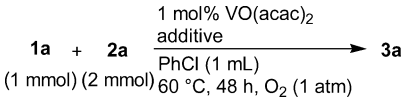
(12) The combination of a stoichiometric amount of I_2 and KI was used in the synthesis of 3-sulfanylindoles from indoles and thiols; see ref 6a and b.

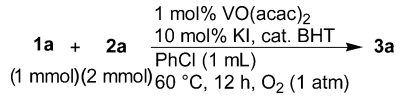
TABLE 3. Effect of Additive



entry	additive (mmol)	conversion of **1a** (%)	isolated yield of **2a** (%)[a]
1	none	65	44
2	**KI (0.1)**	**90**	**66**
3	NaI (0.1)	57	34
4	KBr (0.1)	65	30
5	LiCl (0.1)	64	16
6	*n*-Bu_4NI (0.1)	1	0
7	KI (0.05)	80	60
8	KI (0.2)	69	57

[a] Based on **1a** employed.

TABLE 4. Effect of the Amount of BHT



entry	BHT (mmol)	conversion of **1a** (%)	isolated yield of **3a** (%)[a]
1	0	60	38
2	0.02	97	67
3	**0.05**	**99**	**75**
4	0.05	95	34[b]
5	0.05	99	60[c]
6	0.1	69	47
7	1	58	30

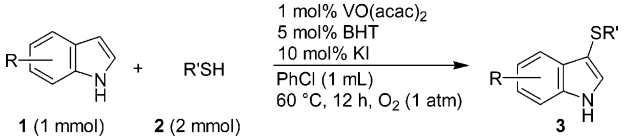
[a] Based on **1a** employed. [b] In the absence of KI. [c] For 24 h.

The reaction in the presence of a radical inhibitor such as 2,6-di-*tert*-butyl-*p*-cresol (butylhydroxytoluene, BHT) was next examined in order to obtain some information about the reaction pathway. Surprisingly, the addition of BHT dramatically accelerated the reaction, and **3a** was obtained in 75% yield within 12 h (entry 3). The combination of BHT and KI was revealed to be essential for obtaining **3a** in higher yield (entry 4). The presence of BHT might prevent the radical reaction of thiols forming diphenyl disulfide. These results show that the optimized reaction condition is the use of indole (1 mmol) and thiol (2 mmol) in the presence of catalytic amounts of $VO(acac)_2$ (1 mol %), KI (10 mol %), and BHT (5 mol %) at 60 °C for 12 h in chlorobenzene (1 mL) under an atmospheric pressure of molecular oxygen.

Results of the synthesis of a variety of 3-sulfanylindoles under the above optimized reaction conditions are summarized in Table 5. Reactions of **1a** with some benzenethiols, except for the one having a substituent at the ortho position (entry 2), smoothly gave the corresponding 3-sulfanylindoles in good yields (entries 3−7). The use of benzyl mercaptan (**2h**) as a substrate also gave the corresponding 3-sulfanylindole (**3h**) in good yield (entry 8). This reaction system could be applied for some alkanethiols such as **2i** and **2j**, giving the corresponding 3-sulfanylindole **3i** and **3j** in moderate yield (entries 9 and 10), whereas the treatment of 2-methyl-2-propanethiol (**2k**) with indole did not give any corresponding product (entry 11). Next, we examined the reaction of substituted indoles with **2a**. In all cases, except for the use of indole having a 2-ethoxycarbonyl group (**1e**), the corresponding 3-sulfanylindoles were obtained in moderate to high yield (entries 12−18).

Vanadium-Catalyzed Synthesis of 1-Sulfanyl-2-naphthols from 2-Naphthols and Thiols under Molecular Oxygen. This vanadium-catalyzed sulfenylation was then applied to 2-naphthol (**4a**). Treatment of **4a** with **2a** in the presence of a catalytic amount of $VO(acac)_2$ in toluene under an atmospheric pressure of molecular

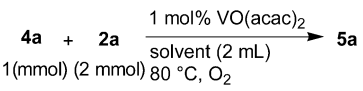
TABLE 5. Vanadium-Catalyzed Synthesis of 3-Sulfanylindoles under Molecular Oxygen



entry	R	R′	time (h)	product	conversion of **1** (%)	isolated yield of **2** (%)[a]
1	H (**1a**)	Ph (**2a**)	12	**3a**	99	75
2	H (**1a**)	2-MeC_6H_4 (**2b**)	12	**3b**	57	29
3	H (**1a**)	3-MeC_6H_4 (**2c**)	12	**3c**	91	80
4	H (**1a**)	4-MeC_6H_4 (**2d**)	12	**3d**	79	65
5	H (**1a**)	4-ClC_6H_4 (**2e**)	12	**3e**	98	74
6	H (**1a**)	4-$MeOC_6H_4$ (**2f**)	12	**3f**	80	70
7	H (**1a**)	4-$NO_2C_6H_4$ (**2g**)	12	**3g**	92	75
8	H (**1a**)	$PhCH_2$ (**2h**)	48	**3h**	58[b]	77
9	H (**1a**)	C_8H_{17} (**2i**)	48	**3i**	99	43[b]
10	H (**1a**)	$(CH_2)_2COOEt$ (**2j**)	48	**3j**	15	45
11	H (**1a**)	^{t}Bu (**2k**)	48	**3k**	49	0
12	*N*-Me (**1b**)	Ph (**2a**)	48	**3l**	93	26
13	2-Me (**1c**)	Ph (**2a**)	12	**3m**	86	85
14	2-Ph (**1d**)	Ph (**2a**)	12	**3n**	22	86
15	2-CO_2Et (**1e**)	Ph (**2a**)	48	**3o**	24	0
16	3-Me (**1f**)	Ph (**2a**)	12	**3p**	54	47[c]
17	5-Me (**1g**)	Ph (**2a**)	12	**3q**	99	70
18	5-Cl (**1h**)	Ph (**2a**)	48	**3r**	80	60

[a] Based on indole employed. [b] Isolated by HPLC. [c] 3-Methyl-2-(phenylsulfanyl)indole.

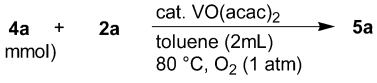
TABLE 6. Solvent Effect



entry	solvent	time (h)	conversion of **4a** (%)	isolated yield of **5a** (%)[a]
1	**toluene**	**24**	**96**	**28**
2	chlorobenzene	24	100	25
3	DMF	21	45	0
4	CH_3CN	21	7	2
5	DMSO	42	62	tr
6	$ClCH_2CH_2Cl$	19	20	10
7[b]	ethanol	93	0	-

[a] Based on **4a** employed. [b] At 70 °C.

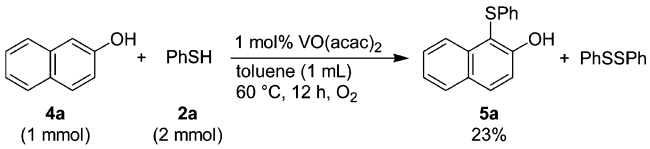
TABLE 7. Optimization of the Reaction



entry	**2a** (mmol)	$VO(acac)_2$ (mol %)	time (h)	conversion of **4a** (%)	isolated yield of **5a** (%)[a]
1	2	1	24	96	28
2	2	2	16	100	34
3	2	**5**	**16**	**100**	**44**
4	2	10	23	95	36
5	1	5	26	91	20
6	5	5	23	100	39
7[b]	2	5	26	93	5
8[c]	2	5	24	5	tr

[a] Based on **4a** employed. [b] KI (0.1 mmol) was added. [c] Under N_2 (1 atm).

SCHEME 2

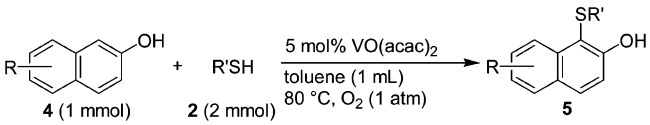


oxygen at 80 °C for 24 h gave 1-(phenylsulfanyl)-2-naphthol (**5a**) in 28% yield (Scheme 2 and Table 6, entry 1). Among solvents examined, toluene was revealed to be the solvent of choice. Similarly to the sulfenylation of indoles, $VO(acac)_2$ was the most efficient catalyst within a variety of vanadium salts examined, such as $V(acac)_3$, $VO(hfac)_2$, $VO(tfac)_2$, $VO(hfdm)_2$, $VOSO_4 \cdot nH_2O$, $VO(C_2O_4)$, and V_2O_5.

Attempts to optimize this reaction are summarized in Table 7. The reaction in the presence of 5 mol % of $VO(acac)_2$ gave **5a** in 44% yield (entries 1−4). Increasing or decreasing of the amount of **2a** did not improve the yield of **3a** (entries 5 and 6). Although the addition of KI was beneficial in the case of indole sulfenylation, a decrease in the yield was observed in the naphthol sulfenylation case (entry 7). When this reaction was carried out under nitrogen atmosphere, **4a** was not converted to **5a** at all (entry 8). This result shows that the presence of molecular oxygen is essential for this reaction as well.

Using 5 mol % catalyst, the reactions of 2-naphthol with some thiols were carried out (Table 8). Although 2-naththol was consumed completely in all cases, the yields of the corresponding 1-sulfanyl-2-naphthols were low (entries 2−6). Interestingly, thiol **2k**, which could not

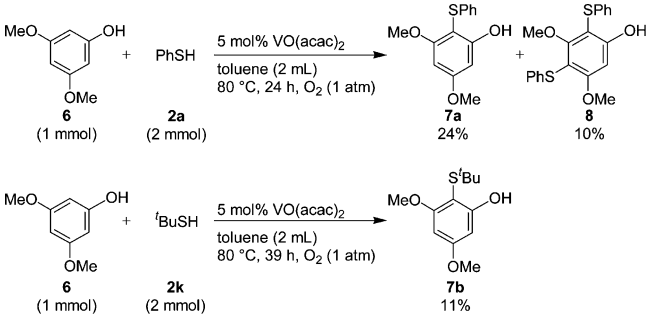
TABLE 8. Vanadium-Catalyzed Synthesis of 1-Sulfanyl-2-naphthol under Molecular Oxygen



entry	R	R′	time (h)	product	isolated yield of **2** (%)[a,b]
1	H (**4a**)	Ph (**2a**)	16	**5a**	44
2	H (**4a**)	4-MeC_6H_4 (**2d**)	26	**5b**	27
3	H (**4a**)	4-ClC_6H_4 (**2e**)	19	**5c**	25
4	H (**4a**)	^{t}Bu (**2k**)	27	**5d**	26
5	H (**4a**)	C_8H_{17} (**2i**)	24	**5e**	24
6	H (**4a**)	Cy (**2l**)	18	**5f**	24
7	6-Br (**4b**)	Ph (**2a**)	19	**5g**	57
8	7-MeO (**4c**)	Ph (**2a**)	19	**5h**	47

[a] Based on **4** employed. [b] **4** was consumed completely in all reactions.

SCHEME 3



react with indole, reacted to give 1-(*tert*-butylsulfanyl)-2-naphthol (**5e**) (entry 5). Next, the reaction of some 2-naphthol derivatives with benzenethiol (**2a**) was examined. Thus, from 6-bromo-2-naphthol (**4b**) and 7-methoxy-2-naphthol (**4c**), 6-bromo-1-(phenylsulfanyl)-2-naphthol (**5g**) and 7-methoxy-1-(phenylsulfanyl)-2-naphthol (**5h**) were obtained in moderate yields (entries 7 and 8). 3,5-Dimethoxyphenol (**6**) could be used as a substrate instead of 2-naphthol, and the reaction of **6** with benzenethiol or 2-methyl-2-propanethiol gave the corresponding 3,5-dimethoxy-2-sulfanylphenol, respectively, but the yield was low (Scheme 3).

Plausible Reaction Pathway. The reaction seems to be electrophilic in nature since (i) the reactivity as well as the orientation of the substituted indoles are similar to those of other known electrophilic substitution reactions of indoles[6a] and (ii) a radical scavenger such as BHT does not inhibit this reaction. A proposed catalytic cycle mechanism is shown in Figure 1 that is a similar to one assumed by Uang[9k] for a vanadium-catalyzed Mannich-type reaction. First, a vanadium(IV) species (**A**) reacts with thiol and molecular oxygen to form a vanadium(V) species (**B**). An electrophilic sulfur moiety in species **B** reacts with indoles or 2-naphthols to give the corresponding 3-sulfanylindoles or 1-sulfanyl-2-naphthols and a hydroxyvanadium(III) species (**C**). Dehydration from species **C** gives an oxovanadium(III) species (**D**). The species **D** is transformed to dioxovanadium(V) species (**E**) by oxidation with molecular oxygen, and the successive reaction of **E** with thiols reproduces species **B**, furnishing a catalytic cycle in vanadium.

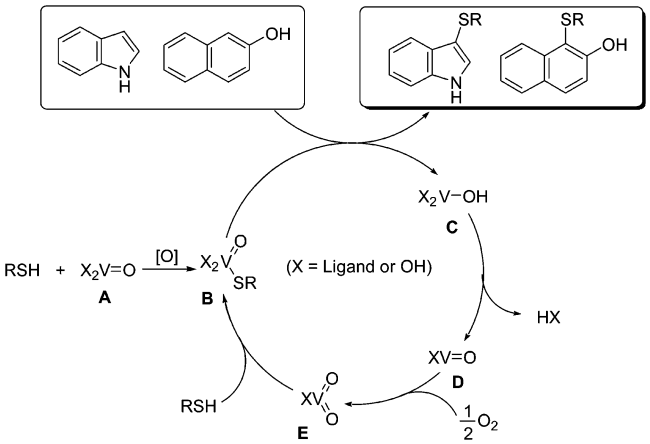


FIGURE 1. Plausible reaction pathway.

Conclusion

We found that vanadium oxyacetylacetonate [VO(acac)$_2$] was an effective catalyst for the direct synthesis of 3-sulfanylindoles (up to 86% yield) and 1-sulfanyl-2-naphthols (up to 57% yield) from the reaction of indoles and 2-naphthols with thiols, respectively, in chlorobenzene or toluene under an atmospheric pressure of molecular oxygen. The addition of catalytic amounts of potassium iodide and 2,6-di-*tert*-butyl-*p*-cresol improved the yield of 3-sulfanylindoles. This catalytic reaction did not proceed at all under a nitrogen atmosphere. The reaction mechanism appears to be electrophilic in nature.

Experimental Section

General Methods. ^{1}H NMR spectra were obtained in $CDCl_3$ at 270, 300, or 400 MHz with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained at 67.5, 75.5, or 100 MHz.

Materials. Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by the usual method before use. VO(tfac)$_2$, VO(hfac)$_2$, and VO(hfdm)$_2$ were synthesized by literature methods.[13] All indoles, 2-naphthols, thiols, and 3,5-dimethoxyphenol were commercial products. Sulfanylindoles **3a**, **3h**, and **3m** were commercial products. Other sulfanylindoles and 1-sulfanyl-2-naphthols **5a**[14] and **5e**[11] are known compounds and characterized by their spectral data. 1-Sulfanyl-2-naphthols **5b**, **5c**, **5d**, **5f**, **5g**, and **5h** and 3,5-dimethoxysulfanylphenols **7a**, **7b**, and **8** are new compounds. Some selected spectral data of sulfanylindoles and 1-sulfanyl-2-naphthols are shown below.

General Procedure for Vanadium-Catalyzed Synthesis of 3-Sulfanylindoles from Indoles and Thiols under Molecular Oxygen. To a solution of VO(acac)$_2$ (2.65 mg, 0.0100 mmol) in chlorobenzene (0.500 mL) in a 20-mL Schlenk flask were added potassium iodide (16.7 mg, 0.100 mmol) and 2,6-di-*tert*-butyl-*p*-cresol (11.0 mg, 0.0500 mmol). Next, indole (1.00 mmol) and thiol (2.00 mmol) in chlorobenzene (0.5 mL) were added, and the resulting mixture was stirred. Oxygen gas was then introduced into the flask from an O_2 balloon under atmospheric pressure, and then the mixture was stirred vigorously for 12 h at 60 °C under oxygen. The mixture was cooled to room temperature and filtered through a pad of Florisil. For isolation of the product, the solvent was evaporated and the residue was purified by column chromatography (*n*-hexane−ethyl acetate as an eluent). Isolation of **3i** was carried out using preparative HPLC after column chromatography because a small amount of unidentified products could not be separated from the major product by column chromatography.

3-(*m*-Tolylsulfanyl)indole[6a] **(3c; Table 5, Entry 3).** White solid; mp 124.4−125.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 3H), 6.85 (t, J = 7.0 Hz, 2H), 7.00−7.03 (m, 2H), 7.13 (td, J = 7.4, 1.1 Hz, 1H), 7.22 (td, J = 7.4, 1.1 Hz, 1H), 7.31 (dd, J = 5.4, 2.6 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 8.12 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.3, 102.6, 111.6, 119.5, 120.8, 122.9, 122.9, 125.7, 126.4, 128.6, 129.0, 130.7, 136.3, 138.4, 138.9.

3-(*p*-Tolylsulfanyl)indole[6a] **(3d; Table 5, Entry 4).** White solid; mp 125.0−126.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 3H), 6.94 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 7.13 (td, J = 1.2, 8.0 Hz, 1H), 7.23 (td, J = 1.2, 8.0 Hz, 1H), 7.31−7.34 (m, 2H), 7.60 (d, J = 8.0 Hz, 1H), 8.14 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.9, 103.1, 111.5, 119.5, 120.7, 122.8, 126.1, 128.9, 129.4, 130.4, 134.5, 135.3, 136.3.

3-(4-Chlorophenylsulfanyl)indole[6a] **(3e; Table 5, Entry 5).** White solid; mp 127.5−128.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (dt, J = 8.8, 2.4 Hz, 2H), 7.09 (dt, J = 8.8, 2.4 Hz, 2H), 7.16 (td, J = 7.2, 1.1 Hz, 1H), 7.26 (td, J = 7.2, 1.1 Hz, 1H), 7.38−7.43 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 8.33 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 102.3, 111.6, 119.4, 121.0, 123.2, 127.0, 128.7, 128.7, 130.5, 136.4, 137.7.

3-(*n*-Octylsulfanyl)indole[5e] **(3i; Table 5, Entry 9).** Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, J = 6.2 Hz, 3H), 1.23−1.35 (m, 10H), 1.53 (quint, J = 7.3 Hz, 2H), 2.69 (t, J = 7.3 Hz, 2H), 7.17−7.34 (m, 4H), 7.77 (d, J = 6.6 Hz, 1H), 8.13 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.1, 22.7, 28.6, 29.2, 29.9, 31.8, 36.5, 106.1, 111.4, 119.3, 120.2, 122.5, 129.1, 129.3, 136.1; IR (neat, cm^{-1}) 3408, 2925, 2853, 1453, 1406, 1340, 1235, 1091, 1008, 1023, 743. Anal. Calcd for $C_{16}H_{23}NS$: C, 73.51; H, 8.87. Found: C, 73.80; H, 9.04.

Ethyl 3-(3-indoylthio)propionate[15] **(3j; Table 5, Entry 10).** Pale green liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (t, J = 7.2 Hz, 3H), 2.53 (t, J = 7.2 Hz, 2H), 2.93 (t, J = 7.2 Hz, 2H), 4.08 (t, J = 7.2 Hz, 2H), 7.19−7.24 (m, 2H), 7.29 (d, J = 2.6 Hz, 1H), 7.33−7.37 (m, 1H), 7.76−7.79 (m, 1H), 8.45 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.1, 31.0, 35.1, 60.6, 104.3, 111.5, 119.1, 120.5, 122.7, 129.3, 130.1, 136.3, 172.2 (C=O); IR (neat, cm^{-1}) 3401, 2979, 1719, 1453, 1410, 1339, 1236, 1094, 1009, 745. Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06. Found: C, 62.88; H, 6.11.

3-Methyl-2-(phenylsulfanyl)indole[5o] **(3p; Table 5, Entry 16).** White solid; mp 73.8−74.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.03−7.31 (m, 8H), 7.60 (d, J = 7.8 Hz, 1H), 7.97 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.4, 110.8, 119.4, 119.6, 119.9, 121.5, 123.5, 125.7, 126.5, 128.5, 129.1, 136.8, 137.1; IR (KBr, cm^{-1}) 3375, 3056, 2908, 1579, 1476, 1448, 1330, 1288, 1239, 1082, 1022, 975, 964, 752, 739, 687, 651, 580, 485. Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47. Found: C, 74.98; H, 5.43.

5-Methyl-3-(phenylsulfanyl)indole[16] **(3q; Table 5, Entry 17).** White solid; mp 153.0−154.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01−7.18 (m, 6H), 7.28 (d, J = 8.0 Hz, 1H), 7.38−7.40 (m, 2H), 8.21 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4, 101.8, 111.2, 119.1, 124.6, 124.7, 125.6, 128.7, 129.3, 130.4, 130.9, 134.7, 139.4.

5-Chloro-3-(phenylsulfanyl)indole[17] **(3r; Table 5, Entry 18).** White solid; mp 112.5−113.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04−7.24 (m, 6H), 7.33 (d, J = 8.6 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.58 (d, J = 1.5 Hz, 1H), 8.43 (br s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 102.8, 112.7, 119.1, 123.5, 125.0,

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125.8, 126.9, 128.8, 130.3, 132.0, 134.8, 138.7; IR (KBr, cm^{-1}) 3401, 3106, 1581, 1477, 1442, 1098, 1024, 890, 870, 803, 743, 735, 689, 585, 515, 496, 425. Anal. Calcd for $C_{14}H_{10}ClNS$: C, 64.73; H, 3.88. Found: C, 64.49; H, 3.99.

General Procedure for Vanadium-Catalyzed Synthesis of 1-Sulfanyl-2-naphthols from 2-Naphthol and Thiols under Molecular Oxygen. To a solution of $VO(acac)_2$ (13.3 mg, 0.0500 mmol) in toluene (1.0 mL) in a 20-mL Schlenk flask were added 2-naphthol (1.00 mmol) and a solution of thiol (2.00 mmol) in toluene (1.0 mL), and the resulting mixture was stirred. Oxygen gas was then introduced into the flask from an O_2 balloon under atmospheric pressure, and then the mixture was stirred vigorously for 16−24 h at 80 °C under oxygen. The mixture was then cooled to room temperature and then filtered through a pad of Florisil. Isolation of the product was carried out as in the case of the reaction using indole as a substrate. Isolation of **5g** was carried out using preparative HPLC after column chromatography.

1-Phenylsulfanyl-2-naphthol[14] (5a; Table 8, Entry 1). White solid, mp = 61.5−62.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00−7.18 (m, 6H), 7.33 (d, J = 8.8 Hz, 1H), 7.35 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.47 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 108.0, 116.8, 123.8, 124.7, 125.9, 126.3, 127.9, 128.5, 129.1, 129.5, 132.8, 135.3, 135.4, 157.0.

1-(*p*-Tolylsulfanyl)-2-naphthol (5b; Table 8, Entry 2). Yellow solid, mp = 72.5−73.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 6.95 (q, J = 8.3 Hz, 4H), 7.21 (s, 1H, OH), 7.32 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 8.22 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 108.6, 116.7, 123.6, 124.6, 126.5, 127.7, 128.4, 129.3, 129.8, 131.6, 132.4, 135.2, 135.7, 156.6; IR (KBr, cm^{-1}) 3377, 1617, 1591, 1492, 1458, 1386, 1194, 1120, 811, 745, 561, 491. Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found C, 76.52; H, 5.30.

1-(4-Chlorophenylsulfanyl)-2-naphthol[11] (5c; Table 8, Entry 3). Yellow solid, mp = 105.0−106.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.93 (d, J = 8.6 Hz, 2H), 7.10 (s, 1H, OH), 7.13 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.4 Hz, 1H), 7.37 (t, J = 7.1 Hz, 1H), 7.59 (t, J = 7.1 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 107.4, 116.7, 123.8, 124.3, 127.4, 127.9, 128.5, 129.1, 129.3, 131.7, 132.9, 133.7, 135.0, 156.8.

1-(*n*-Octylsulfanyl)-2-naphthol (5d; Table 8, Entry 4). Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 6.8 Hz, 3H), 1.21−1.35 (m, 10H), 1.54 (quint, J = 7.2 Hz, 2H), 2.69 (t, J = 7.2 Hz, 2H), 7.25 (d, J = 8.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.40 (s, 1H, OH), 7.55 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 8.34 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.9, 29.2, 29.2, 30.0, 31.8, 36.0, 111.2, 116.2, 123.3, 124.5, 127.2, 128.5, 129.2, 131.2, 135.2, 156.1; IR (neat, cm^{-1}) 3371, 2925, 1619, 1595, 1460, 1384, 1202, 1127, 817. 750. Anal. Calcd for $C_{18}H_{24}OS$: C, 74.95; H, 8.39. Found: C, 74.70; H, 8.38.

1-(*tert*-Butylsulfanyl)-2-naphthol (5e; Table 8, Entry 5). Pale yellow liquid; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.33 (s, 9H), 7.26 (d, J = 8.3 Hz, 1H), 7.33 (ddd, J = 8.3, 7.1, 1.1 Hz, 1H), 7.51 (ddd, J = 8.3, 7.1, 1.1 Hz, 1H), 7.55 (s, 1H, OH), 7.75 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 8.43 (d, J = 8.3 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.5, 50.4, 110.0, 116.2, 123.2, 125.8, 126.9, 128.2, 129.1, 131.9, 136.8, 157.3; IR (neat, cm^{-1}) 3363, 2960, 1618, 1595, 1384, 1207, 1127, 819, 750, 588, 523. Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.29; H, 6.94.

1-Cyclohexylsulfanyl-2-naphthol (5f; Table 8, Entry 6). Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19−1.94 (m, 10H), 2.90 (tt, J = 10.9, 3.7 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 7.35 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.43 (s, 1H, OH), 7.55 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.90 (d, J = 8.3 Hz, 2H), 8.35 (d, J = 8.3 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.5, 26.1, 33.8, 48.2, 110.3, 116.3, 123.4, 125.0, 127.3, 128.5, 129.3, 131.4, 135.9, 156.7; IR (neat, cm^{-1}) 3368, 2929, 1618, 1595, 1384, 1200, 1127, 816, 749. Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02. Found: C, 74.36; H, 7.25.

6-Bromo-1-phenylsulfanyl-2-naphthol (5g; Table 8, Entry 7). White solid, mp = 97.5−98.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (tt, J = 6.8, 1.7 Hz, 2H), 7.04−7.16 (m, 4H), 7.31 (d, J = 9.0 Hz, 1H), 7.48 (dd, J = 9.0, 2.0 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 108.4, 117.7, 118.0, 126.0, 126.3, 126.6, 129.2, 130.4, 130.5, 131.0, 131.7, 134.0, 134.9, 157.1; IR (KBr, cm^{-1}) 3370, 1610, 1587, 1209, 1187, 1131, 934, 815, 734, 687. Anal. Calcd for $C_{16}H_{11}BrOS$: C, 58.02; H, 3.35. Found: C, 57.76; H, 3.14.

7-Methoxy-1-phenylsulfanyl-2-naphthol (5h; Table 8, Entry 8). Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.97−7.19 (m, 8H), 7.53 (d, J = 2.4 Hz, 1H), 7.67 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.2, 103.7, 107.2, 114.1, 116.0, 124.6, 125.9, 126.5, 129.1, 130.1, 132.4, 135.1, 137.1, 157.4, 159.4; IR (neat, cm^{-1}) 3397, 1620, 1513, 1426, 1221, 1194, 1034, 835, 739, 689. Anal. Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00. Found: C, 72.02; H, 5.02.

3,5-Dimethoxy-2-(phenylsulfanyl)phenol (7a). White solid, mp = 66.5−67.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.82 (s, 3H), 6.13 (d, J = 2.4 Hz, 1H), 6.30 (d, J = 2.5 Hz, 1H), 6.91 (s, 1H, OH) 7.04−7.23 (m, 5H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 55.5, 56.2, 91.9, 92.2, 95.6, 125.4, 125.8, 128.8, 135.9, 159.4, 161.7, 163.3; IR (KBr, cm^{-1}) 3395, 1599, 1578, 1477, 1467, 1453, 1439, 1425, 1361, 1312, 1210, 1193, 1157, 1102, 936, 818, 739, 690, 568, 483, 465. Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38. Found: C, 63.88; H, 5.27.

1-(*tert*-Butylsulfanyl)-3,5-dimethoxyphenol (7b). White solid, mp = 82.5−83.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.29 (s, 9H), 3.81 (s, 3H), 3.81 (s, 3H), 6.07 (d, J = 2.5 Hz, 1H), 6.24 (d, J = 2.5 Hz, 1H), 7.31 (s, 1H, OH); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 31.0, 49.1, 55.4, 55.7, 91.4, 91.6, 97.4, 160.0, 162.3, 162.6; IR (KBr, cm^{-1}) 2932, 2856, 2211, 1709, 1671, 1450, 1243, 1165, 974, 894, 725. Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.49. Found: C, 59.24; H, 7.78.

3,5-Dimethoxy-2,4-di-(phenylsulfanyl)phenol (8). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.82 (s, 3H), 6.57 (s, 1H), 7.05−7.25 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.5, 62.5, 95.1, 103.5, 106.3, 124.8, 125.9, 126.1, 126.4, 128.6, 129.1, 135.6, 138.1, 160.6, 164.0, 165.7; IR (neat, cm^{-1}) 3388, 2936, 1586, 1478, 1397, 1299, 1193, 1114, 1023, 926, 824, 738, 689. Anal. Calcd for $C_{20}H_{18}O_3S_2$: C, 64.84; H, 4.90. Found: C, 65.04; H, 4.91.

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