Alkenylation of 1- and 2-Naphthols by Using Magnesium Alkylidene Carbenoids as Electrophilic Alkenylating Agents

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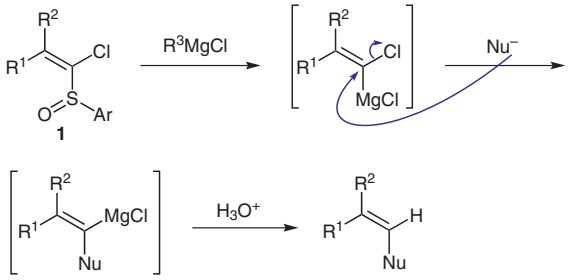
Abstract: 1- and 2-Naphthols were successfully alkenylated in a regioselective manner by treating the corresponding lithium 1- and 2-naphtholates with magnesium alkylidene carbenoids. The magnesium alkylidene carbenoids were generated *in situ* by a sulfoxide–magnesium exchange reaction of 1-chlorovinyl 4-tolyl sulfoxides with isopropylmagnesium chloride. The reaction of magnesium alkylidene carbenoids with lithium 2-naphtholates took place at the 1-position of the naphthyl ring to give 1-(alk-1-enyl)-2-naphthols in respectable yields. The alkenylation of 1-naphthols proceeded at the 2-position of the naphthol ring to give 2-(alk-1-enyl)-1-naphthols in yields of 56–67%. In contrast to the reaction of lithium naphtholates with magnesium alkylidene carbenoids, the reaction of lithium phenolates gave low yields of the corresponding alk-1-enyl aryl ethers.

Key words: alkenation, phenols, carbenoids, sulfoxides, alkenes, arenes, organometallic reagents

ortho-Alkenylphenolic compounds, such as 2-(alk-1-enyl)-1-naphthols and 1-(alk-1-enyl)-2-naphthols, are important synthetic intermediates, especially as precursors of derivatives of benzofurans or naphthofurans.[1] The classical route for the synthesis of such compounds involves allylation of the hydroxy group in a phenolic compound, Claisen rearrangement of the resultant allyl aryl ether, and subsequent transition metal-catalyzed isomerization of the allylarene.[2] The Heck reaction has become the most popular method for the construction of styrene units.[1c,3] A regioselective *ortho*-monohalogenation of electron-rich phenolic compounds is required for the synthesis of *ortho*-alkenylphenolic compounds by means of the Heck reaction.[4] Direct alkenylation with alkynes is a simple and straightforward method for the introduction of alkenyl groups into phenolic compounds.[5] However, because the reaction has to be carried out in the presence of a Lewis acid under harsh reaction conditions, its synthetic scope is limited. Accordingly, the development of an alternative route for the preparation of *ortho*-alkenylphenolic compounds is required.

Previously, we found that treatment of 1-chlorovinyl 4-tolyl sulfoxides **1** with Grignard reagents provides magnesium alkylidene carbenoids as reactive intermediates (Scheme 1).[6] These magnesium alkylidene carbenoids, generated *in situ*, function as electrophilic alkenylating agents for various nucleophiles, including Grignard reagents, aryllithiums, lithium acetylides, lithium amides, lithium thiolates, or lithium enolates,[7] although the nucleophilic substitution reaction does not generally occur at the vinylic carbon atom of the haloalkene. Meanwhile, phenolic compounds are known to act as carbon nucleophiles toward dichlorocarbene in the Reimer–Tiemann reaction.[8] In addition, we recently found that the reaction of lithium phenolates or naphtholates with cyclopropyl- or cyclobutylmagnesium carbenoids gives spirocyclic dienones through a Buchner ring expansion.[9] If phenolic compounds could be alkenylated by magnesium alkylidene carbenoids, then a variety of *ortho*-alkenylphenolic compounds might be directly obtained. Here, we report the synthesis of alkenylated 1- and 2-naphthols through the substitution reaction of lithium 1- and 2-naphtholates with magnesium alkylidene carbenoids. The reaction of lithium phenolates with magnesium alkylidene carbenoids is also reported.



Scheme 1 Reaction of magnesium alkylidene carbenoids with nucleophiles

We examined the alkenylation of 2-naphthol (**2a**) by using the spirocyclic 1-chlorovinyl 4-tolyl sulfoxide **1a** as the source of the corresponding magnesium alkylidene carbenoid (Scheme 2). A solution of isopropylmagnesium chloride in tetrahydrofuran was added to a mixture of lithium 2-naphtholate (1.5 equiv) [prepared from 2-naphthol (**2a**) and butyllithium] and sulfoxide **1a** in tetrahydrofuran at –78 °C, and the reaction mixture was allowed to warm

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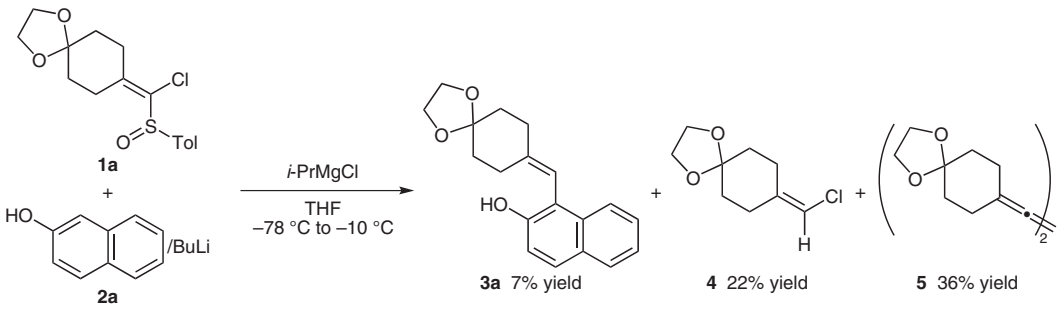
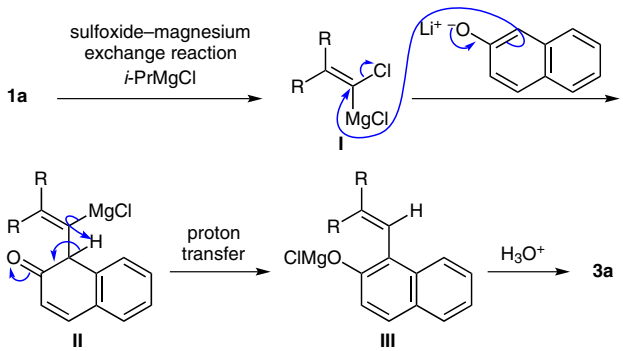


Scheme 2 Alkenylation of 2-naphthol (**2a**) with a magnesium alkylidene carbenoid generated from sulfoxide **1a**

to –10 °C. Acidic workup of the reaction mixture gave the alkenylated 2-naphthol **3a** in 7% yield, together with the chloroalkene **4** (22%) and cumulene **5** (36%).

A comparison of the ^{1}H NMR spectrum of 2-naphthol (**2a**) with that of the product **3a** showed that the signal for the aromatic proton at the 1-position (δ = 7.13 ppm) disappeared and a signal at δ = 6.30 ppm, corresponding to an alkenyl proton, appeared, demonstrating that the alkenyl group had been introduced at the 1-position of the naphthol ring. The presence of a phenolic hydroxy group in product **3a** was confirmed by a H–D exchange experiment with methanol-d_4 and by the iron(III) chloride test.

The alkenylation of 2-naphthol might occur by the following mechanism (Scheme 3). Initially, the magnesium alkylidene carbenoid **I** is generated from sulfoxide **1a** and isopropylmagnesium chloride by a sulfoxide–magnesium exchange reaction.[6] Subsequent nucleophilic substitution of lithium 2-naphtholate by the magnesium alkylidene carbenoid **I** takes place predominantly at the 1-position of the naphthol ring to give cyclohexadienone **II**.[9b,10] The nonaromatic intermediate **II** tautomerizes to the more-stable aromatic 2-naphtholate **III**. Finally, protonation of 2-naphtholate **III** leads to the formation of the 1-(alk-1-enyl)-2-naphthol **3a**.



Scheme 3 A plausible mechanism for the alkenylation of 2-naphthol with magnesium alkylidene carbenoid **I**

We then examined various reaction conditions in an attempt to improve the efficiency of the alkenylation reaction. Chloroalkene **4** and cumulene **5** were the major byproducts in this reaction.[7a] The former seemed to arise from the protonation of magnesium alkylidene carbenoid **I** by water, and the latter appeared to originate from the dimerization of magnesium alkylidene carbenoid **I** as a result of the low nucleophilicity of lithium 2-naphtholate. To eliminate trace amounts of the proton source from the reaction medium, we added *tert*-butylmagnesium chloride, which is not reactive toward sulfoxide **1a**, to the reaction mixture before conducting the sulfoxide–magnesium exchange reaction. We also reduced the concentration of the magnesium alkylidene carbenoid **I** from 0.5 mol/L to 0.1 mol/L in an attempt to limit the self-coupling reaction of magnesium alkylidene carbenoid **I**. Furthermore, we used five equivalents of lithium 2-naphtholate to compensate for its low nucleophilicity. As a result, we obtained the desired 1-(alk-1-enyl)-2-naphthol **3a** in 66% yield, and we reduced the yields of byproducts **4** and **5** to 6% and 7%, respectively (Table 1, entry 1).

We then examined the alkenylation of the substituted 2-naphthols **2b** and **2c** and the related compounds **2d** and **2e** with the magnesium alkylidene carbenoid generated from sulfoxide **1a** under the optimized reaction conditions described above (Table 1, entries 2–5). Alkenylation of 7-methoxy-2-naphthols (**2b**) with the magnesium alkylidene carbenoid gave the corresponding 1-(alk-1-enyl)-2-naphthol **3b** in 78% yield (entry 2). 6-Bromo-2-naphthol (**2c**) similarly gave the 1-(alk-1-enyl)-2-naphthol **3c** in 62% yield (entry 3). 2-Methoxynaphthalene (**2d**) did not react with the magnesium alkylidene carbenoid (entry 4), indicating that a phenolic hydroxy group is essential for the alkenylation reaction to occur. The lithium thiolate prepared from naphthalene-2-thiol (**2e**) exhibited a different reactivity toward the magnesium alkylidene carbenoid (entry 5). In this reaction, the sulfur atom was alkenylated to give alk-1-enyl aryl sulfide **3e′** (Figure 1) in 87% yield, and 1-(alk-1-enyl)naphthalene-2-thiol **3e** was not formed. The trend for the reactivity observed for the reaction of lithium naphthalene-2-thiolate is analogous to that observed for the reaction of lithium benzenethiolates.[7e]

To explore the scope of the alkenylation reaction further, we examined a range of magnesium alkylidene carbenoids as alkenylating agents for lithium 2-naphtholate (Table 2). The reaction of lithium 2-naphtholate with magnesium alkylidene carbenoids generated from sulfoxides **1b–e** containing rings of various sizes gave moderate yields of the corresponding 1-(alk-1-enyl)-2-naphthols **3f–i** (Table 2, entries 1–4). The acyclic 2,2-dialkyl-substi-

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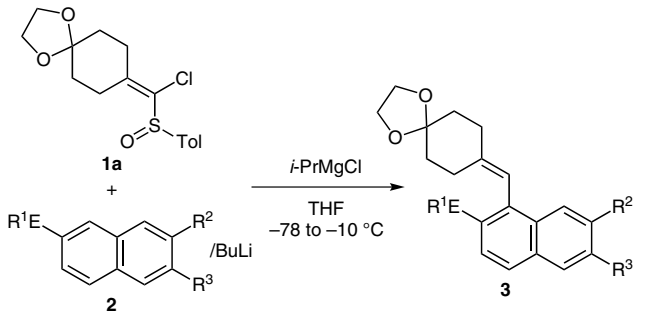
Table 1 Alkenylation of 2-Naphthols and Related Compounds **2a–e** with the Magnesium Alkylidene Carbenoid Generated from Sulfoxide **1a**



Entry	Reactant	ER^1	R^2	R^3	**3**	Yield (%)
1	**2a**	OH	H	H	**3a**	66
2	**2b**	OH	OMe	H	**3b**	78
3	**2c**	OH	H	Br	**3c**	62
4	**2d**	OMe	H	H	**3d**	0[a]
5	**2e**	SH	H	H	**3e**	0[b]

[a] Chloroalkene **4** and cumulene **5** were obtained in 26% and 40% yields, respectively.
[b] Sulfide **3e′** (Figure 1) was obtained in an 87% yield.

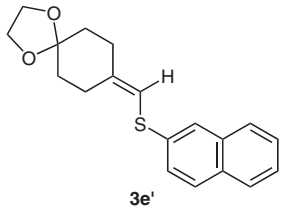
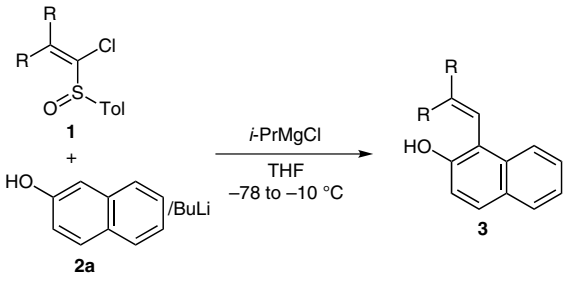


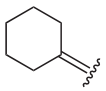
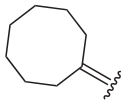
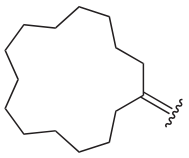
Figure 1 Sulfide byproduct from an alkenylation of naphthalene-2-thiol (**2e**) (Table 1, entry 5)

tuted sulfoxides **1f–h** could also be used in the alkenylation reaction and gave the desired products **3j–l** in 44–53% yield (entries 5–7, respectively), whereas alkenylation using sulfoxide **1i**, which contains two phenyl groups in the β-position, failed due to the ease with which diphenylacetylene is formed through the Fritsch–Buttenberg–Wiechell rearrangement of the resultant magnesium alkylidene carbenoid (entry 8).

In an attempt to synthesize (*E*)- and (*Z*)-1-(alk-1-enyl)-2-naphthols selectively, we examined the reaction of 2-naphthol (**2a**) with the two geometrical isomers of each of the 1-chlorovinyl 4-tolyl sulfoxides **1j–l** bearing two different substituents in the β-position (Table 3).[7f] In all cases, the reaction proceeded with partial geometric isomerization to give the 1-(alk-1-enyl)-2-naphthols **3n–p** as mixtures of (*E*)- and (*Z*)-isomers (entries 1–6). In the case of the reaction with the sulfoxide (*E*)-**1l**, the (*Z*)-1-(alk-1-enyl)-2-naphthol (*Z*)-**3p** was obtained as the major isomer with an *E*/*Z* ratio of 14:86 (entry 5). Similarly, the reaction with the other isomer, (*Z*)-**1l**, preferentially gave the (*E*)-1-(alk-1-enyl)-2-naphthol (*E*)-**3p** with an *E*/*Z* ratio

Table 2 Alkenylation of 2-Naphthol (**2a**) with Magnesium Alkylidene Carbenoids Generated from Sulfoxides **1b–i**



Entry	Reactant	CR_2	Product	Yield (%)
1	**1b**		**3f**	38
2	**1c**		**3g**	50
3	**1d**		**3h**	51
4	**1e**		**3i**	48
5	**1f**	CMe_2	**3j**	61
6	**1g**	CEt_2	**3k**	44
7	**1h**	$C[(CH_2)_2Ph]_2$	**3l**	53
8[a]	**1i**	CPh_2	**3m**	0

[a] 2-Chloro-1,1-diphenylethene and diphenylacetylene were obtained in 22% and 77% yields, respectively.

of 89:11. These geometrical outcomes suggest that the reaction might proceed by an S_N2-type mechanism at the carbenoid carbon atom.[7f,10] The geometry-selective synthesis of 1-(alk-1-enyl)-2-naphthols is difficult to achieve at this stage because the magnesium alkylidene carbenoids gradually isomerize.[7a] For instance, when the reactions shown in entries 1 and 2 were conducted without lithium 2-naphtholate, the chloroalkene was obtained as a mixture of the (*E*)- and (*Z*)-isomers with *E*/*Z* ratios of 72:28 and 59:41, respectively.

We also examined the alkenylation of 1-naphthols **6** (Table 4). 1-Naphthol (**6a**) underwent alkenylation with the magnesium alkylidene carbenoid generated from sulfoxide **1a** to give a 67% yield of the 2-(alk-1-enyl)-1-naphthol **7a** (entry 1). The presence of an electron-donating or electron-withdrawing group at the 4-position had hardly any effect on the efficiency of the reaction (entries 2 and 3). The alkenylation of phenanthren-1-ol (**6d**) took place at the 2-position to provide the 2-(alk-1-enyl)phenanthren-1-ol **7d** in 56% yield (entry 4).

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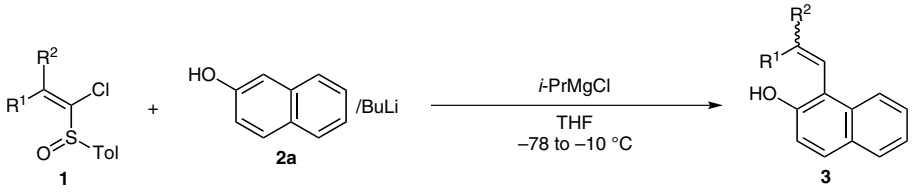
Table 3 Alkenylation of 2-Naphthol (**2a**) with Magnesium Alkylidene Carbenoids Generated from (*E*)- and (*Z*)-1-Chlorovinyl 4-Tolyl Sulfoxides (*E*)- and (*Z*)-**1j**–**l**



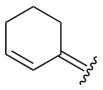
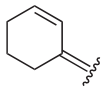
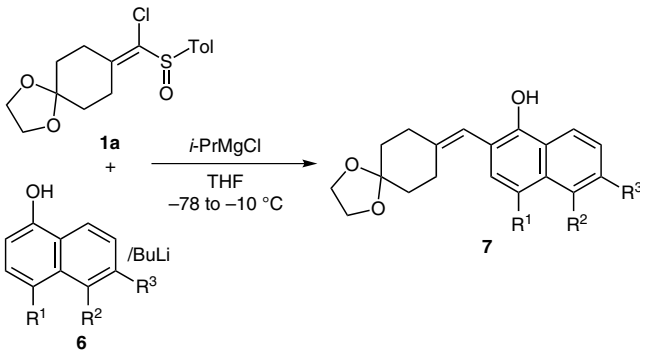
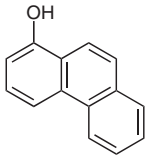
Entry	Reactant	R^1	R^2	Product	Yield (%)	*E*/*Z* ratio
1	(*E*)-**1j**			**3n**	72	31:69
2	(*Z*)-**1j**			**3n**	67	68:32
3	(*E*)-**1k**	$CH=CH_2$	Me	**3o**	48	40:60
4	(*Z*)-**1k**	Me	$CH=CH_2$	**3o**	45	71:29
5	(*E*)-**1l**	$(CH_2)_4Me$	Me	**3p**	43	14:86
6	(*Z*)-**1l**	Me	$(CH_2)_4Me$	**3p**	63	89:11

Table 4 Alkenylation of 1-Naphthols **6** with the Magnesium Alkylidene Carbenoid Generated from Sulfoxide **1a**



Entry	**6**	R^1	R^2	R^3	**7**	Yield (%)
1	**6a**	H	H	H	**7a**	67
2	**6b**	OMe	H	H	**7b**	62
3	**6c**	Cl	H	H	**7c**	63
4	**6d**				**7d**	56

Finally, we subjected phenols **8** to the alkenylation reaction (Table 5). In contrast to the reaction with 1- and 2-naphthols, the reaction with phenol (**8a**) gave the alk-1-enyl phenyl ether **10a** and not the corresponding *ortho*-(alk-1-enyl)phenol **9a** (entry 1). Analysis of the product **10a** by using the iron(III) chloride test showed the absence of a phenolic hydroxy group. The reaction of phenols **8b**–**d** bearing various substituents on the 4-position of the phenol also proceeded at the oxygen atom to give low yields of the corresponding ethers **10b**–**d** (entries 2–4). Although the factor primarily responsible for the difference in the reactivity of lithium phenolates and lithium naphtholates toward magnesium alkylidene carbenoids remains to be clarified,[11] it is noteworthy that a new bond between a vinylic carbon and an oxygen atom was formed directly. However, a significant amount of cumulene **5** was also produced, and this reaction does not, at this stage, appear to have much promise for the synthesis of vinyl ethers.

In summary, we have succeeded in directly alkenylating 1- and 2-naphthols by using magnesium alkylidene carbenoids as alkenylating agents. The present method allowed us to introduce a variety of alkenyl groups onto the naphthol ring in a regiospecific manner. Studies on further applications of the direct alkenylation of nucleophiles with magnesium alkylidene carbenoids are currently ongoing and will be reported in due course.

Melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ soln by using JEOL JNM-LA 300, JEOL JNM-LA 500, and Bruker AV 600 spectrometers. The geometries of (*E*)-**3p** and (*Z*)-**3p** were assigned on the basis of their NOESY spectra. Mass spectra were obtained at 70 eV by direct insertion with a HITACHI M-80B mass spectrometer. IR spectra were recorded on a PerkinElmer Spectrum One FTIR instrument. Silica gel 60 N (Kanto Chemical) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography, and the products that absorbed UV light were detected by UV irradiation. The geometric isomers (*E*)-**3p** and (*Z*)-**3p** were separated by means of recycling gel-permeation chromatography using an LC-9201 system (Japan Analytical Industry Co., Ltd.). Anhyd THF was purchased from Kanto Chemical Co., Inc. and used as supplied. All reactions involving air- or water-sensitive compounds were routinely conducted under a positive pres-

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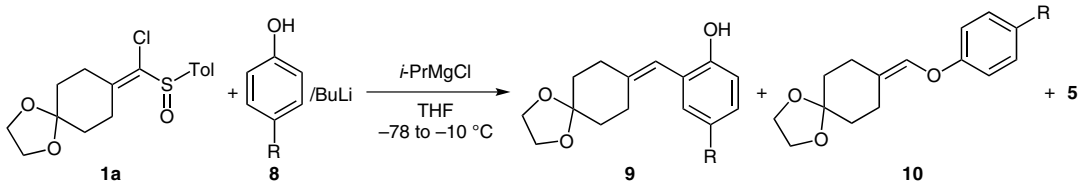
Table 5 Reaction of Phenols **8** with the Magnesium Alkylidene Carbenoid Generated from Sulfoxide **1a**



1a 8 9 10

Entry	Reactant	R	Phenol Product	Yield (%)	Ether Product	Yield (%) of **10**	Yield (%) of **5**
1	**8a**	H	**9a**	0	**10a**	20	22
2	**8b**	OMe	**9b**	0	**10b**	25	19
3	**8c**	F	**9c**	0	**10c**	27	16
4	**8d**	Ph	**9d**	0	**10d**	25	20

sure of argon in glassware that had been flame-dried. Sulfoxides **1** were prepared according to the procedure described in the literature.[12] Sulfoxides **1**[7a,f,12,13] and 1-(alk-1-enyl)-2-naphthols **3g**[14a] and **3j**[14b] are known compounds.

1-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-2-naphthol (3a); Typical Procedure

A 1.65 M soln of BuLi in hexane (0.606 mL, 1.00 mmol) was added dropwise to a soln of 2-naphthol (**2a**; 144 mg, 1.00 mmol) in THF (1.0 mL) at –78 °C, and the mixture was stirred at –78 °C for 10 min. A soln of sulfoxide **1a** (65.4 mg, 0.200 mmol) in THF (1.0 mL) and a 1.03 M soln of *t*-BuMgCl in THF (0.194 mL, 0.200 mmol) were then added to the soln at –78 °C. A 2.0 M soln of *i*-PrMgCl in THF (0.280 mL, 0.56 mmol) was then added dropwise at –78 °C. The mixture was allowed to warm to –10 °C over 1 h then the reaction was quenched with sat. aq NH_4Cl (1.5 mL) and the mixture was extracted with $CHCl_3$ (3 × 7 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane–EtOAc) to give **3a** as a yellow oil [yield: 39.1 mg (0.132 mmol, 66%); R_f = 0.12 (hexane–EtOAc, 5:1)], together with **4** as a colorless oil [yield: 2.2 mg (0.012 mmol, 6%); R_f = 0.39 (hexane–EtOAc, 5:1)], and **5** as a colorless solid [yield: 2.0 mg (0.0066 mmol, 7%); R_f = 0.21 (hexane–EtOAc, 5:1)].

3a

IR (neat): 3411 (OH), 2951, 2885, 1620, 1595, 1269, 1203, 1140, 1121, 1087, 1033, 908, 817, 750 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.62 (t, *J* = 6.5 Hz, 2 H), 1.91 (t, *J* = 6.5 Hz, 2 H), 2.12–2.22 (m, 2 H), 2.66 (dt, *J* = 1.1, 6.5 Hz, 2 H), 3.95–4.01 (m, 4 H), 5.42 (s, 1 H), 6.30 (s, 1 H), 7.19 (d, *J* = 8.8 Hz, 1 H), 7.33 (ddd, *J* = 1.3, 6.9, 8.2 Hz, 1 H), 7.43 (ddd, *J* = 1.3, 6.9, 8.2 Hz, 1 H), 7.67–7.82 (m, 3 H).

H/D exchange experiment: a soln of **3a** (10 mg, 0.034 mmol) in CD_3OD (2 mL) was stirred at r.t. for 24 h. The intensity of the signal at 5.42 ppm decreased to 54%.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.8, 33.3, 35.1, 36.3, 64.4 (2 × C), 108.4, 114.9, 115.9, 117.0, 123.2, 124.1, 126.3, 128.2, 128.7, 128.9, 133.1, 147.7, 150.2.

MS (EI): *m*/*z* (%) = 296 (100) [M^+], 234 (18), 195 (17), 181 (38), 165 (20), 158 (38), 153 (22), 140 (39), 96 (22).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{20}O_3$: 296.1412; found: 296.1412.

1-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-7-methoxy-2-naphthol (3b)

Yield: 50.9 mg (78%); yellow oil.

IR (neat): 3385 (OH), 2951, 2887, 1623, 1513, 1267, 1222, 1139, 1121, 1085, 1032, 909, 831, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.59–1.68 (m, 2 H), 1.90 (t, *J* = 6.5 Hz, 2 H), 2.18 (t, *J* = 6.5 Hz, 2 H), 2.62–2.70 (m, 2 H), 3.88 (s, 3 H), 3.95–4.02 (m, 4 H), 5.39 (s, 1 H), 6.24 (s, 1 H), 6.96–7.08 (m, 3 H), 7.60–7.70 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.8, 33.3, 35.2, 36.5, 55.2, 64.4 (2 × C), 103.2, 108.4, 114.4, 115.0, 115.1, 115.2, 124.1, 128.6, 129.8, 134.4, 147.8, 150.8, 158.2.

MS (EI): *m*/*z* (%) = 326 (100) [M^+], 281 (14), 264 (15), 225 (14), 211 (23), 187 (71), 153 (24), 140 (41), 96 (20).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{20}H_{22}O_4$: 326.1518; found: 326.1517.

1-(1,4-Dioxaspiro[4.5]decan-8-ylidenemethyl)-6-bromonaphthalen-2-ol (3c)

Yield: 46.4 mg (62%); yellow oil.

IR (neat): 3334 (OH), 2951, 2885, 1614, 1589, 1498, 1268, 1204, 1140, 1121, 1090, 1074, 1033, 909, 886, 823, 757, 734 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.62 (t, *J* = 6.5 Hz, 2 H), 1.90 (t, *J* = 6.5 Hz, 2 H), 2.14 (t, *J* = 6.5 Hz, 2 H), 2.61–2.69 (m, 2 H), 3.95–4.02 (m, 4 H), 5.43 (s, 1 H), 6.25 (s, 1 H), 7.20 (d, *J* = 8.9 Hz, 1 H), 7.48 (dd, *J* = 2.0, 8.9 Hz, 1 H), 7.56–7.64 (m, 2 H), 7.92 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.8, 33.3, 35.0, 36.3, 64.4 (2 × C), 108.3, 114.2, 116.2, 117.0, 118.1, 125.9, 127.9, 129.5, 129.9, 130.1, 131.6, 148.4, 150.5.

MS (EI): *m*/*z* (%) = 374 (100) [M^+], 236 (22), 165 (19), 153 (22), 140 (62), 121 (19), 96 (30).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{19}BrO_3$: 374.0518; found: 374.0512.

8-[(2-Naphthylsulfanyl)methylene]-1,4-dioxaspiro[4.5]decane (3e′)

Yield: 54.3 mg (87%); colorless crystals; mp 72.2–73.3 °C (hexane).

IR (KBr): 2950, 1623, 1588, 1136, 1113, 1083, 1036, 942, 910, 853, 825, 810, 741, 682 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.75 (t, *J* = 6.5 Hz, 2 H), 1.79 (t, *J* = 6.5 Hz, 2 H), 2.48 (t, *J* = 6.5 Hz, 2 H), 2.59 (t, *J* = 6.5 Hz, 2 H), 4.00 (s, 4 H), 6.06 (s, 1 H), 7.40 (dd, *J* = 2.3, 8.6 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.71 (br s, 1 H), 7.74 (d, *J* = 7.6 Hz, 1 H), 7.75 (d, *J* = 8.6 Hz, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H).

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^{13}C NMR (126 MHz, $CDCl_3$): δ = 27.0, 33.2, 34.9, 35.9, 64.4 (2 × C), 108.5, 113.7, 125.5, 125.6, 126.4, 126.5, 127.0, 127.7, 128.4, 131.6, 133.8, 134.6, 145.1.

MS (EI): *m*/*z* (%) = 312 (100) [M$^+$], 212 (10), 153 (49), 128 (13), 115 (21), 109 (18), 99 (15).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{19}H_{20}O_2S$: 312.1184; found: 312.1185.

1-(Cyclopentylidenemethyl)-2-naphthol (3f)
Yield: 17.0 mg (38%); yellow oil.

IR (neat): 3507 (OH), 2955, 2868, 1622, 1595, 1516, 1465, 1388, 1265, 1204, 1140, 814, 747 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.69 (quint, *J* = 7.1 Hz, 2 H), 1.79 (quint, *J* = 7.1 Hz, 2 H), 2.07 (br t, *J* = 7.1 Hz, 2 H), 2.63 (br t, *J* = 7.1 Hz, 2 H), 5.52 (s, 1 H), 6.41–6.46 (m, 1 H), 7.19 (d, *J* = 8.9 Hz, 1 H), 7.32 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 7.69 (d, *J* = 8.9 Hz, 1 H), 7.75 (d, *J* = 7.4 Hz, 1 H), 7.76 (d, *J* = 7.4 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.2, 30.6, 34.0, 112.1, 117.0, 117.3, 123.1, 124.1, 126.2, 128.2, 128.6, 128.8, 132.6, 149.8, 154.5.

MS (EI): *m*/*z* (%) = 224 (100) [M$^+$], 195 (17), 181 (62), 165 (18), 157 (20), 152 (15), 144 (16).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{16}O$: 224.1201; found: 224.1205.

1-(Cyclohexylidenemethyl)-2-naphthol (3g)[14a]
Yield: 23.8 mg (50%); yellow oil.

IR (neat): 3510 (OH), 2929, 2854, 1621, 1596, 1516, 1465, 1390, 1203, 1141, 814, 747 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37–1.54 (m, 2 H), 1.57–1.66 (m, 2 H), 1.76 (br quint, *J* = 6.0 Hz, 2 H), 2.00 (t, *J* = 6.0 Hz, 2 H), 2.48 (br s, 2 H), 5.47 (s, 1 H), 6.20 (s, 1 H), 7.19 (d, *J* = 9.0 Hz, 1 H), 7.32 (t, *J* = 7.7 Hz, 1 H), 7.43 (t, *J* = 7.7, Hz, 1 H), 7.70 (d, *J* = 9.0 Hz, 1 H), 7.76 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.4, 27.8, 29.0, 30.3, 36.8, 113.1, 116.2, 116.8, 123.1, 124.2, 126.2, 128.2, 128.6, 128.7, 133.2, 150.0, 150.7.

MS (EI): *m*/*z* (%) = 238 (100) [M$^+$], 195 (16), 181 (49), 165 (13), 157 (53), 152 (14), 144 (17), 128 (13).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1363.

1-(Cyclooctylidenemethyl)-2-naphthol (3h)
Yield: 27.1 mg (51%); yellow oil.

IR (neat): 3511 (OH), 2923, 2854, 1621, 1595, 1516, 1466, 1447, 1388, 1267, 1208, 1141, 814, 747 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21–1.75 (m, 8 H), 1.88 (br s, 2 H), 2.13 (br s, 2 H), 2.55 (br s, 2 H), 5.46 (s, 1 H), 6.35 (s, 1 H), 7.19 (d, *J* = 8.8 Hz, 1 H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 8.8 Hz, 1 H), 7.74 (d, *J* = 7.8 Hz, 1 H), 7.77 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.2, 26.0, 26.7, 27.2, 28.8, 30.8, 36.0, 116.7, 116.9, 117.0, 123.1, 124.1, 126.2, 128.2, 128.7, 128.8, 133.0, 149.8, 153.5.

MS (EI): *m*/*z* (%) = 266 (100) [M$^+$], 207 (21), 195 (19), 181 (65), 164 (21), 157 (69), 152 (18), 144 (28), 128 (13).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{19}H_{22}O$: 266.1671; found: 266.1670.

1-(Cyclopentadecylidenemethyl)-2-naphthol (3i)
Yield: 35.0 mg (48%); yellow oil.

IR (neat): 3514 (OH), 2928, 2857, 1621, 1596, 1516, 1463, 1388, 1348, 1267, 1207, 1141, 815, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02–1.50 (m, 22 H), 1.65–1.74 (m, 2 H), 1.88–2.04 (m, 2 H), 2.33–2.44 (m, 2 H), 5.46 (s, 1 H), 6.25 (s, 1 H), 7.19 (d, *J* = 8.7 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 8.7 Hz, 1 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.76 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.1, 26.4, 26.50, 26.53, 26.7, 27.5, 27.6, 27.7, 31.2, 36.3, 116.4, 116.8, 123.1, 124.2, 126.1, 128.1, 128.6, 128.8, 133.1, 149.7, 152.1.

MS (EI): *m*/*z* (%) = 364 (100) [M$^+$], 181 (37), 157 (25), 144 (20).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{26}H_{36}O$: 364.2766; found: 364.2769.

1-(2-Methylprop-1-en-1-yl)-2-naphthol (3j)[14b]
Yield: 24.2 mg (61%); colorless oil.

IR (neat): 3511 (OH), 2972, 2934, 2912, 1620, 1595, 1516, 1465, 1388, 1267, 1206, 1141, 959, 812, 749 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.61 (s, 3 H), 2.09 (s, 3 H), 5.43 (s, 1 H), 6.28 (s, 1 H), 7.20 (d, *J* = 8.5 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 8.5 Hz, 1 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.77 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.6, 25.5, 116.7, 116.8, 116.9, 123.1, 124.2, 126.2, 128.2, 128.8, 133.0, 142.9, 150.1.

MS (EI): *m*/*z* (%) = 198 (100) [M$^+$], 183 (69), 181 (19), 165 (39), 155 (18), 152 (16), 128 (15).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1049.

1-(2-Ethylbut-1-en-1-yl)-2-naphthol (3k)
Yield: 19.9 mg (44%); yellow oil.

IR (neat): 3512 (OH), 2966, 2934, 1621, 1595, 1516, 1464, 1387, 1267, 1205, 1141, 816, 747 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.6 Hz, 3 H), 1.27 (t, *J* = 7.4 Hz, 3 H), 1.97 (q, *J* = 7.6 Hz, 2 H), 2.41 (dq, *J* = 1.3, 7.4 Hz, 2 H), 5.45 (s, 1 H), 6.19 (s, 1 H), 7.20 (d, *J* = 8.8 Hz, 1 H), 7.32 (ddd, *J* = 1.3, 6.8, 8.1 Hz, 1 H), 7.42 (ddd, *J* = 1.3, 6.8, 8.1 Hz, 1 H), 7.66–7.80 (m, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 12.5, 13.1, 24.6, 28.5, 114.3, 116.7, 116.8, 123.1, 124.1, 126.1, 128.1, 128.6, 128.8, 133.1, 149.8, 154.5.

MS (EI): *m*/*z* (%) = 226 (85) [M$^+$], 197 (100), 181 (30), 179 (22), 169 (20), 165 (17), 157 (19), 152 (20), 144 (24), 141 (19), 128 (19), 115 (15).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1355.

1-[4-Phenyl-2-(2-phenylethyl)but-1-en-1-yl]-2-naphthol (3l)
Yield: 40.1 mg (53%); yellow oil.

IR (neat): 3494 (OH), 3061, 3026, 2926, 2857, 1621, 1595, 1516, 1496, 1464, 1455, 1388, 1207, 1140, 816, 749, 699 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.26 (br s, 2 H), 2.53–2.68 (m, 2 H), 2.79 (br s, 2 H), 3.01 (br s, 2 H), 4.83 (s, 1 H), 6.11 (s, 1 H), 6.87 (d, *J* = 7.4 Hz, 2 H), 7.05–7.14 (m, 4 H), 7.26–7.31 (m, 4 H), 7.31–7.40 (m, 3 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 7.66 (d, *J* = 8.7 Hz, 1 H), 7.72 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 32.6, 33.8, 34.0, 37.6, 116.2, 116.9, 119.0, 123.1, 124.2, 125.9, 126.2, 126.3, 128.0, 128.1, 128.2, 128.5, 128.7, 128.8, 132.9, 141.1, 141.2, 148.3, 149.8.

MS (EI): *m*/*z* (%) = 378 (100) [M$^+$], 195 (25), 181 (22), 157 (74), 143 (23), 129 (17), 105 (33), 91 (41).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{28}H_{26}O$: 378.1984; found: 378.1982.

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1-(Cyclohex-2-en-1-ylidenemethyl)-2-naphthol (3n)
Obtained as a 31:69 mixture of geometric isomers (Table 3, entry 1); yield: 34.0 mg (72%); yellow oil.

IR (neat): 3514 (OH), 2935, 1621, 1594, 1516, 1465, 1388, 1267, 1204, 1141, 958, 816, 750 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) (M: major isomer, m: minor isomer): δ = 1.67 (quint, *J* = 6.2 Hz, 2 H_m), 1.90 (quint, *J* = 6.0 Hz, 2 H_M), 2.15–2.27 (m, 2 H_M, 4 H_m), 2.68 (t, *J* = 6.0 Hz, 2 H_M), 5.34 (s, 1 H_m), 5.53 (s, 1 H_M), 5.93–6.07 (m, 2 H_M, 1 H_m), 6.24 (s, 1 H_M), 6.34 (s, 1 H_m), 6.43–6.47 (m, 1 H_m), 7.194 (d, *J* = 8.4 Hz, 1 H_M), 7.195 (d, *J* = 9.4 Hz, 1 H_m), 7.32 (t, *J* = 7.7 Hz, 1 H_M), 7.33 (t, *J* = 7.7 Hz, 1 H_m), 7.41–7.46 (m, 1 H_M, 1 H_m), 7.712 (d, *J* = 8.4 Hz, 1 H_M), 7.715 (d, *J* = 9.4 Hz, 1 H_m), 7.72 (d, *J* = 7.7 Hz, 1 H_m), 7.74 (d, *J* = 7.7 Hz, 1 H_M), 7.766 (d, *J* = 7.7 Hz, 1 H_M), 7.773 (d, *J* = 7.7 Hz, 1 H_m).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.4, 23.3, 25.7, 26.1, 26.7, 31.9, 115.4, 115.9, 116.9, 117.0, 123.2, 123.3, 124.2, 124.3, 124.9, 126.27, 126.31, 128.1, 128.2, 128.8, 129.0, 129.8, 131.9, 132.9, 134.2, 141.4, 143.6, 150.1, 150.2.

MS (EI): *m*/*z* (%) = 236 (100) [M^+], 219 (12), 207 (39), 194 (14), 181 (29), 165 (13), 157 (25), 152 (12), 129 (12).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{16}O$: 236.1201; found: 236.1199.

1-(2-Methylbuta-1,3-dien-1-yl)-2-naphthol (3o)
Obtained as a 40:60 mixture of geometric isomers (Table 3, entry 3); yield: 20.2 mg (48%); yellow oil.

IR (neat): 3520 (OH), 3060, 2924, 1621, 1595, 1515, 1465, 1388, 1267, 1206, 1141, 818, 748 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) (M: major isomer, m: minor isomer): δ = 1.75 (s, 3 H_m), 2.20 (s, 3 H_M), 5.20 (d, *J* = 11.0 Hz, 1 H_M), 5.26 (s, 1 H_m), 5.28 (d, *J* = 10.6 Hz, 1 H_m), 5.40 (s, 1 H_M), 5.42 (d, *J* = 17.6 Hz, 1 H_m), 5.47 (d, *J* = 17.4 Hz, 1 H_M), 6.35 (dd, *J* = 11.0, 17.4 Hz, 1 H_M), 6.52 (s, 1 H_M), 6.60 (s, 1 H_m), 6.77 (dd, *J* = 10.6, 17.6 Hz, 1 H_m), 7.195 (d, *J* = 9.3 Hz, 1 H_M), 7.204 (d, *J* = 8.7 Hz, 1 H_m), 7.34 (t, *J* = 8.0 Hz, 1 H_M), 7.40 (t, *J* = 8.0 Hz, 1 H_m), 7.44 (t, *J* = 8.0 Hz, 1 H_M, 1 H_m), 7.68 (d, *J* = 8.0 Hz, 1 H_m), 7.71 (d, *J* = 8.0 Hz, 1 H_M), 7.73 (d, *J* = 9.3 Hz, 1 H_M), 7.74 (d, *J* = 8.7 Hz, 1 H_m), 7.776 (d, *J* = 8.0 Hz, 1 H_M), 7.783 (d, *J* = 8.0 Hz, 1 H_m).

MS (EI): *m*/*z* (%) = 210 (38) [M^+], 195 (100), 181 (10), 165 (20), 152 (15).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{15}H_{14}O$: 210.1045; found: 210.1046.

1-[(1*Z*)-2-Methylhept-1-en-1-yl]-2-naphthol [(*Z*)-3p]
Yield: 21.9 mg (43%); yellow oil.

IR (neat): 3512 (OH), 2955, 2929, 2858, 1622, 1595, 1516, 1465, 1388, 1267, 1205, 1141, 815, 747 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.70 (t, *J* = 6.9 Hz, 3 H), 1.00–1.13 (m, 4 H), 1.34 (quint, *J* = 7.4 Hz, 2 H), 1.88–1.99 (m, 2 H), 2.07 (s, 3 H), 5.46 (s, 1 H), 6.23 (s, 1 H), 7.19 (d, *J* = 8.8 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.7, 22.2, 22.9, 27.1, 31.4, 33.0, 116.77, 116.80, 123.1, 124.3, 126.1, 128.1, 128.7, 128.75, 128.81, 133.1, 147.3, 149.9.

MS (EI): *m*/*z* (%) = 254 (100) [M^+], 197 (20), 183 (60), 181 (19), 157 (28), 144 (27).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{22}O$: 254.1671; found: 254.1675.

1-[(1*E*)-2-Methylhept-1-en-1-yl]-2-naphthol [(*E*)-3p]
Yield: 32.0 mg (63%); yellow oil.

IR (neat): 3513 (OH), 2956, 2929, 2857, 1621, 1595, 1517, 1465, 1387, 1266, 1207, 1141, 815, 747 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.97 (br t, *J* = 6.7 Hz, 3 H), 1.36–1.46 (m, 4 H), 1.58 (s, 3 H), 1.65 (quint, *J* = 7.4 Hz, 2 H), 2.37 (t, *J* = 7.4 Hz, 2 H), 5.41 (s, 1 H), 6.28 (s, 1 H), 7.20 (d, *J* = 8.7 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.43 (t, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 8.7 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 17.7, 22.6, 27.8, 31.7, 39.3, 116.3, 116.7, 116.9, 123.1, 124.1, 126.2, 128.2, 128.7, 128.8, 132.9, 147.1, 149.9.

MS (EI): *m*/*z* (%) = 254 (100) [M^+], 197 (30), 183 (90), 181 (33), 179 (21), 165 (20), 157 (41), 152 (18), 144 (44).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{22}O$: 254.1671; found: 254.1675.

2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-1-naphthol (7a)
Yield: 39.7 mg (67%); yellow oil.

IR (neat): 3416 (OH), 2926, 2850, 1718, 1572, 1385, 1271, 1245, 1120, 1085, 1033, 759 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.67 (t, *J* = 6.5 Hz, 2 H), 1.85 (t, *J* = 6.5 Hz, 2 H), 2.31 (t, *J* = 6.5 Hz, 2 H), 2.55 (t, *J* = 6.5 Hz, 2 H), 3.95–4.02 (m, 4 H), 5.52 (s, 1 H), 6.29 (s, 1 H), 7.15 (d, *J* = 8.4 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 7.43–7.50 (m, 2 H), 7.74–7.80 (m, 1 H), 8.19–8.25 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.6, 33.5, 35.2, 36.1, 64.4 (2 × C), 108.4, 117.1, 117.3, 119.5, 122.2, 123.9, 125.2, 126.1, 127.40, 127.44, 133.8, 145.7, 148.0.

MS (EI): *m*/*z* (%) = 296 (100) [M^+], 234 (14), 195 (18), 181 (23), 158 (22), 140 (51), 96 (22).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{20}O_3$: 296.1412; found: 296.1414.

2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)-4-methoxy-1-naphthol (7b)
Yield: 40.4 mg (62%); yellow oil.

IR (neat): 3391 (OH), 2952, 2886, 1621, 1596, 1459, 1390, 1288, 1225, 1122, 1097, 1081, 1033, 759 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.68 (t, *J* = 6.5 Hz, 2 H), 1.85 (t, *J* = 6.5 Hz, 2 H), 2.34 (t, *J* = 6.5 Hz, 2 H), 2.55 (t, *J* = 6.5 Hz, 2 H), 3.94 (s, 3 H), 3.97–4.01 (m, 4 H), 5.17 (s, 1 H), 6.27 (s, 1 H), 6.49 (s, 1 H), 7.43–7.54 (m, 2 H), 8.14–8.20 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.7, 33.4, 35.2, 36.1, 55.7, 64.4 (2 × C), 105.2, 108.4, 116.0, 117.8, 121.7, 122.0, 124.8, 125.4, 125.6, 125.9, 141.8, 145.2, 148.7.

MS (EI): *m*/*z* (%) = 326 (100) [M^+], 280 (14), 225 (11), 211 (11), 202 (14), 187 (23), 140 (62), 99 (29), 96 (20), 86 (11).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{20}H_{22}O_4$: 326.1518; found: 326.1518.

4-Chloro-2-(1,4-dioxaspiro[4.5]dec-8-ylidenemethyl)-1-naphthol (7c)
Yield: 41.6 mg (63%); yellow oil.

IR (neat): 3410 (OH), 2952, 2886, 1595, 1380, 1270, 1215, 1121, 1081, 1033, 760 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.67 (t, *J* = 6.5 Hz, 2 H), 1.85 (t, *J* = 6.5 Hz, 2 H), 2.30 (dt, *J* = 1.1, 6.5 Hz, 2 H), 2.55 (dt, *J* = 1.1, 6.5 Hz, 2 H), 3.96–4.01 (m, 4 H), 5.53 (s, 1 H), 6.21 (s, 1 H), 7.26 (s, 1 H), 7.49–7.63 (m, 2 H), 8.13–8.28 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.7, 33.4, 35.1, 36.1, 64.4 (2 × C), 108.3, 116.2, 117.3, 122.4, 122.7, 124.2, 124.9, 126.0, 127.08, 127.11, 130.6, 146.7, 147.2.

MS (EI): *m*/*z* (%) = 330 (100) [M^+], 268 (16), 215 (18), 206 (29), 193 (18), 165 (18), 140 (79), 99 (34), 96 (30).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{19}ClO_3$: 330.1023; found: 330.1020.

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2-(1,4-Dioxaspiro[4.5]dec-8-ylidenemethyl)phenanthren-1-ol (7d)
Yield: 38.8 mg (56%); colorless oil.

IR (neat): 3419 (OH), 2951, 2886, 1598, 1574, 1462, 1239, 1215, 1137, 1120, 1083, 1033, 753 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.69 (t, *J* = 6.5 Hz, 2 H), 1.87 (t, *J* = 6.5 Hz, 2 H), 2.35 (t, *J* = 6.5 Hz, 2 H), 2.58 (t, *J* = 6.5 Hz, 2 H), 3.97–4.02 (m, 4 H), 5.56 (s, 1 H), 6.34 (s, 1 H), 7.34 (d, *J* = 8.5 Hz, 1 H), 7.58 (t, *J* = 7.7 Hz, 1 H), 7.63 (t, *J* = 7.7 Hz, 1 H), 7.74 (d, *J* = 9.3 Hz, 1 H), 7.89 (d, *J* = 7.7 Hz, 1 H), 8.19 (d, *J* = 9.3 Hz, 1 H), 8.22 (d, *J* = 8.5 Hz, 1 H), 8.64 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.6, 33.5, 35.2, 36.1, 64.4 (2 × C), 108.4, 114.4, 117.0, 119.2, 120.6, 121.4, 122.9, 126.1, 126.4, 126.5, 127.8, 128.5, 130.0, 130.7, 132.0, 146.2, 148.8.

MS (EI): *m*/*z* (%) = 346 (100) [M^+], 284 (15), 245 (19), 231 (21), 215 (13), 208 (42), 202 (17), 140 (35), 96 (27).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{23}H_{22}O_3$: 346.1569; found: 346.1564.

8-(Phenoxymethylene)-1,4-dioxaspiro[4.5]decane (10a)
Yield: 9.8 mg (20%); colorless oil.

IR (neat): 2950, 2882, 1686, 1597, 1492, 1236, 1102, 1078, 1034, 907, 754, 692 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.69 (t, *J* = 6.5 Hz, 2 H), 1.74 (t, *J* = 6.5 Hz, 2 H), 2.27 (t, *J* = 6.5 Hz, 2 H), 2.46 (t, *J* = 6.5 Hz, 2 H), 3.99 (s, 4 H), 6.25 (s, 1 H), 6.98 (d, *J* = 7.9 Hz, 2 H), 7.02 (t, *J* = 7.9 Hz, 1 H), 7.30 (t, *J* = 7.9 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.4, 27.3, 34.8, 36.0, 64.3 (2 × C), 108.9, 115.8, 122.0, 122.5, 129.5, 133.3, 157.7.

MS (EI): *m*/*z* (%) = 246 (55) [M^+], 153 (100), 109 (81), 94 (12), 91 (15), 81 (14), 77 (15).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{15}H_{18}O_3$: 246.1256; found: 246.1251.

8-[(4-Methoxyphenoxy)methylene]-1,4-dioxaspiro[4.5]decane (10b)
Yield: 13.8 mg (25%); yellow oil.

IR (neat): 2961, 2877, 1683, 1505, 1471, 1375, 1219, 1109, 1099, 1029, 908, 833, 683 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.65–1.76 (m, 4 H), 2.24 (dt, *J* = 1.0, 6.4, Hz, 2 H), 2.46 (dt, *J* = 1.0, 6.4, Hz, 2 H), 3.77 (s, 3 H), 3.98 (s, 4 H), 6.15–6.20 (m, 1 H), 6.80–6.94 (m, 4 H).

MS (EI): *m*/*z* (%) = 276 (99) [M^+], 215 (14), 192 (12), 153 (100), 124 (32), 109 (40), 81 (17).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{20}O_4$: 276.1362; found: 276.1364.

8-[(4-Fluorophenoxy)methylene]-1,4-dioxaspiro[4.5]decane (10c)
Yield: 14.3 mg (27%); colorless oil.

IR (neat): 2951, 2883, 1687, 1504, 1444, 1375, 1246, 1204, 1124, 1102, 1034, 907, 831, 756, 681 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.65–1.76 (m, 4 H), 2.25 (dt, *J* = 1.0, 6.4 Hz, 2 H), 2.45 (dt, *J* = 1.0, 6.4 Hz, 2 H), 3.98 (s, 4 H), 6.16–6.19 (m, 1 H), 6.88–7.02 (m, 4 H).

MS (EI): *m*/*z* (%) = 264 (41) [M^+], 153 (100), 112 (9), 109 (26), 99 (10), 81 (13).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{15}H_{17}FO_3$: 264.1162; found: 264.1164.

8-[(Biphenyl-4-yloxy)methylene]-1,4-dioxaspiro[4.5]decane (10d)
Yield: 16.1 mg (25%); colorless oil.

IR (neat): 2956, 2880, 1688, 1606, 1518, 1485, 1375, 1248, 1202, 1101, 1074, 1031, 905, 763 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.67–1.79 (m, 4 H), 2.29 (dt, *J* = 1.0, 6.4 Hz, 2 H), 2.48 (dt, *J* = 1.0, 6.4 Hz, 2 H), 3.99 (s, 4 H), 6.27–6.31 (m, 1 H), 7.01–7.09 (m, 2 H), 7.27–7.35 (m, 1 H), 7.38–7.46 (m, 2 H), 7.49–7.58 (m, 4 H).

MS (EI): *m*/*z* (%) = 322 (100) [M^+], 261 (12), 238 (12), 170 (31), 153 (98), 109 (20).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{21}H_{22}O_3$: 322.1569; found: 322.1569.

Iron(III) Chloride Test
0.1 M aq $FeCl_3$ (1 mL, 0.1 mmol) was added to a soln of **3a** (10.0 mg, 0.034 mmol) in 1:1 H_2O–EtOH (2 mL) at r.t. The color of the soln immediately changed from yellow to green. When a soln of $FeCl_3$ was added to a soln of **10a**, the color of the soln did not change.

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Supporting Information

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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