A Convenient Preparation of Functionalized 1,8-Dioxygenated Naphthalenes from 6-Alkoxybenzocyclobutenones

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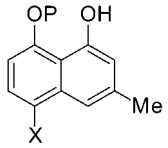
Abstract: An alternate route for the synthesis of naphthalene building blocks **1**−**4** has been developed, starting from readily available 6-alkoxybenzocyclobutenones. As thermolysis of a propynylbenzocyclobutenol only provided the naphthalene in low yield, allenyl-substituted benzocyclobutenols were investigated. The desired allenic precursors were prepared by a two-step procedure, which involved hydroxyl-directed reduction of the chloropropargylbenzocyclobutenols obtained from addition of lithiopropargyl chloride to the benzocyclobutenones. Thermolysis of the allenic alcohols gave the desired naphthalenes in good yields.

1,8-Dioxygenated naphthalenes are a key structural component of the naphthylisoquinoline and michellamine alkaloids. Considerable effort has been expended on the development of efficient syntheses of such compounds (**1**−**4**) for their use in the total synthesis of these natural products.[1,2] Despite this work, there is still a need for an efficient route to the naphthalene core that allows for ready variation of the functionality, particularly in the choice of protecting group.[2a,c]



1 (P = Me, X = Br)
2 (P = iPr, X = Br)
3 (P = Me, X = H)
4 (P = MOM, X = H)

Benzocyclobutenones **5** are versatile precursors to substituted tetralones and naphthalenes. Addition of vinylic and acetylenic nucleophiles to the carbonyl group, followed by thermolysis of these adducts provides a simple and efficient route to these ring systems (Scheme 1).[3] It was envisaged that this strategy could be adapted to allow for the development of a synthesis of 1,8-dioxygenated naphthalenes, which would meet our goal of a flexible, efficient route. Recent work[4] in our group has led to the development of an efficient preparation of 6-alkoxysubstituted benzocyclobutenones (**6a**−**c**). Addition of propynyllithium to the benzocyclobutenones **6a**−**c** and thermolysis of the resulting adducts should afford the desired 1,8-dioxygenated naphthalenes.

Our initial focus was on the preparation of naphthalene **1**,[2a,b,5] as it is a valuable building block for the preparation of korupensamine C and ancistrobrevine B.[6] As it would be difficult to selectively brominate the naphthol **3**, it was decided to investigate functionalization of the benzocyclobutenone prior to thermolysis. This was readily achieved by treating benzocyclobutenone **6a** with benzyltrimethylammonium tribromide and zinc chloride in acetic acid[7] to afford a mixture of para- and ortho-substituted bromides in a 9:1 ratio. Chromatography of the mixture provided the bromide **7a** in 82% yield. The use of other brominating reagents (e.g., Br_2/CCl_4; *N*-bromosuccinimide/DMF) led to lower selectivities and yields.

While the addition of propynyllithium[8] to bromobenzocyclobutenone **7a** in THF at −60 °C proceeded smoothly, thermolysis of the resulting adduct **8** in toluene at reflux resulted in the formation of **1** in a disappointing 20% yield (Scheme 2). The major product of this reaction was the indanone **9** (27% yield), which results from an alternative cyclization onto the adjacent alkynyl carbon.

To prevent the formation of **9**, we investigated the use of an allene as an alternative to the alkyne. It was expected that the high electrophilicity of the central carbon atom of the allene group should ensure an efficient cyclization, even if the reaction should proceed in a nonconcerted fashion.

As the addition of metalated propargylic and allenic compounds to ketones generally yields an inseparable mixture of acetylenic and allenic alcohols,[9] allene **10a** was synthesized by a two-step procedure[10] as detailed in Scheme 2. Addition of lithiated propargyl chloride to ketone **7a** gave the benzocyclobutenol **11a** in 95% yield. Hydroxyl-directed reduction of the acetylene with lithium aluminum hydride in THF gave allenic alcohol **10a** in 95% yield. Pleasingly, thermolysis of allene **10a** went smoothly to afford naphthalene **1** in 84% yield, with no trace of the indanone byproduct. Thus, naphthalene **1** was readily generated in four steps in 62% overall yield from readily available benzocyclobutenone **6a**.

This sequence can also be carried out on 6-isopropoxybenzocyclobutenone **6b**[4] to generate naphthalene **2** in four steps and in 68% overall yield (Scheme 2). O-

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(1) For reviews on the naphthylisoquinoline and michellamine alkaloids, see: (a) Bringmann, G.; Pokorny, F. The Naphthylisoquinoline Alkaloids. In *The Alkaloids*; Cordell, G., Ed.; Academic Press: New York, 1995; Vol. 46, Chapter 4. (b) Rizzacasa, M. A. In *Studies in Natural Product Synthesis, Structure and Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1998; Part F, Vol. 20, p 407.

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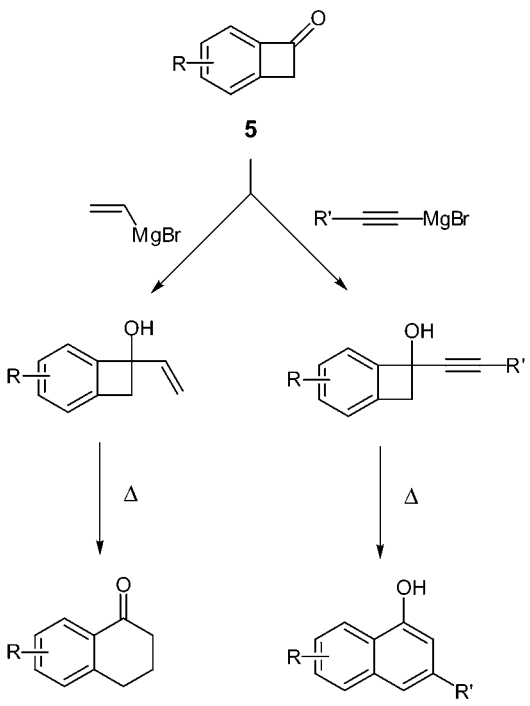
Scheme 1



Methylation of naphthalene **2** would generate **12**, which has been used in the total synthesis[11] of korupensamines A and B, and had previously been synthesized by a 10-step sequence, starting from 3-hydroxybenzaldehdye.[11]

To extend the versatility of this chemistry, benzocyclobutenones **6a** and **6c** were also investigated and the syntheses of naphthalene **3** and **4** are summarized in Scheme 2. These naphthalenes[12] have been used in the total synthesis of stypandrol[13] and dioncophylline B,[14] respectively.

In summary, we have developed an alternate route for the synthesis of naphthalene building blocks **1**−**4**, starting from readily available 6-alkoxybenzocyclobutenones. A significant advantage of our approach is the ability to readily scale-up the sequence. The flexibility of this sequence of reactions should allow access to other substituted naphthalenes, provided the necessary benzocyclobutenone can be generated. The application of this chemistry to the synthesis of naphthylisoquinoline alkaloids is currently under investigation and will be reported in due course.

Experimental Section

General Methods. All reactions were performed in dry glassware under an atmosphere of oxygen-free nitrogen. NMR spectra were recorded on either a Varian Unity 300 or Varian XL300 instrument. All chemical shifts are reported relative to residual $CHCl_3$ (7.26 ppm) for proton and $CDCl_3$ (77.0 ppm) for carbon spectra. Infrared spectra were recorded on a Shimadzu FTIR-8201PC spectrophotometer, either as KBr plates or films. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. HRMS were obtained on a Kratos MS80RFA instrument operating in EI mode at 70 and 4 kV accelerating potential. Flash chromatography was performed using Merck60 silica gel (230−400 mesh). THF and diethyl ether were distilled over sodium/benzophenone immediately before use. Toluene and *N*,*N*-diisopropylamine were distilled from calcium hydride immediately before use. NOTE: All organic extracts were washed with saturated brine solution and dried over $MgSO_4$.

3-Bromo-6-methoxybenzocyclobuten-1-one 7a. Benzyltrimethylammonium tribromide (1.60 g, 4.11 mmol) and $ZnCl_2$ (0.616 g, 4.52 mmol) were added to a stirred solution of 6-methoxybenzocyclobuten-1-one **6a**[4] (0.553 g, 3.74 mmol) in acetic acid (16 mL). The reaction was stirred at room temperature for 24 h, followed by addition of water (20 mL) and 5% w/v $NaHSO_3$ solution (10 mL). The crude product was extracted with ethyl acetate (×4), and the combined organic extracts were washed with water. Removal of the solvent under reduced pressure gave the crude product, which was purified by silica gel flash chromatography. Elution with 10% ethyl acetate/petroleum ether gave the following compounds in order of elution: (i) **3-bromo-6-methoxybenzocyclobuten-1-one 7a** as a white solid (0.698 g, 82%) [mp 74−75 °C (lit.[15] mp 75 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 4.09 (s, 3H), 3.89 (s, 2H)]; and (ii) **5-bromo-6-methoxybenzocyclobuten-1-one** (72 mg, 9%) as a white solid [mp 119−120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 7.3 Hz, 1H), 4.24 (s, 3H), 3.89 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.9, 149.8, 149.5, 140.4, 132.7, 116.1, 109.9, 60.7, 50.6; IR (KBr) 1774 cm^{-1}; HRMS calcd for $C_9H_7{}^{79}BrO_2$ (M^+) 225.9630, found 225.9629].

3-Bromo-6-isopropoxybenzocyclobuten-1-one 7b. 6-Isopropoxybenzocyclobutenone **6b**[4] (0.345 g, 1.96 mmol) was brominated using the procedure detailed for the preparation of **7a**. Purification by silica gel flash chromatography, eluting with 5% ethyl acetate/petroleum ether, gave the following compounds in order of elution: (i) **3-bromo-6-isopropoxybenzocyclobuten-1-one 7b** as a white solid (0.399 g, 80%) [mp 81−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8 Hz, 1H), 6.68 (d, J = 8.8 Hz, 1H), 5.01 (m, 1H), 3.86 (s, 2H), 1.33 (d, J = 5.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.1, 151.4, 149.9, 140.1, 132.2, 119.6, 105.3, 75.2, 51.2, 22.0; IR (KBr) 1762 cm^{-1}; HRMS calcd for $C_{11}H_{11}{}^{79}BrO_2$ (M^+) 253.9943, found 253.9940]; and (ii) **5-bromo-6-isopropoxybenzocyclobuten-1-one** (0.0605 g, 12%) as a colorless oil [^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 7.3 Hz, 1H), 6.88 (d, J = 7.3 Hz, 1H), 5.21 (m, 1H), 3.86 (s, 2H), 1.39 (d, J = 6.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.3, 149.5, 148.6, 140.7, 132.3, 115.4, 110.9, 75.9, 50.4, 22.1; IR (film) 1768 cm^{-1}; HRMS calcd for $C_{11}H_{11}{}^{79}BrO_2$ (M^+) 253.9943, found 253.9940].

3-Bromo-6-methoxy-1-propynylbenzocyclobuten-1-ol 8. A solution of dry diisopropylamine (2.80 mL, 20.0 mmol) in dry THF (20 mL) was cooled to 0 °C. A solution of *n*-butyllithium in hexanes (1.63 M, 12.27 mL, 20.0 mmol) was added dropwise and the resulting mixture stirred at 0 °C for 15 min. This solution was cooled to −60 °C, followed by dropwise addition of 1,2-dibromopropane (0.695 mL, 6.67 mmol), and the solution was stirred for 20 min at 0 °C.[8] The resulting cloudy solution was recooled to −60 °C, and a precooled (−60 °C) solution of benzocyclobutenone **7a** (0.757 g, 3.33 mmol) in dry THF (30 mL) was slowly added. The reaction was maintained at −60 °C for 2 h, followed by dropwise addition of saturated aqueous ammonium chloride solution. Ethyl acetate (50 mL) was added, and the mixture was allowed to warm to room temperature. The aqueous phase was extracted with three further portions of ethyl acetate. Removal of the solvents under reduced pressure and purification of the residue by flash chromatography, eluting with 30% ethyl acetate/petroleum ether, gave propyne **8** as a white solid (0.643 g, 72%): mp 95−96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.8 Hz, 1H), 6.62 (d, J = 8.8 Hz, 1H), 4.04 (s, 3H), 3.60 (d, J = 14.2 Hz, 1H), 3.31 (d, J = 14.2 Hz, 1H), 3.00 (s,

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(12) While **3** and **4** have been generated in one step from the reaction of the lithium enolate of *N*,*N*-diethylsenecioamide with either 3-methoxybenzyne or 3-methoxymethoxybenzene, the yields are low and purification of the material on a large scale would presumably be cumbersome. See: Watanabe, M.; Hisamatsu, S.; Hotokezaka, H.; Furukawa, S. *Chem. Pharm. Bull.* **1986**, *34*, 2810.

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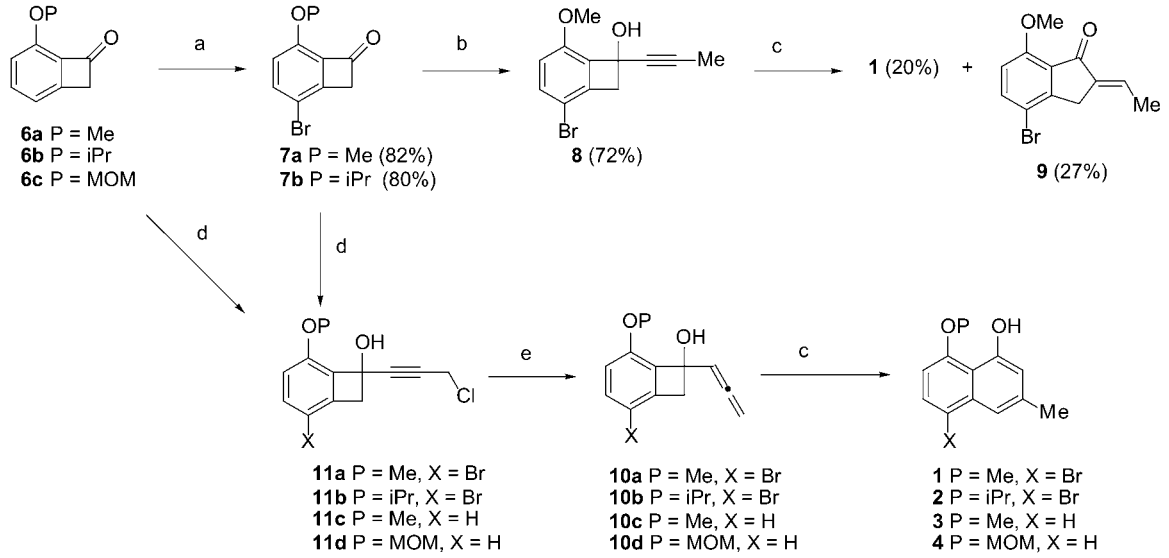
Scheme 2[a]



[a] Steps: (a) $Bn(Me)_3NBr_3/ZnCl_2$/HOAc; (b) $CH_3-CHBr-CH_2Br$/LDA/−60 to 0 °C; **7a**/THF/−60 °C; (c) toluene/reflux (for yields, see Table 1); (d) *n*-BuLi/propargyl chloride/C_6H_6/ether; **6a** (or **6c**, **7a**, **7b**)/THF/−78 to −60 °C (for yields see Table 1); (e) $LiAlH_4$/THF/0 °C (for yields, see Table 1).

Table 1. Summary of Yields (%) for the Preparation of Naphthalenes 1−4

benzocyclobutenone	propyne	allene	naphthalene
7a	**11a** (95)	**10a** (95)	**1** (84)
7b	**11b** (84)	**10b** (99)	**2** (76)
6a	**11c** (76)	**10c** (91)	**3** (80)
6c	**11d** (60)	**10d** (97)	**4** (79)

1H), 1.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 142.7, 133.6, 132.4, 117.1, 106.7, 81.7, 80.0, 69.2, 57.7, 49.6, 3.6. IR (KBr) 3157 cm^{-1}; HRMS calcd for $C_{12}H_{11}{}^{79}BrO_2$ (M^+) 265.9943, found 265.9942.

Thermolysis of Propyne 8. A solution of propyne **8** (0.148 g, 0.555 mmol) in dry toluene (8 mL) was heated at reflux for 18 h. Removal of the solvent under reduced pressure gave two major products in approximately 1:1 ratio as determined by ^{1}H NMR integration. Purification by flash chromatography, eluting with 30% ethyl acetate/petroleum ether, gave **4-bromo-2-ethylidene-7-methoxyindan-1-one 9** as a cloudy oil (40 mg, 27%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 1H), 6.90 (m, 1H), 6.74 (d, J = 8.8 Hz, 1H), 3.94 (s, 3H), 3.51 (m, 2H), 1.96 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.4, 157.8, 150.9, 138.1, 136.7, 132.9, 128.5, 111.4, 111.3, 56.0, 31.1, 15.2. IR (film) 1705 cm^{-1}; HRMS calcd for $C_{12}H_{11}{}^{79}BrO_2$ (M^+) 265.9943, found 265.9942. The remaining fractions from this column were pooled and further purified by flash chromatography, eluting with 20% acetone/petroleum ether, to give **5-bromo-8-methoxy-3-methyl-1-naphthalenol 1** as a white solid (30 mg, 20%): mp 104−105 °C (lit.[2b] mp 105−106 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.54 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 0.98 Hz, 1H), 6.81 (d, J = 1.5 Hz, 1H), 6.51 (d, J = 8.3 Hz, 1H), 3.99 (s, 3H), 2.48 (s, 3H).

Synthesis of Propargyl Chlorides 11a−d. A typical experimental procedure is given for the synthesis of **11a.** A solution of *n*-butyllithium in hexanes (1.55 M, 2.95 mL, 4.57 mmol, 2 equiv) was added dropwise to a solution of propargyl chloride[15] in benzene (43 wt % solution, 0.340 g, 4.57 mmol, 2 equiv) and ether (4.5 mL) at −78 °C. The resulting solution was stirred at −78 °C for 20 min. A precooled (−78 °C) solution of benzocyclobutenone (**7a**) (0.518 g, 2.28 mmol, 1 equiv) in dry THF (12 mL) was added dropwise via cannula. The reaction was allowed to warm slowly to −60 °C over a period of 1 h and maintained at this temperature for a further 3 h. After this time, the reaction was cooled to −78 °C, and water (30 mL) was slowly added. Upon warming to room temperature, the mixture was extracted with ethyl acetate (×4). The organic extracts were filtered through a plug of silica gel (**CAUTION:** *when the filtration was carried out using a sintered glass funnel, it was observed that dry residues ignite upon contact with a metal spatula. If the silica residues are removed while still damp, they present no danger*), and the solvent was removed under reduced pressure to give the crude product as a red oil. Purification by flash chromatography, eluting with 20% ethyl acetate/petroleum ether, gave **3-bromo-1-(3-chloropropynyl)-6-methoxybenzocyclobuten-1-ol 11a** as a pale yellow viscous oil (0.652 g, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 8.8 Hz, 1H), 6.64 (d, J = 9.3 Hz, 1H), 4.18 (s, 2H), 4.03 (s, 3H), 3.65 (d, J = 14.2 Hz, 1H), 3.34 (d, J = 14.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 142.4, 134.0, 131.3, 117.1, 106.7, 86.5, 79.8, 68.6, 57.5, 49.1, 30.1; IR (film) 3375 cm^{-1}; HRMS calcd for $C_{12}H_{10}{}^{79}Br^{35}ClO_2$ (M^+) 299.9553, found 299.9553.

3-Bromo-1-(3-chloropropynyl)-6-isopropoxybenzocyclobuten-1-ol 11b: brown viscous oil (84%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 9.3 Hz, 1H), 6.64 (d, J = 9.3 Hz, 1H), 4.82 (m, 1H), 4.18 (s, 2H), 3.63 (d, J = 14.2 Hz, 1H), 3.34 (d, J = 14.2 Hz, 1H), 2.92 (br s, 1H), 1.35 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9, 142.5, 134.0, 132.1, 118.7, 106.6, 85.8, 79.4, 72.7, 68.9, 49.0, 30.0, 22.7, 22.3; IR (film) 3396 cm^{-1}; HRMS calcd for $C_{14}H_{14}{}^{79}Br^{35}ClO_2$ (M^+) 327.9866, found 327.9863.

1-(3-Chloropropynyl)-6-methoxybenzocyclobuten-1-ol 11c: colorless viscous oil (76%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, J = 8.3, 7.3 Hz), 6.75 (d, J = 7.3 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 4.19 (s, 2H), 4.06 (s, 3H), 3.74 (d, J = 14.2 Hz, 1H), 3.43 (d, J = 13.7 Hz, 1H), 2.91 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 143.0, 131.8, 130.3, 115.9, 114.4, 87.4, 79.3, 70.1, 57.2, 49.5, 30.3; IR (film) 3383 cm^{-1}; HRMS calcd for $C_{12}H_{11}{}^{35}ClO_2$ (M^+) 222.0448, found 222.0448.

1-(3-Chloropropynyl)-6-methoxymethoxybenzocyclobuten-1-ol 11d: pale yellow viscous oil (60%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 1H), 6.82 (m, 2H), 5.82 (d, J = 7.3 Hz, 1H), 5.00 (d, J = 7.3 Hz, 1H), 4.18 (m, 1H), 3.63 (d, J = 14.2 Hz, 1H), 3.56 (s, 3H), 3.44 (d, J = 14.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 143.5, 131.5, 130.8, 117.4, 116.5, 94.5, 88.7, 78.9, 69.7, 56.3, 47.4, 30.4; IR (film) 3423 cm^{-1}; HRMS calcd for $C_{13}H_{13}{}^{35}ClO_3$ (M^+) 252.0553, found 252.0553.

Synthesis of Allenes 10a−d. A typical experimental procedure is given for the synthesis of **10a**. A solution of chloropropyne **11a** (0.650 g, 2.16 mmol) in dry THF (20 mL) was added dropwise to a suspension of $LiAlH_4$ (0.164 g, 4.31 mmol, 2 equiv) in dry THF (20 mL) at 0 °C. The resulting solution was allowed to warm to room temperature and stirred for 30 min. Upon cooling to 0 °C, the reaction mixture was quenched via dropwise addition of 1 M HCl solution (20 mL). Water (20 mL) was added and the product extracted with ethyl acetate (×4). The solvent was removed under reduced pressure to give **3-bromo-6-**

methoxy-1-propadienylbenzocyclobuten-1-ol 10a as a pale yellow viscous oil (0.548 g, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.8 Hz, 1H), 6.61 (d, J = 8.8 Hz, 1H), 5.64 (dd, J = 6.4, 6.8 Hz, 1H), 5.00 (m, 2H), 3.89 (s, 3H), 3.43 (d, J = 14.7 Hz, 1H), 3.25 (d, J = 14.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 153.1, 142.2, 133.6, 133.2, 116.2, 106.8, 96.2, 79.3, 75.3, 57.1, 47.0; IR (film) 3383 cm^{-1}; HRMS calcd for $C_{12}H_{11}{}^{79}BrO_2$ (M^+) 265.9943, found 265.9942.

3-Bromo-6-isopropoxy-1-propadienylbenzocyclobuten-1-ol 10b: brown viscous oil (99%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.8 Hz, 1H), 6.60 (d, J = 8.8 Hz, 1H), 5.60 (dd, J = 6.4, 6.8 Hz, 1H), 5.00 (m, 2H), 4.66 (m, 1H), 3.41 (d, J = 14.2 Hz, 1H), 3.24 (d, J = 14.7 Hz, 1H) 2.80 (br s, 1H), 1.31 (d, J = 5.9 Hz), 1.28 (d, J = 5.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.1, 151.6, 142.4, 134.4, 133.4, 117.9, 106.7, 95.6, 79.5, 75.5, 72.0, 47.0, 22.5, 22.1; IR (film) 3400 cm^{-1}; HRMS calcd for $C_{14}H_{15}{}^{79}BrO_2$ (M^+) 294.0256, found 294.0253.

6-Methoxy-1-propadienylbenzocyclobuten-1-ol 10c: pale yellow viscous oil (91%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (dd, J = 8.3, 8.3 Hz, 1H), 6.73 (m, 2H), 5.68 (dd, J = 6.8, 6.4 Hz, 1H), 4.99 (m, 2H), 3.92 (s, 3H), 3.52 (d, J = 14.2 Hz, 1H), 3.34 (d, J = 14.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 153.6, 142.7, 132.5, 131.1, 115.8, 113.5, 96.9, 79.2, 76.5, 56.8, 47.4; IR (film) 3404 cm^{-1}; HRMS calcd for $C_{12}H_{12}O_2$ (M^+) 188.0837, found 188.0837.

6-Methoxymethoxy-1-propadienylbenzocyclobuten-1-ol 10d: pale brown viscous oil (97%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (dd, J = 8.3, 7.3 Hz, 1H), 6.80 (m, 2H), 5.67 (dd, J = 6.4, 6.8 Hz, 1H), 5.54 (d, J = 6.8 Hz, 1H), 4.97 (d, J = 6.8 Hz, 1H), 4.92 (m, 2H), 4.75 (br s, 1H), 3.51 (s, 3H), 3.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.7, 149.5, 143.0, 132.5, 130.9, 117.1, 115.9, 98.0, 94.1, 78.6, 76.5, 56.0, 46.4; IR (film) 3425 cm^{-1}; HRMS calcd for $C_{13}H_{14}O_3$ (M^+) 218.0943, found 218.0943.

Synthesis of Naphthalenes 1−4. A typical experimental procedure is given for the synthesis of **1**. A solution of allene **10a** (0.512 g, 1.92 mmol) in dry toluene (20 mL) was heated at reflux for a period of 2.5 h. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel, using 15% ethyl acetate/petroleum ether, to give **5-bromo-8-methoxy-3-methyl-1-naphthalenol 1** as a white solid (0.429 g, 84%): mp 104−105 °C (lit.[2b] 105−106 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.54 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 0.98 Hz, 1H), 6.81 (d, J = 1.5 Hz, 1H), 6.51 (d, J = 8.3 Hz, 1H), 3.99 (s, 3H), 2.48 (s, 3H).

5-Bromo-8-isopropoxy-3-methyl-1-naphthalenol 2 (5% ethyl acetate/petroleum ether; white solid, 76%): mp 118−119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.47 (d, J = 0.98 Hz, 1H), 6.78 (d, J = 1.5 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 4.81 (m, 1H), 2.47 (s, 3H), 1.49 (d, J = 6.4 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 153.9, 139.3, 134.5, 129.4, 117.7, 114.9, 114.0, 113.0, 105.9, 73.0, 21.9, 21.8; IR (KBr) 3360 cm^{-1}; HRMS calcd for $C_{14}H_{15}{}^{79}BrO_2$ (M^+) 294.0256, found 294.0253.

8-Methoxy-3-methyl-1-naphthalenol 3 (15% ethyl acetate/petroleum ether; white solid, 80%): mp 93−94 °C (lit.[5] mp 92−94 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.32 (dd, J = 8.3, 1.5 Hz, 1H), 7.26 (dd, J = 7.8, 7.8 Hz, 1H), 7.09 (br s, 1H), 6.73 (d, J = 1.5 Hz, 1H), 6.70 (dd, J = 7.3, 0.98 Hz, 1H), 4.04 (s, 3H), 2.42 (s, 3H).

8-Methoxymethoxy-3-methyl-1-naphthalenol 4 (10% ethyl acetate/petroleum ether, pale yellow solid, 79%): mp 48−49 °C (lit.[12] mp 58 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.38 (d, J = 8.3, Hz, 1H), 7.26 (dd, J = 8.3, 7.8 Hz, 1H), 7.11 (s, 1H), 6.97 (d, J = 7.3 Hz, 1H), 6.76 (d, J = 0.98 Hz, 1H), 5.43 (s, 2H), 3.58 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 153.4, 137.5, 136.8, 125.6, 121.9, 118.3, 113.3, 112.2, 106.6, 95.3, 56.5, 21.4; IR (film) 3416 cm^{-1}; HRMS calcd for $C_{13}H_{14}O_3$ (M^+) 218.0943, found 218.0943.

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Supporting Information Available: Copies of the ^{1}H and ^{13}C NMR spectra for all new compounds and naphthalene **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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