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# A One-Flask Synthesis of Dihydronaphthalenemethanols by Directed Addition of Organolithium Reagents to BHA Naphthalenecarboxylates

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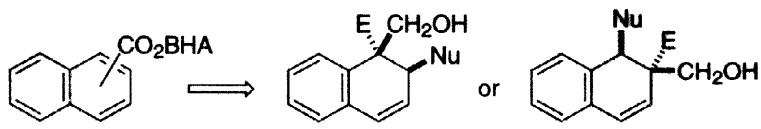
***Abstract***: The 1,4-addition reaction of organolithium reagents with 2,6-bis(*tert*-butyl)-4-methoxyphenyl naphthalenecarboxylates gave regioselectively substituted dihydronaphthalenecarboxylates in high yields. Successive treatment of the esters with organolithiums in THF, lithium triethylborohydride, methyl iodide, and finally sodium borohydride in methanol, provided regio- and stereoselectively the corresponding 1,1,2- and 1,2,2-trisubstituted dihydronaphthalenylmethanols in good yields. This one-flask process is constituted from a sequence of five reactions involving a reductive generation of an aldehyde metal enolate from a ketene as the key step. 

Keywords: Addition reactions; Esters; Ketene; Naphthalenes

## Introduction

An efficient construction of a carbon skeleton has been one of the challenging targets of synthetic and medicinal chemistry. Elaboration of an aromatic ring with an electrophile has been the established methodology as shown in the Friedel Crafts-type reaction. The electrophilic aromatic substitution reaction of a naphthalene, however, needs to be combined with a reducing process for the construction of dihydronaphthalenes that are useful skeletons for the synthesis of biologically active cyclic molecules. Another promising way is the use of a carbonucleophile. Addition of organometallics to a naphthalene nucleus provides the way for the construction of dihydronaphthalene. Recent progress in the field has been paved by Meyers based on oxazoline[1,2] and imine[3,4] chemistry.[5] The reaction of unmodified-naphthalenecarboxylic acids with a limited group of organolithiums[6] and intramolecular addition of naphthalenecarboxamide[7] have been developed. Here we describe that 2,6-bis(*tert*-butyl)-4-methoxyphenyl (BHA)[8] naphthalenecarboxylate serves as the efficient acceptor for the directed 1,4-addition reaction of organolithiums.[9] Furthermore, successive treatment of the esters with organolithiums, super hydride, alkyl halide, and finally sodium borohydride in methanol, provides regio- and stereoselectively 1,1,2- and 1,2,2-trisubstituted dihydronaphthalenylmethanols in one-flask. The one-flask process is constituted from a sequence of five reactions involving a reductive generation of an aldehyde metal enolate[10] from a ketene as the key step.

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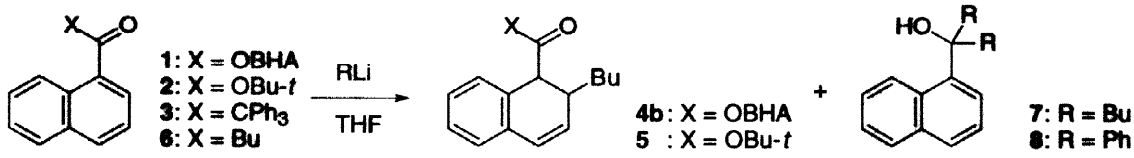
**The BHA ester as a sterically controllable activating group of a naphthalene nucleus**

The general idea under consideration for the addition of organometallics to a naphthalene nucleus relies on a steric control, allowing a conjugate-type addition by sterically inhibiting the nucleophilic attack of the organolithium to the carbonyl carbon. Pioneering reports by Seebach[11] and Cooke[12] have demonstrated that sterically hindered α,β-unsaturated trityl ketones and BHA esters serve as the Michael acceptors to afford the 1,4-addition products.[13]

The three 1-naphthalene carbonyl candidates, BHA ester **1**, *tert*-butyl ester **2**, and trityl ketone **3** were prepared from 1-naphthalenecarbonyl chloride. The reaction of **2** with butyllithium in THF gave the desired product **5** in only 4% yield, and the undesired carbonyl-addition products **6** and **7** in 7 and 73% yields. The reaction of **3** with phenyllithium also afforded **8** without production of the desired 1,4-adduct. Contrary to the unfavorable behavior of **2** and **3**, BHA ester **1** serves as an excellent acceptor.

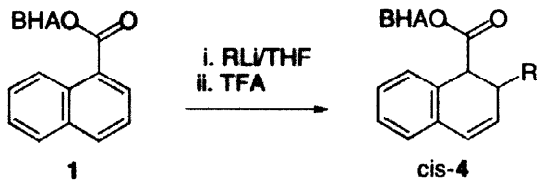
The reaction of **1** with butyllithium in THF at −78 °C afforded quantitatively **4b**. The major stereoisomer was cis-**4b** formed in 70% yield, and the minor was trans-**4b** formed in 30% yield.




**Addition of organolithium reagents to BHA 1- and 2-naphthalenecarboxylates**

As summarized in Table 1, the 1,4-addition of alkyl-, vinyl-, and aryllithiums to **1** took place regioselectively at the C2 position to afford **4** in high yields. In every case, the major product was cis-**4**, arising from the reasonably anticipated stereoselective protonation of the lithium enolate with trifluoroacetic acid.[14] Epimerization of cis-**4** into trans-**4** confirms the stereochemistry of **4**.[15] The 1,6-addition product was not observed.

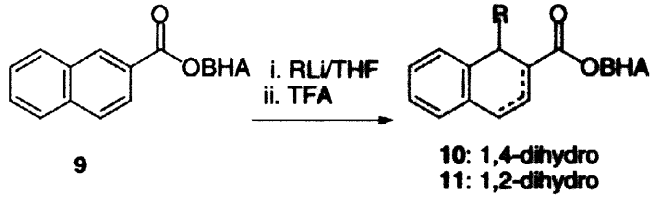
**Table 1.** Addition of Organolithium Reagents to **1**




**1** cis-**4**

| R | temp/°C | time/h | 4 | cis-/trans-4 | yield/% |
|---|---|---|---|---|---|
| Me | −23 | 1 | a | 2.3 | >99 |
| Bu | −78 | 1 | b | 2.3 | >99 |
| Vinyl | −45 | 1 | c | 1.8 | >99 |
| Ph | −45 | 2 | d | 3.6 | >99 |
| 1-Naph | −45 | 4 | e | >99 | 98 |

**Table 2.** Addition of Organolithium Reagents to **9**




**9** **10**: 1,4-dihydro
**11**: 1,2-dihydro

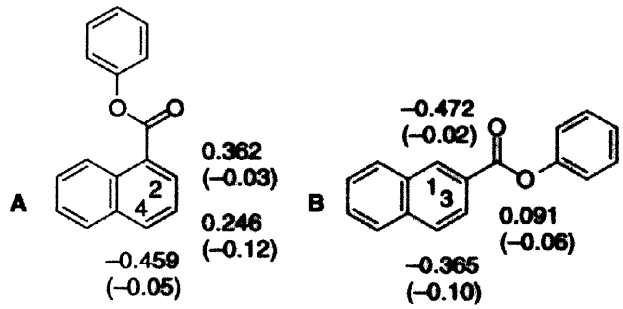
| R | temp/°C | time/h | 10, 11 | 10/11 | yield/% |
|---|---|---|---|---|---|
| Me | −23 | 1.5 | a | 4.0 | >99 |
| Bu | −78 | 0.5 | b | 4.3 | >99 |
| Ph | −45 | 2 | d | 2.0 | >99 |
| 1-Naph | −45 | 2 | e | 2.0 | 83 |

The reaction with BHA 2-naphthalenecarboxylate **9** also gave regioselectively 1-substituted dihydro-2-naphthalenecarboxylates **10** and **11** in high yields as summarized in Table 2. The major product was 1,4-dihydronaphthalenecarboxylate **10**, arising from a protonation at the C4 position. The steric bulk around the enolate may direct the protonation at the C4, not the C2 position.

**Origin of regioselectivity in the addition of organolithium to naphthalenecarboxylates**

The addition of organolithium reagents to 1- and 2-naphthalenecarboxylates is a regioselective process. 1-Naphthalenecarboxylate **1** favors an attack at the C2 position, and 2-naphthalenecarboxylate **9** does so at the C1 position. Theoretical calculations of the LUMO coefficients of phenyl 1- and 2-naphthalenecarboxylates were performed using semiempirical MO PM3, in precise mode.[16] The orientation of the carbonyl group has little influence on the results. Therefore, **A** and **B** are presented for 1- and 2- naphthalenecarboxylates.

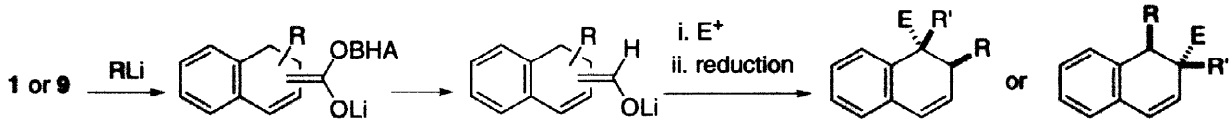
The magnitude of the coefficients suggests that the most reactive position of **A** is the C4 position, followed by the C2 position where the reaction of **1** was observed. In **B**, C1 is the most favored reaction site, which is the observed reaction site of **9**. The charge is not meaningful. Calculation of the corresponding methyl ester and aldehyde also gave the similar results. These calculations indicate that coordination of the carbonyl oxygen of **1** or **9** to the lithium of organolithium is involved in the initial stage of the reaction, then the proximity effect is operative.[3,17]




LUMO coefficients and charges (in parentheses).

**Design of the one-flask process based on a successive generation and reduction of a ketene**

The versatility of the above reaction depends on the functional conversion of the BHA ester group to other functions such as an aldehyde or an alcohol. However, attempted conversion of the BHA group of **4** into the carboxylic acid by ceric ammonium nitrate oxidation or the alcohol by lithium aluminium hydride reduction suffered from aromatization to give a mixture of products.[18] The thermally induced cleavage of the ester lithium enolate to a ketene followed by *in situ* reaction with organolithium reagents has been reported to provide the corresponding ketone lithium enolate.[19,20] We extended the 1,4-addition of organolithium reagents with the BHA ester into a one-flask process that provides 1,1,2- and 1,2,2-trisubstituted dihydronaphthalenes **12-15** from **1** and **9**. The process involves a generation of an aldehyde metal enolate by the reduction of the ketene[21] with lithium triethylborohydride.

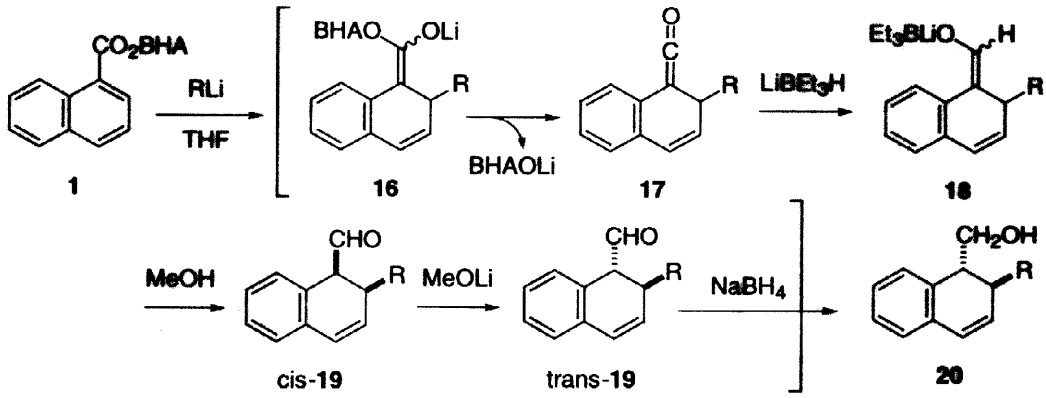



**12**: R' = CHO
**13**: R' = $CH_2OH$
**14**: R' = CHO
**15**: R' = $CH_2OH$

**The one-flask synthesis of 2-substituted 1,2-dihydro-1-naphthalenylmethanol**

The one-flask process is exemplified by the conversion of **1** to **20b** (R = Bu). A hexane solution of 1.2 equiv of butyllithium was added to a solution of **1** in THF at –78 °C. After stirring at –78 °C for 40 min, a THF solution of 3 equiv of lithium triethylborohydride was added and the mixture was stirred under reflux for 1.5 h to generate an aldehyde metal enolate **18b**. The mixture was then diluted with methanol at –50 °C and stirred for 1 h at rt to epimerize cis-**19b** to trans-**19b**. Then, the mixture was treated with sodium borohydride at rt. The mixture was then quenched with 10% aqueous HCl and extracted with benzene. Concentration and

silica gel column chromatography afforded **20b** in 81% yield. Reduction with diisobutyl aluminium hydride was not satisfactory and gave **20b** in only 30% yield.




The one-flask process involves five operations, (1) an addition of organolithium to form the lithium enolate **16**, (2) formation of a ketene **17** by eliminating BHA phenoxide, (3) reduction to an aldehyde enolate **18**, (4) protonation to cis-**19** and epimerization to trans-**19**, and finally (5) reduction to the alcohol **20**.

The epimerization of cis-**19** with lithium methoxide was easily carried out by treatment of the reduction mixture with methanol at rt for 1 h to afford trans-**19**. Without this isomerization step, a mixture of cis- and trans-**20** was obtained.[22] Results using alkyl-, vinyl-, and aryllithiums are summarized in Table 3.

**Table 3.** The one-flask synthesis of **20** from **1**

| R | 20 | yield/% |
|---|---|---|
| Me | a | 71 |
| Bu | b | 81 |
| Vinyl | c | 61 |
| Ph | d | 85 |
| 1-Naph | e | 82 |

## Synthesis of 1,2-disubstituted 1,2-dihydro-1-naphthalenylmethanol

A stereoselective construction of the consecutive quaternary and tertiary carbon centers is possible by a treatment of the aldehyde enolate **18**[23] with an electrophile in the presence of HMPA to give 1,2-disubstituted 1,2-dihydro-1-naphthalenecarbaldehyde **12**.

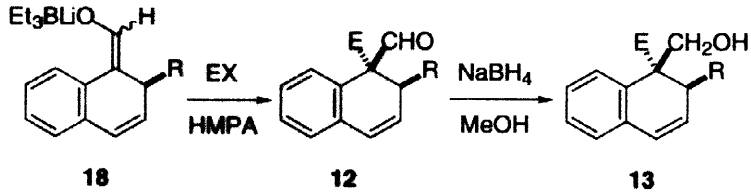



**Table 4.** The one-flask synthesis of **13** from **1**

| R | EX | 13 | yield/% |
|---|---|---|---|
| Me | MeI | a | 55 |
| Bu | MeI | b | 75 |
| Bu | BnBr | bb | 53 |
| Vinyl | MeI | c | 42 |
| Ph | MeI | d | 65 |

The electrophile was stereoselectively introduced from the bottom face of the enolate **18**, avoiding the steric repulsion of the initially introduced R group. The one-flask process gave the corresponding alcohol **13** in a reasonably good yield.[24] Results of the one-flask reaction are summarized in Table 4. The oxidation of the alcohol **13** with PCC gave back the corresponding aldehyde **12**. Stereochemistry was determined by NOE and confirmed by comparison with those reported.[1]

### Synthesis of 1,2-disubstituted 1,2-dihydro-2-naphthalenylmethanol

The one-flask process was extended to the synthesis of 1,2-disubstituted 1,2-dihydro-2-naphthalenylmethanol **15**. Some of the reaction results are summarized in Table 5.

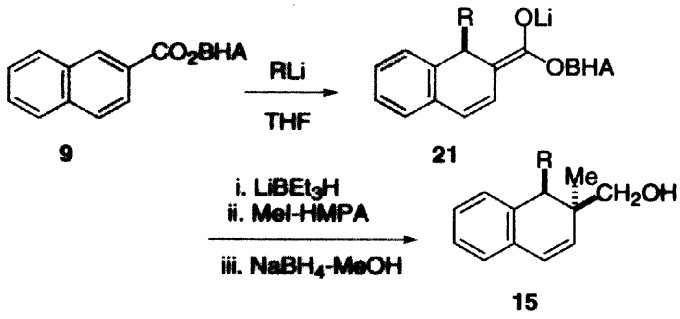



Table 5. The one-flask synthesis of **15** from **9**

| R | 15 | yield/% |
|---|---|---|
| Me | a | 45 |
| Bu | b | 93 |
| Vinyl | c | 52 |
| Ph | d | 66 |
| 1-Naph | e | 51 |

It is important to note that the methylation of the aldehyde enolate proceeded exclusively at the C2 position to give regio- and stereoselectively the alcohol **15**, whereas the protonation of the BHA enolate **21** took place at the C4 to give the 1,4-dihydro-isomer **10** as the major product, probably due to the steric hindrance at the C2 by the bulky BHA group.[25] The oxidation of the alcohol **15** with PCC gave back the corresponding aldehyde **14**.

## Conclusion

The BHA group exerts a remarkable activating and directing effects on the reaction of naphthalenecarboxylate with an organolithium reagent. Reductive generation and subsequent protonation or alkylation of the aldehyde metal enolate are carried out in a one-flask operation. The one-flask process to 1,2-di-, 1,1,2- and 1,2,2-trisubstituted dihydronaphthalenes from the BHA naphthalenecarboxylates is an alternative to the elegant scheme developed by Meyers based on the oxazoline and imine chemistry. Extension of this process to the enantioselective one-flask process is the target of our continuing efforts.[26]

**Acknowledgment**: We gratefully acknowledge financial support from Japan Society for Promotion of Science (RFTF-96P00302), the Ministry of Education, Science, Sports and Culture, and the Science and Technology Agency, Japan.

## Experimental[27]

**2,6-Bis(*tert*-butyl)-4-methoxyphenyl 1-naphthalenecarboxylate (1)**. A hexane solution of butyllithium (12 mL, 19 mmol) was added dropwise at 0 °C to a solution of BHA (4.31 g, 18 mmol) in THF (20 mL). After stirring for 0.5 h at 0 °C, a solution of 1-naphthoyl chloride[28] (4.0 g, 21 mmol) in THF (20 mL) was added dropwise to the white suspension. After stirring for 48 h at rt, satd $NH_4Cl$ was added and the mixture was extracted with benzene. Concentration and recrystallization from AcOEt gave **1** (5.72g, 81%) as colorless prisms of mp 189-190 °C. $^1$H-NMR: 1.37 (18H, s), 3.85 (3H, s, Me), 6.89 (2H, s), 7.54-7.71 (2H, m), 7.89-7.99 (2H, m), 8.14 (1H, brd), 8.64 (1H, dd, *J*=7.4, 1.5), 9.04-9.20 (1H, m). $^{13}$C-NMR: 31.5 (q), 35.7 (s), 55.3 (q), 111.7 (d), 124.7 (d), 125.9 (d), 126.0 (s), 126.4 (d), 128.4 (d), 128.7 (d), 131.6 (d), 132.2 (s), 134.1 (s), 134.5 (d), 141.7 (s), 143.8 (s), 156.4 (s), 167.2 (s). IR (KBr): 1727, 1585 cm$^{-1}$. MS *m/z*: 390 ($M^+$). Anal. Calcd. for $C_{26}H_{30}O_3$: C, 79.96; H, 7.74. Found: C, 79.71; H, 7.73.

**1-Naphthalenyl triphenylmethyl ketone (3)**. A hexane solution of butyllithium (56.4 mL, 0.09 mol)

was added dropwise at –78 °C to a solution of triphenylmethane (21.5 g, 0.09 mol) in THF (200 mL). The red solution was stirred for 1 h at 0 °C. A solution of 1-naphthoyl chloride (25.2 g, 0.13 mol) in THF (20 mL) was added dropwise over 0.5 h at –70 °C. After stirring for 2 h at –70 °C, the mixture was allowed to warm up to rt. The red mixture was stirred for 12 h at rt. After addition of satd $NaHCO_3$, the mixture was stirred vigorously for 2.5 h at rt. The mixture was extracted with AcOEt. Concentration and chromatography (hexane-hexane/AcOEt, 50/1-20/1) gave **3** (5.93g, 17%) as colorless prisms of mp 158-160 °C (AcOEt/hexane, 1/1). $^1$H-NMR: 6.8-8.0 (m). IR ($CHCl_3$): 1680, 1590, 1490 $cm^{-1}$. MS *m/z*: 397 ($M^+$-1), 243 ($Tr^+$). Anal. Calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 90.47, H, 5.57.

**Reaction of 2 with butyllithium**. A hexane solution of butyllithium (0.82 mL, 1.3 mmol) was added at –78 °C to a solution of **2**[29] (228 mg, 1.0 mmol) in THF (10 mL). The mixture was stirred for 0.7 h at –78 °C and an additional butyllithium (0.63 mL, 1.0 mmol) was added. The mixture was allowed to warm up to rt and then treated with satd $NH_4Cl$. The mixture was extracted with ether. Concentration and chromatography (hexane/AcOEt, 50/1) gave a mixture of **5** (10 mg, 4%), **6** (14 mg, 7%), and **7** (197 mg, 73%). **5**: $^1$H-NMR: 0.50-2.65 (19H, m), 7.15-8.05 (6H, m), 8.40-8.75 (1H, m). IR (neat): 3500, 2980, 1600, 1510 $cm^{-1}$. MS *m/z*: 270 ($M^+$), 213. Anal. Calcd. for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.42, H, 9.78.

**Reaction of 3 with phenyllithium**. To a solution of **3** (399 mg, 1.0 mmol) in THF (10 mL) at –78 °C was added a solution of phenyllithium (0.53 mL, 1.2 mmol) in cyclohexane/ether (7/3). The mixture was stirred for 7 h at –78 °C to 0 °C, and then treated with trifluoroacetic acid (TFA) (0.8 mL) and diluted with ether. Concentration and chromatography (hexane/ether, 30/1) gave **3** (0.27g, 68%) and **8** (90 mg, 29%) as powder of mp 137.5-138.5 °C (hexane/ether). $^1$H-NMR: 3.32 (1H, s, OH), 7.2-7.4 (13H, m), 7.5-7.9 (3H, m), 7.95-8.10 (1H, m). IR ($CHCl_3$): 3633, 1600, 1500 $cm^{-1}$. MS *m/z*: 310 ($M^+$), 292.

***cis*- and *trans*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-methyl-1,2-dihydro-1-naphthalenecarboxylates (4a)**. An ether solution of methyllithium (1.0 mL, 1,5 mmol, low halide) was added to a solution of **1** (391 mg, 1.0 mmol) in THF (10 mL) at –23 °C. After stirring for 1.5 h at –23 °C, the yellow green mixture was quenched with TFA (0.8 mL). The mixture was diluted with ether, and washed with 10% HCl, satd $NH_4Cl$, brine, and dried over $MgSO_4$. Concentration and chromatography (hexane/ether, 40/1) gave cis-**4a** (280 mg, 70%) of mp 130-132 °C and trans-**4a** (126 mg, 30%) as colorless prisms of mp 117.5-118.5 °C.

cis-**4a**: $^1$H-NMR: 0.82 and 1.40 (each 9H, s), 2.86-3.16 (1H, m), 3.75 (3H, s, Me), 3.87 (1H, brd, *J*=6 Hz,), 5.93 (1H, ddd, *J*=1, 3, 10 Hz), 6.40 (1H, dd, *J*=3, 9 Hz), 6.75 and 6.83 (each 1H, d, *J*=3 Hz), 7.0-7.6 (4H, m). $^{13}$C-NMR: 16.8 (q), 30.6 (q), 31.4 (q), 32.1 (d), 34.9 (s), 35.4 (s), 50.9 (d), 55.2 (q), 111.4 (d), 126.0 (d), 126.2 (d), 127.2 (d), 128.1 (d), 130.1 (d), 131.7 (s), 134.7 (s), 135.6 (d), 142.0 (s), 143.0 (s), 144.2 (s), 156.0 (s), 169.7 (s). IR (KBr): 2980, 1760, 1590 $cm^{-1}$. MS *m/z*: 406 ($M^+$), 391 ($M^+$-Me), 236. Anal. Calcd. for $C_{27}H_{34}O_3$ 1/4$H_2O$: C, 78.89; H, 8.46. Found: C, 78.92; H, 8.36.

trans-**4a**: $^1$H-NMR: 0.89 and 1.35 (each 9H, s), 3.26 (1H, m), 3.76 (4H, s, OMe, CHCO), 6.06 (1H, dd, *J*=6, 10 Hz, olefin), 6.38 (1H, d, *J*=10 Hz, olefin), 6.75 and 6.82 (each 1H, d, *J*=3 Hz), 7.0-7.5 (4H, m). $^{13}$C-NMR: 18.2 (q), 29.9 (d), 30.7 (q), 31.4 (q), 35.0 (s), 35.5 (s), 51.9 (d), 55.2 (q), 111.3 (d), 111.4 (d), 125.6 (d), 126.1 (d), 127.2 (d), 128.1 (d), 128.5 (s), 131.8 (d), 133.1 (s), 133.5 (s), 142.4 (s), 143.1 (s), 143.7 (s), 156.0 (s), 172.2 (s). IR (KBr): 2940, 1785, 1585 $cm^{-1}$. MS *m/z*: 406 ($M^+$), 236. Anal. Calcd. for $C_{27}H_{34}O_3$: C, 79.76; H, 8.43. Found: C, 79.51; H, 8.45.

***cis*- and *trans*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-butyl-1,2-dihydro-1-naphthalenecarboxylates (4b)**. A hexane solution of butyllithium (0.82 mL, 1.3 mmol) was added to a solution of **1** (391 mg, 1.0 mmol) in THF (10 mL) at –78 °C. The workup as above and chromatography (hexane/ether, 30/1) gave cis-**4b** (309 mg, 70%) of mp 118.5-120.0 °C and trans-**4b** (136 mg, 30%) of mp 104-105 °C.

cis-**4b**: $^1$H-NMR: 0.70-1.59 (7H, m), 0.81 and 1.39 (each 9H, s), 1.70-2.05 (2H, m), 2.60-2.90 (1H, m, H). 3.75 (3H, s), 3.91 (1H, brd, *J*=5 Hz), 6.01 (1H, brd, *J*=10 Hz), 6.41 (1H, dd, *J*=3, 10 Hz), 6.73 and 6.82 (each 1H, d, *J*=3 Hz), 6.98-7.32 (3H, m), 7.38-7.54 (1H, m). $^{13}$C-NMR: 14.2 (q), 22.8 (t), 30.2 (t x 2), 30.7 (q), 31.5 (q), 35.0 (s), 35.5 (s), 37.8 (d), 49.9 (d), 55.2 (q), 111.3 (d x 2), 125.8 (d), 126.4 (d), 127.0 (d), 128.0 (d), 130.0 (d), 132.1 (d), 134.5 (s), 134.9 (s), 141.9 (s), 142.8 (s), 144.0 (s), 155.9 (s), 169.6 (s). IR (KBr): 1743, 1590 cm$^{-1}$. MS *m/z*: 448 ($M^+$), 237, 236. Anal. Calcd. for $C_{30}H_{40}O_3$: C, 80.31; H, 8.99. Found: C, 80.11; H, 9.03.

trans-**4b**: $^1$H-NMR: 0.68-1.60 (7H, m) 0.92 and 1.36 (each 9H, s), 2.96-3.22 (1H, m), 3.76 (3H, s), 3.83 (1H, brs), 6.09 (1H, dd, *J*=7, 10 Hz), 6.40 (1H, d, *J*=10 Hz), 6.75 and 6.82 (each 1H, d, *J*=3 Hz), 6.96-7.50 (4H, m). $^{13}$C-NMR: 14.1 (q), 22.8 (t), 29.3 (t x 2), 30.8 (q), 31.5 (q), 32.6 (s), 35.0 (s), 35.6 (d), 50.2 (d), 55.2 (q), 111.2 (d), 111.4 (d), 125.9 (d), 126.0 (d), 127.1 (d), 127.9 (d), 128.9 (d), 131.4 (d), 132.2 (s), 142.3 (s), 142.9 (s), 143.6 (s), 155.1 (s), 162.0 (s). IR (KBr): 1780, 1585 cm$^{-1}$. MS *m/z*: 448 ($M^+$), 390, 237, 236. Anal. Calcd. for $C_{30}H_{40}O_3$: C, 80.31; H, 8.99. Found: C, 80.30; H, 9.01.

***cis*- and *trans*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-vinyl-1,2-dihydro-1-naphthalenecarboxylates (4c)**. An ether solution of methyllithium (0.9 mL, 1.2 mmol, low halide) was added to a solution of **1** (391 mg, 1.0 mmol) and tetravinyltin (0.07 mL, 0.4 mmol) in THF (10 mL) at –78 °C. The mixture was stirred for 3.5 h at –78 to -20 °C. The reaction was quenched with TFA (0.8 mL). The workup as above and chromatography (hexane/ether, 30/1-10/1) gave cis-**4c** (0.27 g, 64%) as colorless prisms of mp 99-100 °C (MeOH) and trans-**4c** (0.15 g, 36%) as colorless prisms of mp 91-92 °C (MeOH).

cis-**4c**: $^1$H-NMR: 0.80 and 1.36 (each 9H, s), 3.4-3.8 (1H, m), 3.75 (3H, s, OMe), 3.98 (1H, brd, *J*=4 Hz, CHCO). 5.12 and 5.24 (each 1H, m, $CH_2$=), 6.00 (1H, m, olefin), 6.27-6.63 (2H, m, olefin), 6.74 and 6.82 (each 1H, d, *J*=3 Hz) 6.9-7.6 (4H, m). $^{13}$C-NMR: 30.5 (q), 31.4 (q), 34.8 (s), 35.3 (s), 42.4 (d), 51.7 (d), 55.1 (q), 111.3 (d), 111.4 (d), 116.9 (t), 126.1 (d), 126.4 (d), 127.4 (d), 128.3 (d), 130.1 (d), 131.1 (s), 132.6 (d), 34.4 (s), 138.9 (d), 141.9 (s), 143.1 (s), 144.1 (s), 156.0 (s), 169.4 (s). IR (KBr): 1750, 1588 cm$^{-1}$. MS *m/z*: 418 ($M^+$), 403 ($M^+$-Me). Anal. Calcd. for $C_{28}H_{34}O_3$: C, 80.34; H, 8.19. Found: C, 80.22; H, 8.14.

trans-**4c**: $^1$H-NMR: 0.89 and 1.36 (each 9H, s), 3.5-3.9 (2H, m), 3.76 (3H, s, OMe), 4.93-5.22 (2H, m, $CH_2$=), 5.59-6.07 (2H, m), 6.48 (1H, d, *J*=10 Hz, olefin), 6.75 and 6.83 (each 1H, d, *J*=3 Hz), 6.9-7.5 (4H, m). $^{13}$C-NMR: 30.6 (q), 31.4 (q), 35.0 (s), 35.5 (s), 39.2 (d), 50.4 (d), 55.2 (q), 111.3 (d), 111.5 (d), 115.7 (t), 126.3 (d), 127.1 (d), 127.5 (d), 128.2 (d), 128.6 (s), 129.1 (d), 131.4 (s), 133.7 (s), 136.9 (d), 142.4 (s), 143.1 (s), 143.7 (s), 156.1 (s), 171.7 (s). IR (KBr): 1753, 1590, 1415 cm$^{-1}$. MS *m/z*: 418 ($M^+$), 236. Anal. Calcd. for $C_{28}H_{34}O_3$: C, 80.34; H, 8.19. Found: C, 80.48; H, 8.16.

***cis*- and *trans*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-phenyl-1,2-dihydro-1-naphthalenecarboxylates (4d)**. A solution of phenyllithium (1.1 mL, 2.2 mmol) in cyclohexane-ether was added to a solution of **1** (391 mg, 1.0 mmol) in THF (10 mL) at –78 °C. After stirring for 2 h at –78 °C, the yellow green mixture was quenched with TFA (0.8 mL). The workup as above and chromatography (hexane/ether, 20/1) gave cis-**4d** (363 mg, 78%) as powder of mp 130-132 °C and trans-**4d** (102 mg, 22%) as powder of mp 149.5-151.5 °C.

cis-**4d**: $^1$H-NMR: 0.77 and 0.92 (each 9H, s), 3.69 (3H, s, OMe), 4.19 (1H, brd, *J*=5 Hz, PhCH), 4.33 (1H, brd, *J*=5 Hz, CHCO), 6.54 (2H, brs, olefin), 6.68 (2H, s), 7.0-7.6 (9H, m). $^{13}$C-NMR: 30.4 (q), 30.8 (q), 34.8 (s), 35.0 (s), 43.7 (d), 53.0 (d), 55.1 (q), 111.2 (d), 126.2 (d), 126.6 (d), 127.0 (d), 127.5 (d), 128.0 (d), 128.6 (d), 130.0 (d), 130.4 (d), 130.9 (d), 131.9 (d), 134.7 (s), 140.5 (s), 141.7 (s), 143.2 (s), 144.0 (s), 155.9 (s), 168.5 (s). IR (KBr): 2950, 1753, 1592 cm$^{-1}$. MS *m/z*: 468 ($M^+$), 237, 236. Anal. Calcd. for $C_{32}H_{36}O_3$: C, 82.01; H, 7.74. Found: C, 81.90, H, 7.72.

trans-**4d**: $^1$H-NMR: 0.91 and 1.38 (each 9H, s), 3.77 (3H, s, OMe), 4.09 (1H, brs, CHCO), 4.48 (1H, brd,

*J*=6 Hz, PhCH), 6.13 (1H, ddd, *J*=1, 6, 10 Hz, olefin), 6.66 (1H, brd, *J*=10 Hz, olefin), 6.77 and 6.85 (each 1H, d, *J*=3 Hz), 7.0-7.5 (9H, m). $^{13}$C-NMR: 30.6 (q), 31.4 (q), 35.0 (s), 35.5 (s), 40.9 (d), 52.8 (d), 55.2 (q), 111.4 (d), 111.5 (d), 126.2 (d), 127.0 (d), 127.5 (d), 127.68 (d), 127.73 (d), 128.1 (d), 128.3 (d), 128.7 (d), 129.7 (d), 131.7 (s), 133.8 (d), 141.1 (s), 142.5 (s), 143.1 (s), 143.7 (s), 156.1 (s), 172.1 (s). IR (KBr): 1740, 1590 cm$^{-1}$. MS *m/z*: 468 ($M^+$). Anal. Calcd. for $C_{32}H_{36}O_3$: C, 82.01; H, 7.74. Found: C, 81.73; H, 7.71.

***cis*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-naphthalenyl-1,2-dihydro-1-naphthalenecarboxylate (4e).** A hexane solution of butyllithium (2.1 mL, 3.0 mmol) was added to a solution of 1-bromonaphthalene (0.42 mL, 3.0 mmol) in ether (5 mL) at –78 °C. After stirring for 1.3 h at –78 °C, the yellow heterogeneous mixture was added to a solution of **1** (391 mg, 1.0 mmol) in THF (10 mL) at –78 °C. The yellow suspension was stirred at –45 °C for 4 h. The reaction was quenched with TFA (0.8 mL). Usual workup and chromatography (hexane/ether, 20/1) gave cis-**4e** (508 mg, 98%) as colorless prisms of mp 215-216. °C (EtOH). The trans isomer was not detected. $^1$H-NMR: 0.53 and 0.78 (each 9H, s), 3.66 (3H, s, OMe), 4.50 (1H, d, *J*=5 Hz), 5.14 (1H, d, *J*=5 Hz, CHCO), 6.59 and 6.65 (each 1H, d, *J*=3 Hz), 6.66 (2H, s, olefin), 7.18-8.11 (11H, m). $^{13}$C-NMR: 30.4 (q), 34.7 (s), 34.8 (s), 39.2 (d), 50.6 (d), 55.0 (q), 111.2 (d), 111.4 (d), 122.0 (d), 125.1 (d), 125.5 (d), 126.3 (d), 126.4 (d), 127.1 (d), 127.4 (d), 127.6 (d), 128.7 (d), 129.2 (d), 129.5 (d), 130.4 (d), 130.5 (d), 131.7 (s), 132.8 (s), 133.7 (s), 134.8 (s), 135.3 (s), 141.5 (s), 143.1 (s), 144.0 (s), 155.9 (s), 168.6 (s). IR (KBr): 1755, 1590 cm$^{-1}$. MS *m/z*: 518 ($M^+$), 255. Anal. Calcd. for $C_{36}H_{38}O_3$: C, 83.36; H, 7.39. Found: C, 83.45; H, 7.46.

**2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-naphthalenecarboxylate (9).** Prepared in 90% yield from 2-naphthoyl chloride by the same procedure for **1**. Colorless needles of mp 164-165 °C (AcOEt-MeOH, 1/2.5). $^1$H-NMR: 1.35 (18H, s), 3.84 (3H, s), 6.93 (2H, s), 7.52-8.10 (5H, m), 7.89-7.99 (2H, m), 8.26 (1H, dd, *J*=2, 9 Hz), 8.81 (1H, brs). IR (KBr): 1730, 1587 cm$^{-1}$. MS *m/z*: 390 ($M^+$). Anal. Calcd. for $C_{26}H_{30}O_3$: C, 79.96; H, 7.74. Found: C, 79.74, H, 7.85.

**2,6-Bis(*tert*-butyl)-4-methoxyphenyl 1-methyl-1,2-dihydro-2-naphthalenecarboxylate (11a) and 2,6-bis(*tert*-butyl)-4-methoxyphenyl 1-methyl-1,4-dihydro-2-naphthalenecarboxylate (10a).** Prepared by the same procedure for **10b** and **11b**. Chromatography (hexane/$CHCl_3$/ether, 80/20/1) gave **11a** (20%) as colorless prisms of mp 149-150 °C (EtOH) and **10a** (79%) as colorless prisms of mp 185-186 °C (EtOH).

**11a**: $^1$H-NMR: 1.23 (3H, d, *J*=7 Hz, Me), 1.33 and 1.34 (each 9H, s), 3.45 (1H, dq, *J*=7, 7 Hz, CHMe), 3.80 (3H, s), 3.91 (1H, m), 6.45 (1H, dd, *J*=1, 7 Hz), 6.60 (1H, dd, *J*=3, 7 Hz), 6.88 (2H, s), 7.0-7.3 (4H, m). IR (KBr): 1750, 1587 cm$^{-1}$. MS *m/z*: 406 ($M^+$), 236. Anal. Calcd. for $C_{27}H_{34}O_3$: C, 79.76; H, 8.43. Found: C, 79.46, H, 8.45.

**10a**: $^1$H-NMR: 1.2-1.4 (3H, m, 2 x Me), 1.28 and 1.35 (each 9H, s), 3.52-3.82 (2H, m), 3.81 (3H, s, OMe), 3.88-4.12 (1H, m), 6.88 (2H, s), 7.1-7.3 (4H, m), 7.50 (1H, dd, *J*=3, 5 Hz). $^{13}$C-NMR: 23.8 (q), 31.2 (t), 31.38 (q), 31.41 (q), 34.6 (d), 35.5 (s), 35.6 (s), 55.2 (q), 111.5 (d), 111.6 (d), 126.1 (d), 126.8 (d), 127.8 (d), 128.0 (d), 132.0 (s), 135.5 (s), 139.0 (d), 140.5 (s), 141.8 (s), 143.6 (s), 143.9 (s), 156.2 (s), 166.3 (s). IR (KBr): 1723, 1588 cm$^{-1}$. MS *m/z*: 406 ($M^+$), 236. Anal. Calcd. for $C_{27}H_{34}O_3$ 1/4$H_2O$: C, 78.89; H, 8.46. Found: C, 79.02, H, 8.54.

**2,6-Bis(*tert*-butyl)-4-methoxyphenyl 1-butyl-1,2-dihydro-2-naphthalenecarboxylate (11b) and 2,6-bis(*tert*-butyl)-4-methoxyphenyl 1-butyl-1,4-dihydro-2-naphthalenecarboxylate (10b).** To a solution of **9** (391 mg, 1.0 mmol) in THF (10 mL) at –78 °C was added a hexane solution of butyllithium (0.8 mL, 1.3 mmol). After stirring for 0.5 h at –78 °C, the mixture was quenched with TFA (0.8 mL). The workup as above and chromatography (hexane/ether, 50/1) gave **11b** (85 mg, 19%) as amorphous and **10b** (364 mg, 81%) as amorphous.

**11b**: $^1$H-NMR: 0.6-1.9 (9H, m), 1.32 and 1.35 (each 9H, s), 3.17 (1H, m), 3.80 (3H, s), 3.96 (1H, m), 6.45 (1H, ddd, $J$=1, 2.5, 10 Hz), 6.64 (1H, dd, $J$=2.5, 10 Hz), 6.88 (2H, s), 7.0-7.5 (4H, m). $^{13}$C-NMR: 13.9 (q), 22.7 (t), 28.1 (t), 29.5 (t), 31.2 (q), 31.4 (q), 35.5(s), 35.6 (s), 39.6 (d), 47.2 (d), 55.2 (q), 111.68 (d), 111.74 (d), 124.3 (d), 126.6 (d), 126.7, 126.9, 128.3 129.1, 132.7 (s), 138.5 (s), 141.8 (s), 143.4 (s), 143.5 (s), 156.3 (s), 172.4 (s). IR (neat): 1760, 1600 cm$^{-1}$. MS *m/z*: 448 ($M^+$), 433 ($M^+$-Me), 236. Anal. Calcd. for $C_{30}H_{40}O_3$: C, 80.31; H, 8.99. Found: C, 80.20, H, 9.00.

**10b**: $^1$H-NMR: 0.78 (3H, t, $J$=7 Hz), 1.02-1.55 (4H, m), 1.27 and 1.36 (each 9H, s), 1.75 (2H, m), 3.62 (1H, ddd, $J$=2, 6, 22 Hz), 3.72 (1H, ddd, $J$=3, 3, 22 Hz), 3.81 (3H, s), 4.07 (1H, br), 6.87 and, 6.89 (each 1H, d, $J$=3 Hz), 7.19 -7.26 (4H, m), 7.58 (1H, dd, $J$=2, 6 Hz). $^{13}$C-NMR: 14.0 (q), 22.6 (t), 27.1 (t), 31.38 (q), 31.43 (q), 31.7 (t), 35.5 (s), 35.6 (s), 36.2 (t), 39.5 (d), 55.2 (q), 111.56 (d), 111.62 (d), 126.0 (d), 126.4 (d), 127.6 (d), 128.4 (d), 133.1 (s), 134.2 (s), 138.8 (s), 140.1 (d), 141.8 (s), 143.5 (s), 143.9(s), 156.2 (s), 166.3 (s). IR (KBr): 1730, 1590 cm$^{-1}$. MS *m/z*: 448 ($M^+$), 433, 236. Anal. Calcd. for $C_{30}H_{40}O_3$: C, 80.31; H, 8.99. Found: C, 80.11, H, 8.98.

**2,6-Bis(*tert*-butyl)-4-methoxyphenyl 1-phenyl-1,2-dihydro-2-naphthalenecarboxylate (11d) and 2,6-bis(*tert*-butyl)-4-methoxyphenyl 1-phenyl-1,4-dihydro-2-naphthalenecarboxylate (10d)**. Prepared by the same procedure for **10b** and **11b**. Chromatography (hexane/acetone/chloroform, 200/6/3) gave **10d** (67%) as colorless needles of mp 127-127.5 °C (EtOH) and **11b** (33%) as colorless prisms of mp 132-133 °C (EtOH).

**11d**: $^1$H-NMR: 0.90 and 1.28 (each 9H, s), 3.76 (3H, s), 4.21-4.38 (1H, m), 4.67 (1H, brd, $J$=3 Hz), 6.65 (1H, ddd, $J$=1, 2, 10 Hz), 6.72-6.89 (3H, m), 7.0-7.5 (9H, m). IR (KBr): 1753 cm$^{-1}$. MS *m/z*: 468 ($M^+$), 453. Anal. Calcd. for $C_{32}H_{36}O_3$: C, 82.01; H, 7.74. Found: C, 81.73, H, 7.74.

**10d**: $^1$H-NMR: 0.99 and 1.26 (each 9H, s), 3.76 (3H, s), 3.92 (2H, m), 5.22 (1H, t, $J$=3 Hz), 6.78 and 6.83 (each 1H, d, $J$=3 Hz), 7.0-7.4 (9H, m), 7.60 (1H, dd, $J$=3, 5 Hz). $^{13}$C-NMR: 31.0 (q), 31.4 (q), 31.6 (t), 35.2 (s), 35.6 (s), 45.6, 55.2 (q), 111.5 (d), 126.3 (d), 126.4 (d), 127.1 (d), 128.0 (d), 128.2 (d), 128.6 (d), 129.5 (d), 131.3 (s), 133.9 (s), 138.1 (s), 138.3 (d), 143.6 (s), 143.7 (s), 144.6 (s), 156.1 (s), 166.0 (s). IR (KBr): 1722, 1590 cm$^{-1}$. MS *m/z*: 468 ($M^+$). Anal. Calcd. for $C_{32}H_{36}O_3$ 1/5$H_2O$: C, 81.39; H, 7.77. Found: C, 81.21, H, 7.82.

**2,6-Bis(*tert*-butyl)-4-methoxyphenyl 1-naphthalenyl-1,2-dihydro-2-naphthalenecarboxylate (11e) and 2,6-bis(*tert*-butyl)-4-methoxyphenyl 1-naphthalenyl-1,4-dihydro-2-naphthalenecarboxylate (10e)**. Prepared by the same procedure for **10b** and **11b**. Chromatography (hexane/acetone, 80/1) gave **11e** (28%) as amorphous and **10e** (55%) as colorless prisms of mp 220-220.5 °C (AcOEt/EtOH).

**10e**: $^1$H-NMR: 0.82 and 1.23 (9H, s), 3.70 (3H, s), 3.93 and 4.17 (each 1H, ddd, $J$=5, 5, 24 Hz), 6.10 (1H, brs), 6.67 and 6.77 (1H, d, $J$=3 Hz), 7.03 (1H, dd, $J$=7, 7 Hz), 7.15 (1H, ddd, $J$=7, 7, 7 Hz), 7.20 (1H, d, $J$=8 Hz), 7.27 (4H, m), 7.41 and 7.52 (each 1H, dd, $J$=7, 7 Hz), 7.62 (1H, dd, $J$=4, 4 Hz), 7.71 (1H, dd, $J$=2, 5 Hz), 7.76 (1H, d, $J$=8 Hz), 8.56 (1H, br). $^{13}$C-NMR: 30.9 (q), 31.3 (q), 31.5 (t), 35.1 (s), 35.5 (s), 39.8 (d), 55.2 (q), 111.4 (d), 124.3 (d), 125.2 (d), 125.3 (d), 126.1 (d), 126.4 (d), 127.0(d), 128.2 (d), 128.5 (d), 128.7 (d), 130.4 (s), 131.6 (s), 134.1 (s), 138.6 (s), 141.6 (s), 143.64 (s), 156.0 (s), 166.1 (s). IR (KBr): 1717, 1590 cm$^{-1}$. MS *m/z*: 518 ($M^+$), 503 ($M^+$-Me). Anal. Calcd. for $C_{36}H_{38}O_3$: C, 83.36; H, 7.39. Found: C, 83.38, H, 7.39.

**11e**: $^1$H-NMR: 0.77 and 1.19 (each 9H, s), 3.69 (3H, s), 4.55 (1H, ddd, $J$=3, 3, 7 Hz), 5.67 (1H, d, $J$=7 Hz), 6.65 and 6.75 (each 1H, d, $J$=3 Hz), 6.79 and 6.88 (1H, dd, $J$=3, 10 Hz), 7.06 (1H, m), 7.17-7.26 (4H, m), 7.40 (1H, m), 7.53 (1H, m), 7.62 and 7.73 (each 1H, d, $J$=8 Hz), 7.92 (1H, dd, $J$=6, 7 Hz), 8.62 (1H, d, $J$=8 Hz). $^{13}$C-NMR: 30.9 (q), 31.3 (q), 35.1 (s), 35.3 (s), 37.2 (d), 48.2 (d), 55.1 (q), 111.5 (d), 111.6 (d),

124.1 (d), 124.3 (d), 125.0 (d), 125.2 (d), 126.0 (d), 126.6 (d), 127.1(d), 127.5 (d), 127.6 (d), 128.1 (d), 128.2 (d), 128.4 (d), 130.5 (d), 131.8 (s), 132.4 (s), 134.0 (s), 137.6 (s), 139.4 (s), 141.5 (s), 143.1 (s), 143.7 (s), 156.1 (s), 170.6 (s). IR (KBr): 1745, 1590 $cm^{-1}$. MS *m/z*: 518 ($M^+$), 503 ($M^+$-Me). Anal. Calcd. for $C_{36}H_{38}O_3$: C, 83.36; H, 7.39. Found: C, 83.14, H, 7.40.

***trans*-2-Methyl-1,2-dihydro-1-naphthalenylmethanol (20a).**[1] Prepared under the same conditions for trans-**20b** using methyllithium. Chromatography (hexane/ether, 5/1) gave trans-**20a** (71%). $^1$H-NMR: 0.95 (3H, d, *J*=7 Hz, Me), 1.55 (1H, brs, OH), 2.3-2.9 (2H, m, CH), 3.53 (2H, brd, $CH_2O$), 5.85 (1H, dd, *J*=5, 10 Hz, olefin), 6.35 (1H, d, *J*=10 Hz), 6.8-7.4 (4H, m). IR (neat): 3350, 1485, 1450 $cm^{-1}$. MS *m/z*: 174 ($M^+$).

***trans*-2-Butyl-1,2-dihydro-1-naphthalenylmethanol (20b) (reduction by super hydride and isomerization).**[1] To a solution of **1** (391 mg, 1.0 mmol) in THF (10 mL) at –78 °C was added a hexane solution of butyllithium (0.8 mL, 1.2 mmol). After stirring for 40 min at –78 °C, a THF solution of $LiEt_3BH$ (3 mL, 3 mmol) was added dropwise to the yellow green solution. After refluxing for 1.5 h, to the mixture was added methanol (5 mL) dropwise (a gas evolution was observed.) at –50 °C. The mixture was stirred for 1 h at rt. Then, $NaBH_4$ (0.38 g, 10 mmol) was added at –50 °C. The mixture was allowed to warm up to rt, and then 10% HCl (50 mL) was added slowly. The mixture was extracted with benzene. Concentration and chromatography (hexane/ether, 5/1) gave trans-**20b** (175 mg, 81%) as a pale yellow oil. $^1$H-NMR: 0.8-0.9 (3H, m), 1.2-1.6 (7H, m), 2.82 (1H, t, *J*=8 Hz), 3.5-3.6 (2H, m), 5.96 (1H, dd, *J*=8, 12 Hz), 6.37 (1H, d, *J*=8 Hz), 7.0-7.4 (4H, m). $^{13}$C-NMR: 14.0 (q), 22.7 (t), 29.1 (t), 33.6 (t), 35.1 (d), 45.9 (d), 65.3 (t), 125.3 (d, 2 carbons), 126.0 (d), 126.8 (d), 129.2 (d), 131.3 (d), 132.7 (s), 134.1 (s). IR (neat) 3350, 1450 $cm^{-1}$. HRMS *m/z*: Calcd. for $C_{15}H_{20}O$: 216.1515. Found 216.1560.

cis-**20b**: Colorless needles of mp 51-52 °C (hexane). $^1$H-NMR: 0.7-2.0 (10H, m), 2.4-3.0 (2H, m), 3.75 (2H, brd, *J*=7 Hz), 5.79 (1H, dd, *J*=2, 10 Hz), 6.42 (1H, dd, *J*=3, 10 Hz), 6.9-7.5 (4H, m). $^{13}$C-NMR: 14.1 (q), 22.7 (t), 29.6 (t), 30.2 (t), 36.5 (d), 43.8 (d), 60.9 (t), 126.3 (d), 126.9 (d x 2), 127.3 (d), 128.5 (d), 132.9 (d), 133.9 (s), 136.5 (s). IR (KBr): 3280, 1450 $cm^{-1}$. MS *m/z*: 216 ($M^+$). Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.21, H, 9.38.

***trans*-1,2-Dihydro-2-vinyl-1-naphthalenylmethanol (20c).** To a solution of **1** (391 mg, 1.0 mmol) and tetravinyltin (0.07 mL, 0.4 mmol) in THF (10 mL) at –45 °C was added an ether solution of methyllithium (0.9 mL, 1.2 mmol, low halide). After stirring for 0.8 h at –45 °C and for 2 h at –23 °C, a THF solution of $LiEt_3BH$ (4 mL, 4 mmol) was added dropwise. The same treatment with that for **20b** and chromatography (hexane/ether, 4/1) gave **20c** (114 mg, 61%) as a pale yellow oil. $^1$H-NMR: 1.47 (1H, s, OH), 2.84-3.20 (2H, m), 3.65 (2H, m), 4.91 (1H, ddd, *J*=1, 2, 10 Hz), 5.06 (1H, ddd, *J*=1, 2, 18 Hz), 5.73 (1H, ddd, *J*=7, 10, 18 Hz), 5.85 (1H, ddd, *J*=1, 6, 9 Hz), 6.48 (1H, d, *J*=9 Hz), 6.8-7.3 (4H, m). $^{13}$C-NMR: 39.2 (d), 46.1 (d), 64.8 (t), 114.5 (t), 126.4 (d), 126.7 (d), 127.2 (d), 127.3 (d), 128.2 (d), 129.1 (d), 132.9 (s), 133.7 (s), 138.4 (d). IR (KBr): 3360, 1635, 1490, 1450 $cm^{-1}$. MS *m/z*: 186 ($M^+$), 168 ($M^+$-$H_2O$). HRMS *m/z*: Calcd. for $C_{13}H_{14}O$: 186.1044. Found: 186.1061.

***trans*-2-Phenyl-1,2-dihydro-1-naphthalenylmethanol (20d).**[1] Prepared under the same conditions for **20b** using phenyllithium. Chromatography (hexane/ether, 10/1-4/1-3/1) gave **20d** (85%) as a pale yellow oil. IR (neat): 3260, 1600, 1490 $cm^{-1}$. $^1$H-NMR: 1.56 (1H, s), 3.08 (1H, brt, *J*=7 Hz), 3.6-3.9 (3H, m), 5.99 (1H, ddd, *J*=1, 6, 10 Hz), 6.61 (1H, d, *J*=10 Hz), 7.0-7.2 (9H, m). $^{13}$C-NMR: 41.3 (d), 48.6 (d), 65.7 (t), 126.3 (d), 126.8(d), 127.1 (d), 127.3 (d), 127.4 (d), 128.3 (d), 128.9 (d), 129.0 (d), 132.9 (s), 133.2 (s), 142.6 (s). HRMS *m/z*: Calcd for $C_{17}H_{16}O$: 236.1202. Found 236.1182.

***trans*-2-(1-Naphthalenyl)-1,2-dihydro-1-naphthalenylmethenol (20e).** Prepared under the same conditions for **20b** using 1-naphthalenyllithium, generated from 1-bromonaphthalene and butyllithium in

ether. Chromatography (hexane/ether, 15/1) gave **20e** (72%) as colorless needles of mp 88-89 °C (ether/hexane). $^1$H-NMR: 1.62 (1H, s, OH), 3.25 (1H, dd, *J*=7, 7 Hz), 3.80 and 3.91 (each 1H, dd, *J*=7, 11 Hz), 4.73 (1H, d, *J*=6 Hz), 6.05 (1H, dd, *J*=6, 10 Hz), 6.77 (1H, d, *J*=10 Hz), 6.8-8.4 (11H, m). $^{13}$C-NMR: 35.8 (d), 47.7 (d), 66.0 (t), 123.3 (d), 125.0 (d), 125.3 (d), 125.4 (d), 126.0 (d), 126.5 (d), 127.1 (d), 127.2 (d), 127.5 (d), 128.1 (d), 128.6 (d), 128.9 (d), 129.3 (d), 131.0 (s), 132.8 (s), 133.5 (s), 134.2 (s), 136.9 (s). IR (KBr): 3300, 1590 cm$^{-1}$. MS *m/z*: 286 ($M^+$), 268 ($M^+$-OH), 255 ($M^+$-$CH_2OH$). Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.81, H, 6.38.

**(1*RS*,2*RS*)-1,2-Dimethyl-1,2-dihydro-1-naphthalenylmethanol (13a).**[3b] To a solution of **1** (391 mg, 1.0 mmol) in THF (10 mL) at –23 °C was added an ether solution of methyllithium (1.2 mL, 1.5 mmol, LiBr complex). After stirring for 1 h at –23 °C, a THF solution of $LiEt_3BH$ (3 mL, 3 mmol) was added dropwise. After refluxing for 5 h, HMPA (3.5 mL, 20 mmol) and methyl iodide (1.25 mL, 20 mmol) were added and the mixture was stirred for 11 h at rt. Then, methanol (5 mL) and $NaBH_4$ (0.20 g) was added at 0 °C. The mixture was stirred for 0.5 h at 0 °C, and then 10% HCl was added slowly. The mixture was extracted with benzene. Chromatography (hexane/ether, 5/1) gave **13a** (104 mg, 55%) as a pale yellow oil. $^1$H-NMR: 1.09 (3H, d, *J*=7 Hz), 1.30 (1H, s, OH), 1.36 (3H, s), 3.64 and 3.88 (each 1H, d, *J*=11 Hz), 5.80 (1H, dd, *J*=4, 10 Hz), 6.39 (1H, dd, *J*=2, 10 Hz), 6.96-7.33 (4H, m). $^{13}$C-NMR: 14.4 (q), 21.9 (q), 37.0 (d), 41.2 (s), 65.9 (t), 125.5 (d), 126.0 (d), 126.5 (d), 126.6 (d), 127.3 (d), 133.2 (s), 134.0 (d), 139.7 (s). IR (KBr): 3440, 1485, 1450 cm$^{-1}$. MS *m/z*: 188 ($M^+$), 157 ($M^+$-$CH_2OH$). HRMS *m/z*: Calcd. for $C_{14}H_{16}O$: 188.1200. Found: 188.1216.

**(1*RS*,2*RS*)-2-Butyl-1-methyl-1,2-dihydro-1-naphthalenylmethanol (13b).** Prepared under the same conditions for **13a** using butyllithium. Chromatography (hexane/ether, 5/1) gave **13b** (75%) as a pale yellow oil. $^1$H-NMR: 0.6-1.8 (10H, m), 1.36 (3H, s), 2.22 (1H, m), 3.61 and 3.88 (each 1H, d, *J*=11 Hz), 5.94 (1H, dd, *J*=4, 10 Hz), 6.43 (1H, dd, *J*=2, 10 Hz), 6.9-7.3 (4H, m). $^{13}$C-NMR: 14.1 (q), 22.0 (q), 22.8 (t), 28.3 (t), 30.0 (t), 41.6 (s), 42.1 (d), 66.1 (t), 125.4 (d), 126.5 (d), 126.6 (d), 126.7 (d), 127.3 (d), 132.1 (d), 133.4 (s), 140.0 (s). IR (KBr): 3450, 1500, 1035 cm$^{-1}$. MS *m/z*: 230 ($M^+$), 212 ($M^+$-$H_2O$). HRMS *m/z*: Calcd. for $C_{16}H_{22}O$: 230.1670. Found: 230.1655.

**(1*RS*,2*RS*)-1-Benzyl-2-butyl-1,2-dihydro-1-naphthalenylmethanol (13bb).** Prepared under the same conditions for **13b** using benzyl bromide. Chromatography (hexane/ether, 10/1-5/1-4/1) gave **13bb** (53%) as a pale yellow oil. $^1$H-NMR: 0.73-1.68 (10H, m), 2.40 and 3.15 (each 1H, d, *J*=13 Hz), 3.85 and 4.01 (each 1H, d, *J*=11), 6.22 (1H, dd, *J*=6, 10 Hz), 6.4-7.4 (10H, m). $^{13}$C-NMR: 14.1 (q), 23.1 (t), 29.0 (t), 29.6 (t), 39.5 (d), 40.0 (t), 45.3 (s), 62.6 (t), 125.8 (d), 126.3 (d), 126.4 (d), 126.5 (d), 126.6 (d), 127.4 (d), 130.6 (d), 132.5 (d), 133.2 (, s), 137.7 (s), 138.3 (s). IR (KBr): 3500, 1600, 1495, 1455 cm$^{-1}$. MS *m/z*: 306 ($M^+$). HRMS *m/z*: Calcd. for $C_{22}H_{26}O$: 306.1982. Found: 306.1992.

**(1*RS*,2*RS*)-1-Methyl-2-vinyl-1,2-dihydro-1-naphthalenylmethanol (13c).** Prepared under the same conditions for **13b**. Chromatography (hexane/ether, 5/1) gave **13c** (42%) as a pale yellow oil. $^1$H-NMR: 1.31 (3H, s), 1.52 (1H, s, OH), 3.00 (1H, dd, *J*=4, 8 Hz), 3.77 and 3.90 (each 1H, d, *J*=11 Hz), 5.08 (1H, dd, *J*=2, 7 Hz), 5.21 (1H, dd, *J*=2, 14 Hz), 5.63-5.99 (2H, m), 6.45 (1H, dd, *J*=1, 9 Hz), 6.9-7.3 (4H, m). $^{13}$C-NMR: 22.8 (q), 41.6 (s), 48.6 (d), 67.1 (t), 116.8 (t), 125.2 (d), 126.7 (d), 126.86 (d), 126.92 (d), 127.7 (d), 129.5 (d), 133.0 (s), 137.5 (d), 139.5 (s). IR (KBr): 3450, 1630, 1480, 1450 cm$^{-1}$. MS *m/z*: 200 ($M^+$), 182 ($M^+$-$H_2O$). HRMS *m/z*: Calcd. for $C_{14}H_{16}O$: 200.1200. Found: 200.1197.

**(1*RS*,2*SR*)-1-Methyl-2-phenyl-1,2-dihydro-1-naphthalenylmethanol (13d).** Prepared under the same conditions for **13b**. Chromatography (hexane/ether, 10/1-5/1) gave **13d** (65%) as colorless needles of mp 101-102 °C (hexane). $^1$H-NMR: 1.13 (1H, br, OH), 1.37 (3H, s), 3.50 and 3.90 (each 1H, d, *J*=11 Hz), 3.63 (1H,

dd, *J*=2, 4 Hz), 6.05 (1H, dd, *J*=4, 10 Hz), 6.57 (1H, dd, *J*=2, 10 Hz), 7.09-7.42 (9H, m). $^{13}$C-NMR: 24.2 (q), 42.7 (s), 50.6 (d), 66.6 (t), 125.5 (d), 126.8 (d x 4), 127.8 (d), 128.2 (d), 129.1 (d), 131.6 (d), 133.2 (s), 139.3 (s), 140.2 (s). IR (KBr): 3200, 1450 cm$^{-1}$. MS *m/z*: 250 ($M^+$), 233 ($M^+$-OH). Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.38, H, 7.24.

**(1*RS*,2*RS*)-2-Butyl-1-methyl-1,2-dihydro-1-naphthalenecarbaldehyde (12b).** A solution of **13b** (86 mg, 0.37 mmol) in $CH_2Cl_2$ (0.5 mL) was added to a suspension of PCC (120 mg 0.56 mmol) in $CH_2Cl_2$ (1 mL). After stirring for 2.5 h at rt, the mixture was diluted with ether and decanted. Concentration and chromatography (hexane/ether, 60/1) gave **12b** (40 mg, 47%) as a colorless oil. $^1$H-NMR: 0.93-2.00 (9H, m), 1.63 (3H, s), 2.58-2.86 (1H, m), 6.19, (1H, dd, *J*=4, 10 Hz), 6.69 (1H, dd, *J*=2, 10 Hz), 7.22-7.61 (4H, m), 9.80 (1H, s). IR (KBr): 1720, 1480, 1470, 1440 cm$^{-1}$. MS *m/z*: 228 ($M^+$), 199 ($M^+$-CHO). HRMS *m/z*: Calcd for $C_{16}H_{20}O$; 228.1513. Found: 228.1515.

**(1*RS*,2*RS*)-1-Methyl-2-vinyl-1,2-dihydro-1-naphthalenecarbaldehyde (12c).**[1] Oxidized as above for **12b**. Chromatography (hexane/ether, 60/1) gave **12c** (38%) as a colorless oil. $^1$H-NMR: 1.31 (3H, s), 3.14 (1H, ddd, *J*=2, 4, 9 Hz), 5.16 (1H, dd, *J*=1, 17 Hz), 5.25 (1H, dd, *J*=1, 9 Hz), 5.83 (1H, m), 5.86 (1H, dd, *J*=4, 10 Hz), 6.51 (1H, dd, *J*=2, 10 Hz), 6.99-7.33 (4H, m), 9.78 (1H, s). IR (KBr): 1720, 1640, 1490, 1450 cm$^{-1}$. MS *m/z*: 200 ($M^+$+2), 199 ($M^+$+1), 198 ($M^+$).

**(1*RS*,2*RS*)-1,2-Dimethyl-1,2-dihydro-2-naphthalenylmethanol (15a).** Prepared from **9** under the same conditions for **13b**. Chromatography (hexane/ether, 30/1-5/1) gave **15a** (45%) as a pale yellow oil. $^1$H-NMR: 1.06 (3H, s), 1.16 (3H, d, *J*=7 Hz), 1.50 (1H, s, OH), 2.80 (1H, q, *J*=7 Hz), 3.58 and 3.65 (each 1H, d, *J*=11 Hz), 5.62 and 6.45 (each 1H, d, *J*=10 Hz), 6.95-7.30 (4H, m). $^{13}$C-NMR: 15.7 (q), 22.2 (q), 39.9 (s), 40.7 (d), 67.6 (t), 126.1 (d), 126.2 (d), 126.6 (d), 127.2 (d), 127.6 (d), 132.2 (s), 133.0 (d), 140.5 (s). IR ($CHCl_3$): 3440, 1490, 1455 cm$^{-1}$. MS *m/z*: 189 ($M^+$+1), 188 ($M^+$), 171 ($M^+$-OH). HRMS *m/z*: Calcd. for $C_{13}H_{16}O$: 188.1200. Found: 188.1175.

**(1*RS*,2*SR*)-1-Butyl-2-methyl-1,2-dihydro-2-naphthalenylmethanol (15b).** Prepared under the same conditions for **13b**. Chromatography (hexane/ether, 10/1-3/1) gave **15b** (93%) as a pale yellow oil. $^1$H-NMR: 0.69-1.67 (10H, m), 1.00 (3H, s), 2.53 (1H, ddd, *J*=1, 5, 9 Hz), 3.59 and 3.83 (each 1H, d, *J*=11 Hz), 5.59 (1H, dd, *J*=1, 10 Hz), 6.40 (1H, dd, *J*=10 Hz), 6.96-7.23 (4H, m). $^{13}$C-NMR: 14.1 (q), 21.8 (q), 23.2 (t), 28.5 (t), 30.2 (t), 40.3 (s), 46.1 (d), 67.7 (t), 126.2 (d x 4), 129.3 (d), 132.4 (s), 133.0 (d), 138.0 (s). IR (KBr): 3400, 1480, 1460, 1450 cm$^{-1}$. MS *m/z*: 230 ($M^+$), 199 ($M^+$-$CH_2OH$). Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.13, H, 9.71.

**(1*RS*,2*SR*)-2-Methyl-1-vinyl-1,2-dihydro-2-naphthalenylmethanol (15c).** Prepared under the same conditions for **13b**. Chromatography (hexane/ether, 10/1-3/1) gave **15c** (52%) as a colorless oil. $^1$H-NMR: 1.05 (3H, s), 1.52 (1H, s, OH), 3.30 (1H, d, *J*=10 Hz), 3.56 and 3.58 (each 1H, d, *J*=11 Hz), 5.07 (1H, dd, *J*=2, 10 Hz), 5.18 (1H, dd, *J*=2, 16 Hz), 5.67 (1H, d, *J*=10 Hz), 5.99 (1H, ddd, *J*=10, 10, 16 Hz), 6.48 (1H, dd, *J*=10 Hz), 6.98-7.28 (4H, m). $^{13}$C-NMR: 21.9 (q), 40.2 (s), 52.8 (d), 68.2 (t), 116.1 (t), 126.2 (d), 126.8 (d), 126.9 (d), 127.8 (d), 128.1 (d), 132.2 (s), 133.3 (d), 136.5 (s), 138.1 (d). IR (KBr): 3400, 1630, 1480, 1450 cm$^{-1}$. MS *m/z*: 200 ($M^+$), 183 ($M^+$-OH), 169 ($M^+$-$CH_2OH$). HRMS *m/z*: Calcd. for $C_{14}H_{16}O$: 200.1200. Found: 200.1265.

**(1*RS*,2*SR*)-2-Methyl-1-phenyl-1,2-dihydro-2-naphthalenylmethanol (15d).** Prepared under the same conditions for **13b**. Chromatography (hexane/ether, 4/1) gave **15d** (66%) as colorless prisms of mp 94.5-95.0 °C (hexane). $^1$H-NMR: 1.14 (3H, s), 1.28 (1H, brs, OH), 3.38 (2H, d, *J*=2 Hz), 3.92 (1H, s), 5.76 and 6.60 (each 1H, d, *J*=10 Hz), 6.89-7.34 (9H, m). $^{13}$C-NMR: 23.7 (q), 41.6 (s), 53.6 (d), 68.2 (t), 126.5 (d), 126.7 (d), 126.8 (d), 127.5 (d), 127.8 (d), 128.4 (d), 129.0 (d), 129.1 (d), 132.5 (s), 133.5 (d), 137.7 (s), 140.9 (s). IR

(KBr): 3300, 1485, 1445 $cm^{-1}$. MS *m/z*: 250 ($M^+$), 233 ($M^+$-OH). Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.41, H, 7.26.

**(1*RS*,2*RS*)-2-Methyl-1-(1-naphthalenyl)-1,2-dihydro-2-naphthalenylmethanol (15e).** Prepared under the same conditions for **13b**. Chromatography (hexane/ether, 5/1) gave **15e (65%) as amorphous.** $^1$H-NMR: 0.87 (1H, brs, OH), 1.26 (3H, s), 3.31 (2H, brs), 4.98 (1H. s), 5.83 and 6.67 (each 1H, d, *J*=9 Hz), 6.92-7.86 (10H, m), 8.41 (1H, d, *J*=9 Hz). $^{13}$C-NMR: 24.3 (q), 42.5 (s), 45.3 (d), 68.3 (t), 123.1 (d), 125.3 (d), 125.5 (d), 126.3 (d), 126.7 (d x 2), 127.2 (d), 127.3 (d), 127.4 (d), 127.8 (d), 129.2 (d), 131.8 (s), 132.6 (s), 133.5 (s), 134.0 (s). IR ($CHCl_3$): 3400, 1590 $cm^{-1}$. MS *m/z*: 300 ($M^+$), 282 ($M^+$-$H_2O$), 296 ($M^+$-$CH_2OH$). Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.68, H, 6.83.

**(1*RS*,2*SR*)-2-Methyl-1-phenyl-1,2-dihydro-2-naphthalenecarbaldehyde (14a).**[1] Oxidized as above for **12b**. Chromatography (hexane/ether, 60/1) gave **14a** (84%) as a colorless solid of mp 72-76 °C. $^1$H-NMR: 1.20 (3H, s), 4.27 (1H, s), 5.94 and 6.75 (1H, d, *J*=10 Hz), 6.86-7.38 (9H, m), 9.60 (1H, s). IR ($CHCl_3$): 1730, 1600 $cm^{-1}$. MS *m/z*: 248 ($M^+$), 233 ($M^+$-Me), 219 ($M^+$-CHO).

**(1*RS*,2*SR*)-1-Butyl-2-methyl-1,2-dihydro-2-naphthalenecarbaldehyde (14b).**[1] Oxidized as above for **12b**. Chromatography (hexane/ether, 20/1) gave **14b** (71%) as a colorless oil. $^1$H-NMR: 0.60-2.00 (9H, m) 1.08 (3H, s), 2.60-3.00 (1H, m), 6.20 and 6.50 (each 1H, d, *J*=9 Hz), 7.0-7.5 (4H, m), 9.65 (1H, s). IR (neat): 1730, 1450 $cm^{-1}$. MS *m/z*: 228 ($M^+$), 213 ($M^+$-Me). Data are identical with those reported.

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