Synthesis of 1,2-Disubstituted Naphthalenes and Tetrahydronaphthalenes from Dihydronaphthalenes Obtained by Conjugate Addition of Organolithium Reagents to 2,6-Bis(*tert*-butyl)-4-methoxyphenyl Naphthalenecarboxylates

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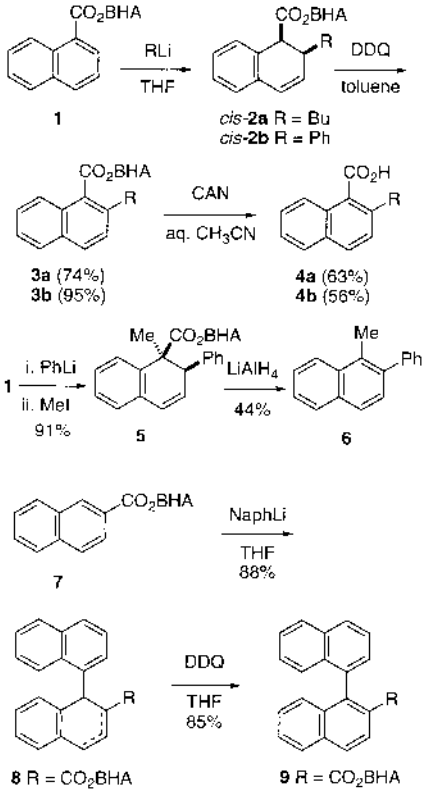
Received April 9, 1999; accepted June 10, 1999

A method of the conversion of 2,6-bis(*tert*-butyl)-4-methoxyphenyl dihydronaphthalenecarboxylates into substituted naphthalenes and tetrahydronaphthalenes was developed. Aromatization of substituted dihydronaphthalenecarboxylates with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and subsequent treatment with ceric ammonium nitrate (CAN) gave the corresponding substituted naphthalenecarboxylic acids. Alternatively, hydrogenolysis and subsequent treatment with CAN provided a way to tetrahydronaphthalenemethanols in good yields.

Key words addition reaction; naphthalene; ester; alkylation; oxidation; hydrogenolysis

Efficient construction of a carbon skeleton has been one of the challenging targets of synthetic chemistry. Addition reaction of organometallics to a naphthalene nucleus provides the methodology for construction of dihydronaphthalenes that are useful starting materials for synthesis of biologically active cyclic molecules. Recent progress in the field has been developed by Meyers based on oxazoline[1] and imine[2] chemistry. Chromium carbonyl chemistry has been applied to the addition reaction of organolithiums with naphthalene.[3] Naphthalenecarboxylic acid has been shown to be a good substrate for a limited kind of organolithiums.[4] Intramolecular nucleophilic attack of lithiated moiety to naphthalene nucleus has also been reported.[5] We have been involved in the field and developed an efficient addition reaction of organolithiums to 2,6-bis(*tert*-butyl)-4-methoxyphenyl (BHA)[6] 1- and 2-naphthalenecarboxylates to afford 2- and 1-substituted dihydronaphthalenecarboxylates in high yields.[7] Having established that the BHA ester serves as the activating and directing group for reaction of naphthalenecarboxylates **1** and **7** with organolithium reagents, the next goal is the development of an efficient way for construction of requisite naphthalene skeletons bearing reasonably manipulatable functionality. One drawback of the reaction scheme, however, is the BHA group, against which nucleophilic attack is hard due to its bulkiness. Already we have developed a methodology for direct conversion of BHA dihydronaphthalenecarboxylates to the corresponding dihydronaphthalenecarboxaldehydes and alcohols through reductive generation of aldehyde enolate.[8] Our studies are directed toward general entry for all types of naphthalene derivatives such as aromatized, dihydro-, and tetrahydronaphthalenes. Therefore, synthesis of aromatized and tetrahydronaphthalenes from dihydronaphthalenes achieves this goal based on conjugate addition of organolithium reagent to naphthalene nucleus. We describe herein that BHA dihydronaphthalenecarboxylates serve as the starting materials for synthesis of disubstituted naphthalenes and tetrahydronaphthalenes through aromatization and hydrogenolysis as a key step of conversion.

1,2-Disubstituted Naphthalenes through Aromatization Aromatization of **2a**,**b** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing toluene gave the corresponding 2-substituted 1-naphthalenecarboxylates **3a**,**b** in 74 and 95% yields, respectively. Oxidative hydrolysis of **3a**,**b** with ceric ammonium nitrate (CAN)[9,10] in aqueous acetonitrile at room temperature smoothly afforded 2-substituted 1-naphthalenecarboxylic acids **4a**,**b** in 63 and 56% yields. Alternatively, concomitant aromatization and hydrolysis of BHA ester proceeded in a single operation by direct treatment of **2b** with CAN to afford the corresponding carboxylic acid. Subsequent methylation with diazomethane provided methyl ester of aromatized naphthalenecarboxylic acid **4b** in



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49% overall yield.

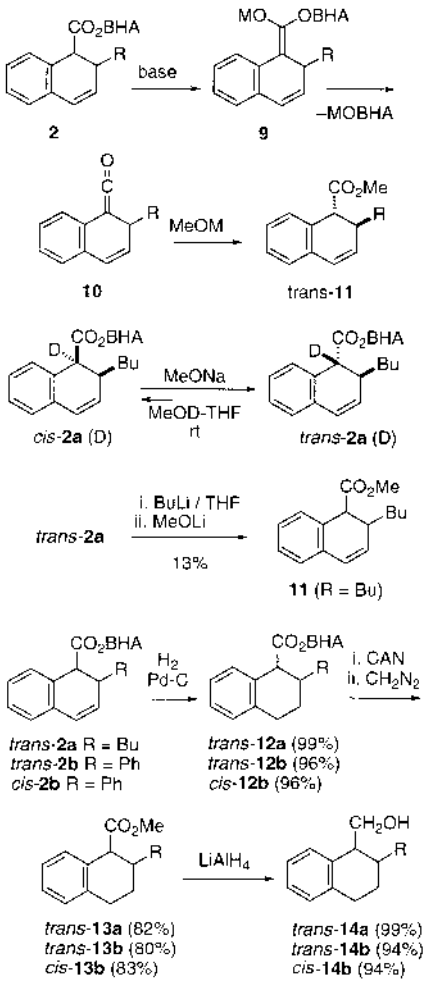
Oxidative removal of the BHA group of **5** bearing a quaternary carbon, obtained by the tandem dialkylation of **1** with phenyllithium and methyl iodide in 91% yield,[5] was unsuccessful and gave a mixture of many products. However, it is noteworthy that reductive treatment of **5** with lithium aluminium hydride in refluxing tetrahydrofuran (THF) gave **6** as a decarboxylated and aromatized product in 44% yield. The mechanistic aspect for production of **6** is unclear at the present time.

DDQ oxidation of 1-naphthalenyldihydronaphthalene **8**, obtained by reaction of 1-naphthyllithium with BHA 2-naphthalenecarboxylate **7** in 88% yield, provided biphenyl derivative **9** in 85% yield. It is interesting that this may open a synthetic way to optically active binaphthyl employing an asymmetric technique.[11]

1,2-Disubstituted 1,2,3,4-Tetrahydronaphthalenes through Hydrogenolysis Conversion of **2** into methyl ester of dihydronaphthalenecarboxylate **11** was attempted through a ketene **10**[12] generated from **9**.[13] Treatment of *cis*-**2a** with NaOMe in a mixture of MeOH and THF at room temperature afforded epimerized *trans*-**2a** in 87% yield. Deuterium incorporation at the C1 was observed in the epimerization starting from either *cis*- or *trans*-**2a** in MeOD. The observed epimerization indicates formation of **9** by deprotonation at the C1 position, assuring the possibility of the formation of ketene **10**. However, successive treatment of **2a** with butyllithium in THF and then lithium methoxide in refluxing THF gave the expected **11** in only 13% yield as the isolable dihydronaphthalenic compound.

After unsuccessful attempts to convert the BHA group of dihydronaphthalenes into other less sterically demanding esters without concomitant aromatization, hydrogenolysis prior to CAN treatment was found to solve the problem. Hydrogenolysis of **2a**,**b** gave the tetrahydronaphthalenecarboxylates **12a**,**b**. Treatment with CAN and subsequent methylation with diazomethane gave methyl ester **13a**,**b**. Reduction with $LiAlH_4$ gave the corresponding alcohols **14a**,**b** in high overall yields. Conversion of BHA dihydronaphthalenecarboxylate **2** to the alcohols **14** proceeded without epimerization to afford the corresponding stereoisomers as shown in the conversion of *cis*- and *trans*-**2b** to *cis*- and *trans*-**14**, respectively.

Conclusion Aromatization of substituted dihydronaphthalenecarboxylates with DDQ and subsequent treatment with CAN gave the corresponding substituted naphthalenecarboxylic acids. Alternatively, hydrogenolysis to tetrahydronaphthalenecarboxylates followed by CAN, and then $LiAlH_4$ treatments provided the way to tetrahydronaphthalenemethanols. It is also important to note that a chiral tetrahydronaphthalene has become available using an external chiral ligand-controlled asymmetric reaction which is our current focus.[14,15]



IR (KBr): 1730 cm^{-1}. MS *m/z*: 446 (M^+), 431 (M^+-Me). *Anal*. Calcd for $C_{30}H_{38}O_3$: C, 80.68; H, 8.58. Found: C, 80.60, H, 8.63.

2-Butyl-1-naphthalenecarboxylic Acid (4a) A solution of **3a** (15 mg, 0.034 mmol) and ceric ammonium nitrate (55 mg, 0.1 mmol) in a mixture of CH_3CN (0.2 ml) and water (0.1 ml) was stirred for 0.5 h at room temperature. After addition of mannitol and water, the mixture was poured onto 10% HCl, and diluted with ether. After usual workup, concentration and chromatography (benzene-ether, 2 : 1) gave **4a** (5 mg, 63%) as an oil. ^{1}H-NMR: 0.9—1.7 (7H, m), 2.93 (2H, m), 7.2—8.1 (7H, m). IR ($CHCl_3$): 1690 cm^{-1}. MS *m/z*: 228 (M^+). HRMS Calcd for $C_{15}H_{16}O_2$ *m/z*: 228.1150. Found: 228.1147.

2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-Phenyl-1-naphthalenecarboxylate (3b) Prepared under the same conditions as for **3a**. Chromatography (hexane–ether, 30 : 1) gave **3b** (106 mg, 95%) from *cis*-**2b** as colorless prisms of mp 135.5—136 °C (EtOH). ^{1}H-NMR: 1.17 (18H, s), 3.77 (3H, s), 6.85 (2H, s), 7.2—7.6 (8H, m), 7.7—8.0 (2H, m), 8.9—9.0 (1H, m). IR (KBr): 1720 cm^{-1}. MS *m/z*: 465 (M^+-1), 451 (M^+-Me). *Anal*. Calcd for $C_{32}H_{34}O_3$: C, 82.37; H, 7.34. Found: C, 82.35, H, 7.30.

2-Phenyl-1-naphthalenecarboxylic Acid (4b) Prepared under the same conditions as for **4a**. Chromatography (benzene–ether, 1 : 1) gave **4b** (56%) as an oil. ^{1}H-NMR: 6.7—8.3 (12H, m). IR ($CHCl_3$): 1690 cm^{-1}. MS *m/z*: 228 (M^+).

2,6-Bis(*tert*-butyl)-4-methoxyphenyl (1*RS*,2*RS*)-1-Methyl-2-phenyl-1,2-dihydro-1-naphthalenecarboxylate (5) To a solution of **1** (391 mg, 1.0 mmol) in THF (10 ml) at −78 °C was added a solution of phenyllithium (0.82 ml, 1.8 mmol). After stirring for 3.5 h at −45 °C, methyl iodide (0.3 ml, 5 mmol) and HMPA (0.9 ml, 5 mmol) were at −20 °C and the mixture was allowed to warm up to 0 °C over 1.5 h, diluted with ether, and washed with satd $NaHCO_3$, 10% $Na_2S_2O_3$, and brine. Concentration and chromatography (hexane–ether, 30 : 1) gave **5** (440 mg, 91%) as colorless needles of mp 129.5—130 °C (MeOH). ^{1}H-NMR: 0.75 and 0.91 (each 9H, s), 2.01 (3H, s), 3.72 (3H, s, OMe), 3.95 (1H, m), 6.39 (1H, dd, *J*=1, 9 Hz), 6.45 (1H, dd, *J*=2, 9 Hz), 6.72 (2H, s), 6.98—7.60 (9H, m). ^{13}C-NMR: 23.0

Experimental[16]

2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-Butyl-1-naphthalenecarboxylate (3a) A solution of *cis*-**2a**[5] (75 mg, 0.17 mmol) and DDQ (60 mg, 0.26 mmol) in toluene (3 ml) was refluxed for 2.5 h. The mixture was diluted with ether. After usual workup, concentration and chromatography (hexane–ether, 40 : 1) gave **3a** (55 mg, 74%) as colorless needles of mp 78—79 °C (EtOH). ^{1}H-NMR: 0.70—1.92 (25H, m), 3.19 (2H, m), 3.84 (3H, s, OMe), 6.97 (2H, s), 7.40—7.60 (3H, m), 7.70—8.11 (2 H, m), 8.95—9.12 (1H, m).

(q), 30.3 (q), 30.9 (q), 34.8 (s), 35.2 (s), 50.8 (s), 51.9 (d), 55.0 (q), 111.2 (d), 11.3 (d), 126.1 (d), 126.8 (d), 126.9 (d), 127.6 (d), 127.7 (d), 127.8 (d), 128.4 (d), 132.3 (d), 134.4 (d), 135.0 (s), 135.4 (s), 139.8 (s), 142.6 (s), 143.4 (s), 144.3 (s), 155.8 (s), 170.5 (s). IR (KBr): 1745 cm^{-1}. MS *m/z*: 482 (M^+), 467 (M^+-Me). *Anal*. Calcd for $C_{33}H_{38}O_3$: C, 82.12; H, 7.94. Found: C, 82.31; H, 7.99.

2,6-Bis(*tert*-butyl)-4-methoxyphenyl 1,1′-Binaphthalene-2-carboxylate (9) A mixture of **8**[5] (31 mg, 0.06 mmol, 1,2-/1,4-dihydro-, 4/3) and DDQ (17 mg, 0.07 mmol) in THF (1 ml) was stirred under reflux for 2 h, then diluted with benzene. After usual workup, concentration and chromatography (hexane–ether, 15/1) gave **9** (26 mg, 85 %) as colorless prisms of mp 214—215 °C (EtOH). ^{1}H-NMR: 1.19 and 1.28 (each 9H, s, *tert*-Bu), 3.70 (3H, s, OMe), 6.72 and 6.76 (each 1H, d, *J*=3 Hz), 7.07 (1H, d, *J*=8 Hz), 7.14 (1H, ddd, *J*=1, 7, 7 Hz), 7.22—7.30 (4H, m), 7.36 (1H, ddd, *J*=1, 7, 7 Hz), 7.48 (1H, m), 7.58 (each 1H, m), 7.85 (1H, dd, *J*=5, 8 Hz), 7.99 (1H, d, *J*=8 Hz), 8.13 (1H, d, *J*=9 Hz), 8.62 (1H, d, *J*=8 Hz). ^{13}C-NMR: 31.5 (q), 35.5 (q), 55.2 (q), 111.5 (d), 125.1 (d), 125.4 (d), 125.4 (d), 125.5 (d), 125.9 (d), 126.2 (d), 126.3 (d), 126.4 (d), 126.8 (d), 127.6 (d), 127.7 (d), 128.1 (d), 128.3 (d), 128.5 (d), 132.8 (s), 133.3 (s), 133.8 (s), 135.3 (s), 137.0 (s), 141.6 (s), 143.5 (s), 144.2 (s), 156.1 (s), 165.2 (s). IR (KBr): 1740 cm^{-1}. MS *m/z*: 516 (M^+), 501 (M^+-Me). *Anal*. Calcd for $C_{36}H_{36}O_3$: C, 83.69; H, 7.02. Found: C, 83.57, H, 6.94.

1-Methyl-2-phenylnaphthalene (6) Reduction of 5 with $LiAlH_4$ to **6**: A mixture of BHA 1-methyl-2-phenyldihydronaphthalenecarboxylate **5** (11 mg, 0.02 mmol) and $LiAlH_4$ (6 mg) in THF (0.5 ml) was stirred under reflux for 1 h, and then successively treated with water (0.01 ml), 15% NaOH (0.01 ml), and water (0.03 ml). Filtration, concentration, and chromatography (hexane) gave **6** (2.1 mg, 44%) as a colorless oil. ^{1}H-NMR: 2.61 (3H, s, Me), 7.22—8.14 (11H, m). IR ($CHCl_3$): 1590 cm^{-1}. MS *m/z*: 218 (M^+).

Epimerization of *cis*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-Butyl-1,2-dihydro-1-naphthalenecarboxylates (*cis*-2a) to *trans*-2a A mixture of *cis*-**2a**[5] (288 mg, 0.64 mmol) and sodium methoxide (3.2 mmol) in a mixture of MeOH (3 ml) and THF (2.5 ml) was stirred at room temperature for 1 h and quenched with satd. NH_4Cl. The mixture was extracted with ether. Concentration and chromatography (hexane–ether, 30 : 1) gave *trans*-**2a** (251 mg, 87%). ^{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, OMe), 3.83 (1H, br s), 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. *Anal*. Calcd for $C_{30}H_{40}O_3$: C, 80.31; H, 8.99. Found: C, 80.30; H, 9.01.

Methyl 2-Butyl-1,2-dihydronaphthalenecarboxylates (11) A hexane solution of butyllithium (1.1 ml, 1.7 mmol) was added to a solution of *trans*-**2a** (586 mg, 1.5 mmol) in dry THF (15 ml) at −78 °C. After stirring for 0.5 h at −78 °C, a solution of MeOLi (15 mmol)[17] was added. After refluxing for 4 h, the mixture was poured onto satd NH_4Cl and extracted with benzene. Concentration and chromatography (hexane–benzene, 2 : 1) gave **11** (48 mg, 13%) as a mixture of two stereoisomers: upper isomer (5%): ^{1}H-NMR: 0.7—1.9 (9H, m), 2.80 (1H, m, CHBu), 3.60 (3H, s, MeO), 3.75 (1H, d, *J*=6 Hz), 5.80 and 6.40 (each 1H, dd, *J*=2, 9 Hz), 6.9—7.3 (4H, m). IR (KBr): 1745 cm^{-1}. MS *m/z*: 244 (M^+); lower isomer (8%): ^{1}H-NMR: 0.6—1.9 (9H, m), 2.75 (1H, m, CHBu), 3.62 (3H, s, MeO), 3.84 (1H, m), 5.95 (1H, dd, *J*=5, 9 Hz, olefin), 6.40 (1H, d, *J*=9 Hz), 6.8—7.4 (4H, m). IR (KBr): 1745 cm^{-1}. MS *m/z*: 244 (M^+).

***trans*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-Butyl-1,2,3,4-tetrahydro-1-naphthalenecarboxylate (*trans*-12)** A mixture of *trans*-**2a** (171 mg, 0.38 mmol) and 10% Pd-C (50 mg) in AcOEt (2 ml) was stirred for 0.5 h under H_2. Usual workup and chromatography (hexane–ether, 2 : 5) gave *trans*-**12a** (170 mg, 99%) as an oil. ^{1}H-NMR: 0.60—1.80 (27H, m), 1.90—2.38 (2H, m), 2.40—2.80 (3H, m), 3.6—3.9 (1H, m), 3.77 (3H, s), 6.77 and 6.85 (each 1H, d, *J*=3 Hz), 6.9—7.5 (4H, m). ^{13}C-NMR: 14.0 (q), 22.7 (t), 23.5 (t), 24.8 (t), 29.6 (t), 30.6 (q), 31.4 (q), 32.0 (t), 32.9 (d), 35.0 (s), 35.5 (s), 50.7, 55.1 (q), 111.3(d), 111.5 (d), 125.6 (d), 127.0 (d), 128.8 (d), 130.8 (d), 132.6 (d), 137.8 (s), 142.3 (d), 143.2 (s), 143.7 (s), 156.0 (s), 173.3 (s). IR (KBr): 1755 cm^{-1}. MS *m/z*: 450 (M^+). *Anal*. Calcd for $C_{30}H_{42}O_3$: C, 79.96; H, 9.39. Found: C, 79.84, H, 9.44.

***trans*-2-Butyl-1,2,3,4-tetrahydro-1-naphthalenelmethanol (*trans*-14a)** A mixture of *trans*-**12a** (157 mg, 0.35 mmol) and ceric ammonium nitrate (0.69 g, 1.25 mmol) in a mixture of CH_2Cl_2 (0.9 ml), CH_3CN (2.8 ml), and water (2.8 ml) was stirred for 2.5 h at room temperature, and mannitol (150 mg) was added. The mixture was poured onto 10% HCl and extracted with ether. Concentration gave a yellow oil, which was dissolved in ether (10 ml) and treated with a solution of diazomethane at 0 °C. Usual workup and concentration gave *trans*-**13a** as a yellow oil. Reduction with $LiAlH_4$ in THF gave *trans*-**14a** (81%) as an oil. ^{1}H-NMR: 0.7—2.2 (13H, m), 2.4—3.0 (3H, m), 3.5—4.0 (2H, m), 7.0—7.4 (4H, m). ^{13}C-NMR: 14.1 (q), 22.9 (t), 24.0, (t), 26.2 (t), 29.6 (t), 33.2 (t), 33.5 (d), 46.5 (d), 67.4 (t), 125.7 (d), 126.0 (d), 129.0 (d), 136.2 (s), 138.0 (s). IR (neat): 3380 cm^{-1}. MS *m/z*: 218 (M^+), 187 (M^+-CH_2OH). *Anal*. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.49, H, 10.17.

***trans*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-Phenyl-1,2,3,4-tetrahydro-1-naphthalenecarboxylates (*trans*-12b)** Prepared under the same conditions as for **12a**. Chromatography (hexane–ether, 20 : 1) gave *trans*-**12b** (96%) as colorless prisms of mp 126—130 °C. ^{1}H-NMR: 0.92 and 1.33 (each 9H, s, *tert*-Bu), 1.85—1.90 (1H, m), 2.44—2.60 (2H, m), 2.70 (1H, dt, *J*=6, 16 Hz), 3.77 (3H, s, OMe), 406 (1H, dt, *J*=2, 6 Hz), 4.29 (1H, br d, *J*=2 Hz), 6.78 and 6.84 (each 1H, d, *J*=3 Hz), 7.11—7.27 (8H, m), 7.67 (1H, m). ^{13}C-NMR: 26.1 (t), 28.3 (t), 30.7 (q), 31.4 (q), 35.1 (s), 35.1 (s), 39.6 (d), 50.9 (d), 55.2 (q), 111.4 (d), 111.6 (d), 126.2 (d), 127.3 (d), 127.5 (d), 128.4 (d), 128.7 (d), 131.1 (s), 132.1, 139.1 (s), 142.1 (s), 143.1 (s), 143.1 (s), 144.1 (s), 156.1 (s), 173.1 (s). IR (KBr): 1745, 1590, 1127 cm^{-1}. MS *m/z*: 470 (M^+), 455 (M^+-Me). *Anal*. Calcd for $C_{32}H_{38}O_3$: C, 81.66; H, 8.14. Found: C, 81.38, H, 8.21.

***trans*-Methyl 2-Phenyl-1,2,3,4-tetrahydro-1-naphthalenecarboxylates (*trans*-13b)** Prepared by the same procedure for **13a**. Chromatography (hexane–ether, 25 : 1) gave *trans*-**13b** (80%) as colorless prisms of mp 87.5—88 °C (EtOH). ^{1}H-NMR: 1.8—2.3 and 2.7—3.1 (each 2H, m), 3.36 (1H, ddd, *J*=4, 10, 10 Hz), 3.59 (3H, s, OMe), 4.04 (1H, br d, *J*=10 Hz), 7.0—7.4 (9H, m). ^{13}C-NMR: 29.5 (t×2), 44.1 (d), 51.8 (d), 53.3 (d), 126.2 (d), 126.7 (d), 126.9 (d), 127.2 (d), 127.8 (d), 128.6 (d), 129.3 (d), 133.5 (s), 136.4 (s), 144.0 (s), 174.6 (s). IR (KBr): 1725, 1594 cm^{-1}. MS *m/z*: 266 (M^+), 207 (M^+-CO_2Me). *Anal*. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.94, H, 6.83.

***trans*-2-Phenyl-1,2,3,4-tetrahydro-1-naphthalenemethanol (*trans*-14b)** Reduced under the same conditions for *trans*-**14a** in 94% yield. A colorless oil. ^{1}H-NMR: 1.20 (1H, br, OH), 1.70—2.20 and 2.73—2.90 (each 2H, m), 3.00—3.20 (2H, m), 3.72 (1H, dd, *J*=3, 11 Hz), 3.97 (1H, dd, *J*=4, 11 Hz), 7.0—7.4 (9H, m). ^{13}C-NMR: 29.0 (t), 29.7 (t), 42.1 (d), 46.9 (d), 65.0 (t), 126.1 (d), 126.2 (d), 127.7 (d), 127.9 (d), 128.4 (d), 129.2 (d), 136.3 (s), 138.8 (s), 145.9 (s). IR (neat): 3400 cm^{-1}. MS *m/z*: 239 (M^++1), 238 (M^+). *Anal*. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.43, H, 7.57.

***cis*-2,6-Bis(*tert*-butyl)-4-methoxyphenyl 2-Phenyl-1,2,3,4-tetrahydro-1-naphthalenecarboxylates (*cis*-12b)** Prepared under the same conditions for *trans*-**12b**. Chromatography (hexane–ether, 25 : 1) gave *cis*-**12b** (96%) as colorless prisms of mp 160—161 °C. ^{1}H-NMR: 0.81 and 0.98 (each 9H, s), 1.12 (1H, m), 2.8—3.3 (4H, m), 3.71 (3H, s, OMe), 4.34 (1H, m), 6.70 (2H, s), 7.0—7.7 (9H, m). ^{13}C-NMR: 21.9 (t), 28.6 (t), 30.5 (q), 30.9 (q), 34.9 (s), 35.1 (s), 42.3 (d), 52.5 (s), 55.1 (q), 111.3 (d), 111.4 (d), 125.8 (d), 126.2 (d), 127.7 (d), 127.8 (d), 129.0 (d), 129.3 (d), 132.0 (d), 133.0 (s), 137.4 (s), 141.7 (s), 142.6 (s), 143.4 (s), 143.9 (s), 156.0 (s), 170.4 (s). IR (KBr): 1755 cm^{-1}. MS *m/z*: 470 (M^+), 455 (M^+-Me). *Anal*. Calcd for $C_{32}H_{38}O_3$: C, 81.66; H, 8.14. Found: C, 81.54, H, 8.18.

***cis*-Methyl 2-Phenyl-1,2,3,4-tetrahydro-1-naphthalenecarboxylates (*cis*-13b)** Prepared by the same procedure for *trans*-**13b**. Chromatography (hexane–ether, 25 : 1) gave *cis*-**13b** (83%) as colorless solid. ^{1}H-NMR: 2.04, 2.85, and 2.96 (each 1H, m), 3.10 (1H, ddd, *J*=3, 6, 17 Hz), 3.24 (1H, ddd, *J*=3, 6, 13 Hz, CHPh), 3.35 (3H, s, OMe), 4.11 (1H, d, *J*=6 Hz), 7.13—7.36 (9H, m). ^{13}C-NMR: 22.8 (t), 29.5 (t), 42.2 (d), 51.4 (q and d), 125.8 (d), 126.7 (d), 127.2 (d), 127.4 (d), 128.3 (d), 129.1 (d), 129.6 (d), 133.6 (s), 136.8 (s), 142.9(s), 173.2 (s). IR (neat): 1735 cm^{-1}. MS *m/z*: 267 (M^++1), 266 (M^+), 207 (M^+-CO_2Me). *Anal*. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.03, H, 6.85.

***cis*-2-Phenyl-1,2,3,4-tetrahydro-1-naphthalenemethanol (*cis*-14b)** Reduced under the same conditions for *trans*-**14b** in 94% yield. ^{1}H-NMR: 1.22 (1H, br, OH), 1.95—2.76 (2H, m), 2.90—3.43 (4H, m), 3.54 (1H, dd, *J*=5, 11 Hz), 3.76 (1H, dd, *J*=6, 11 Hz), 7.0—7.5 (9H, m). ^{13}C-NMR: 23.3 (t), 29.6 (t), 42.3 (d), 47.0 (d), 65.0 (t), 125.8 (d), 126.5 (d), 126.0 (d), 127.6 (d), 128.4 (d), 128.7 (d), 129.3 (d), 129.6 (d), 137.1 (s), 137.6 (s), 144.0 (s). IR ($CHCl_3$): 3640, 1600 cm^{-1}. MS *m/z*: 238 (M^+). *Anal*. Calcd for $C_{17}H_{18}O\cdot 1/8H_2O$: C, 84.87; H, 7.64. Found: C, 84.90, H, 7.63.

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

References and Notes

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