# Preparation and Determination of Absolute Rotations and Configurations of 6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl Derivatives[1]

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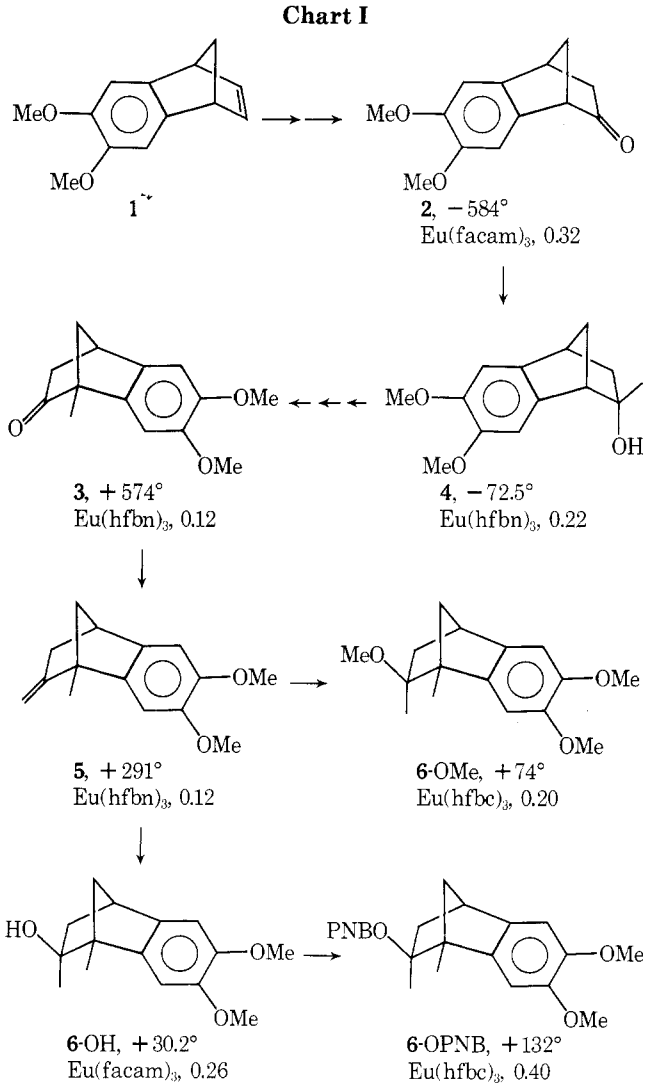
6,7-Dimethoxybenzonorbornadiene (1) has been prepared and converted to racemic and optically active 6,7-dimethoxy-2-benzonorbornenone (2). The latter was converted to 6,7-dimethoxy-1-methyl-2-methylenebenzonorbornene (5) in five steps, which in turn was converted to various racemic or optically active 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl derivatives (6-OMe, 6-OH, and 6-OPNB). The absolute configuration of 2, and thus of all subsequent compounds in the series, can be deduced from the asymmetric hydroboration involved in the preparation of 2. Enantiomeric compositions of all active compounds were determined with optically active NMR lanthanide shift reagents.

We have recently investigated the symmetry properties of ionic intermediates in the 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl system.[2] This paper reports the synthesis of the necessary compounds and the correlation of optical configurations and rotations required for that investigation.

6,7-Dimethoxybenzonorbornadiene (1) was prepared from 4,5-dimethoxyanthranilic acid[3] and cyclopentadiene and converted to racemic and optically active 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl derivatives (6) as outlined in Chart I.

**Chart I**




The key intermediate in this synthesis is 6,7-dimethoxy-1-methyl-2-methylenebenzonorbornene (5), which was obtained from 6,7-dimethoxy-1-methyl-2-benzonorbornenone (3) by the Wittig reaction. The latter was prepared by the series of reactions used earlier to convert norcamphor to 1-methyl-2-norbornanone[4,5] and 2-benzonorbornenone to 1-methyl-2-benzonorbornenone.[6] This sequence involves conversion of 1 to 6,7-dimethoxy-2-benzonorbornenone (2) in two steps, hydroboration followed by oxidation of the resulting 6,7-dimethoxy-*exo*-2-benzonorbornenol. Asymmetric hydroboration with tetraisopinocamphenyldiborane[7] led to optically active 2, which was the precursor for all of the active compounds. The most active samples were about 60% optically pure.

Conversion of 2 to 6,7-dimethoxy-2-methyl-*endo*-2-benzonorbornenol (4) with methylmagnesium bromide followed by acid-catalyzed rearrangement of 4 in acetic acid gave 6,7-dimethoxy-1-methyl-*exo*-2-benzonorbornenyl acetate. This step results in the configurational change shown in Chart I. Reductive cleavage of the acetate with lithium aluminum hydride followed by Oppenauer oxidation gave 3.

Absolute configurations and rotations are shown in Chart I. The configurational assignments are based on the assumption that asymmetric hydroboration of 1 and benzonorbornadiene[6,8] give similar enantiomeric compositions. In each case hydroboration with tetraisopinocamphenyldiborane derived from (−)-$\alpha$-pinene leads to the (−) ketone and magnitudes of induced asymmetry are similar for the two systems. It has been shown[8] that the absolute configuration of (−)-2-benzonorbornadiene corresponds to the structure for (−)-2 in Chart I.

The absolute rotations were determined from rotations and enantiomeric compositions of homogeneous optically active samples. Enantiomeric compositions were determined directly with optically active NMR lanthanide shift reagents.[9,10] From induced shifts of the various signals it is apparent that the binding constant for the ortho methoxyl groups is larger than for the keto (2 and 3), hydroxyl (4 and 6), or ester (6-OPNB) groups.[11] Several optically active shift reagents were investigated, including tris(3-trifluoroacetyl-*d*-camphorato)europium(III) [Eu(facam)$_3$],[10] tris(3-heptafluorobutyryl-*d*-camphorato)europium(III) [Eu(hfbc)$_3$],[10] tris(3-pentafluorobenzoyl-*d*-camphorato)europium(III) [Eu(fbc)$_3$], and tris(3-heptafluorobutyryl-*d*-nopinato)europium(III) [Eu(hfbn)$_3$]. The shift reagent giving the maximum nonequivalence of one set of enantiotopic methoxyl signals, and the magnitudes of the nonequivalences ($\Delta\Delta\delta$ in parts per million) are included in Chart I.

Optically active 5 was converted to 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenol (6-OH) by oxymercura-

tion–demercuration.[12] The enantiomeric composition of the product was the same as that of the reactant. Similarly, 6,7-dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl methyl ether (**6**-OMe) was prepared from **5** without change in optical purity by methoxymercuration–demercuration.[6,13] 6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoate (**6**-OPNB) was prepared from **6**-OH and purified by recrystallization, which increases the optical purity. The most active samples were about 70% optically pure.

6,7-Dimethoxy-2-benzonorbornenone (**2**) was also converted to 6,7-dimethoxy-2-methylenebenzonorbornene (Wittig reaction), which in turn was converted to 6,7-dimethoxy-2-methyl-*exo*-2-benzonorbornenol (the exo isomer of **4**) by oxymercuration–demercuration.

## Experimental Section

**6,7-Dimethoxybenzonorbornadiene (1).** This compound was prepared by the Diels–Alder addition of 4,5-dimethoxybenzyne to cyclopentadiene. The benzyne was derived from 4,5-dimethoxyanthranilic acid, mp 185° (lit. mp 186°),[3] which was prepared by catalytic hydrogenation (45 psi, $PtO_2$,30 min) of 6-nitroveratric acid, mp 189° (lit. mp 189–190°).[3] The latter was obtained by oxidation (basic permanganate) of 6-nitroveratraldehyde.[14]

4,5-Dimethoxyanthranilic acid was converted to **2-carboxy-4,5-dimethoxybenzenediazonium chloride** as follows. In a typical preparation[15,16] a solution of 80 g (0.41 mol) of 4,5-dimethoxyanthranilic acid in 600 ml of absolute ethanol was cooled to 10° and 40 ml of concentrated hydrochloric acid was added with vigorous stirring. To the resulting pasty mixture was added 59 ml of isoamyl nitrite, after which stirring was continued and 600 ml of anhydrous ether was added. The diazonium chloride was filtered, washed with anhydrous ether, dried briefly under reduced pressure, and stored in a refrigerator until used. The yield of crude diazonium chloride was 102 g (0.42 mol). The diazonium chloride was prepared shortly (<24 hr) before use.

The Diels–Alder addition of 4,5-dimethoxybenzyne to cyclopentadiene was carried out as follows. To a stirred suspension of 25 g of the above diazonium chloride in 160 ml of 1,2-dichloroethane at 85° was added 9 ml of freshly distilled cyclopentadiene followed by 13.6 ml of propylene oxide. The refluxing mixture was stirred until gas evolution ceased (ca. 2.5 hr). Then the reaction mixture was neutralized with aqueous sodium hydroxide and steam distilled. After removal of most of the solvent the temperature rose to 98° and the subsequent fraction contained essentially pure **1**, which separates as a solid. Extraction with ether followed by drying and removal of the ether gave 7 g (35%) of residual **1**, which after purification by recrystallization from an ether–pentane mixture followed by sublimation had mp 82–83°; NMR ($CDCl_3$) $\delta$ 2.23 (m, 2 H), 3.81 (s, 8-H), 6.78 (m, 2 H), 6.92 (s, 2 H).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93. Found: C, 77.33; H, 7.09.

**6,7-Dimethoxy-2-benzonorbornenone (2).** Racemic and optically active **2** were prepared from **1** in about 80% yield by procedures described earlier[8] for conversion of benzonorbornadiene to racemic and optically active 2-benzonorbornenone. This method involves hydroboration with diborane in tetrahydrofuran for racemic products or with tetraisopinocamphenyldiborane in diglyme for active products, followed by oxidation of the resulting dimethoxy-*exo*-2-benzonorbornenol. The product (**2**), mp 106–107°, was purified by recrystallization from ether–pentane mixtures followed by sublimation. The NMR spectrum ($CDCl_3$) had overlapping methoxyl singlets at $\delta$ 3.80 and an aromatic singlet (2 H) at $\delta$ 6.87.

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.40; H, 6.47.

Asymmetric hydroboration of **1** with tetraisopinocamphenyldiborane, derived from (+)-$\alpha$-pinene, $[\alpha]^{25}D$ 40.2° (neat) (~78% optically pure), led to (+)-**2**, $[\alpha]^{25}D$ 351° (*c* 2.9, $CHCl_3$) (60% optically pure).[17] Similar results were obtained in several other preparations. These results are similar to those reported earlier[6,8] for the parent benzonorbornadiene system with regard to signs of rotations and magnitudes of the induced asymmetry.

**6,7-Dimethoxy-2-methyl-*endo*-2-benzonorbornenol (4).** A solution of 13 g (0.06 mol) of 6,7-dimethoxy-2-benzonorbornenone (**2**) in 60 ml of dry tetrahydrofuran was added at room temperature to 60 ml (0.18 mol) of 0.3 *M* methylmagnesium bromide in ether. The mixture (under dry nitrogen) was stirred during the addition and stirring was continued for an additional 30 min, after which the reaction mixture was refluxed for 2 hr. The excess methylmagnesium bromide was decomposed by careful addition of a saturated aqueous solution of ammonium chloride, after which 10% hydrochloric acid was added to dissolve the precipitate. The resulting solution was extracted with three 200-ml portions of ether and the ether extract was dried and concentrated to 13 g (93%) of a brown residual syrup which consisted of 93% **4** contaminated with 7% of the endo isomer. Recrystallization from ether followed by vacuum distillation gave **4**: mp 60–61°; NMR ($CCl_4$) $\delta$ 1–2 (m, 5 H), 1.45 (s, 3 H), 2.88 (s, 1 H), 3.12 (s, 1 H), 3.74 (s, 6 H), 6.75 (2 s, 2 H).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 71.60; H, 7.53.

By the above procedure, except that the reflux period was increased to 5 hr, 20 g of homogeneous (+)-**2**,[17] $[\alpha]^{25}D$ 351° (*c* 2.9, $CHCl_3$), was converted to 19.3 g (90%) of (+)-**4**. A homogeneous sample of (+)-**4**,[17] $[\alpha]^{25}D$ 44.8° (*c* 1.0, $CHCl_3$), was obtained by preparative GC (10% FAPP on 45/60 Chromosorb W). The NMR spectrum in the presence of Eu(hfbn)$_3$ indicated that this sample was 62% optically pure.

**6,7-Dimethoxy-1-methyl-2-benzonorbornenone (3).** Crude **4** was converted to **3** in 56% overall yield by the three-step process described earlier for the parent benzonorbornenyl system[6] (the two intermediates were not purified). The product (**3**) was purified by recrystallization (and decolorizing with Norite) from ether at −78° followed by sublimation and had mp 102–103°; NMR ($CCl_4$) $\delta$ 1.38 (s, 3 H), 1.7–2.4 (m, 4 H), 3.41 (s, 1 H), 3.78 (s, 6 H), 6.72 (2 s, 2 H).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.41; H, 6.90. Found: C, 72.61; H, 6.80.

In the same manner 17.6 g of the (+)-**4** described above was converted to 15.7 g (90%) of crude (−)-**3**. A homogeneous sample of (−)-**3**,[17] $[\alpha]^{25}D$ −342° (*c* 0.98, $CHCl_3$), was obtained by preparative GC (10% FAPP on 45/60 Chromosorb W). The NMR spectrum in the presence of Eu(hfbn)$_3$ indicated the sample to be 60% optically pure.

**6,7-Dimethoxy-1-methyl-2-methylenenorbornene (5).** This compound was prepared from the above ketone (**3**) by the Wittig reaction using the procedure described earlier for similar transformations in the 1-methylnorbornyl[5] and 1-methylbenzonorbornenyl[6] systems. The yield of **5**, after purification by recrystallization from ether, was 75%: mp 39–41°; NMR ($CCl_4$) $\delta$ 1.52 (s, 3 H), 1.6–2.5 (m, 4 H), 3.2 (s, 1 H), 3.72 (s, 6 H), 4.5–4.8 (2 t, 2 H), 6.55 (2 s, 2 H).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.47; H, 7.86.

By the same procedure 6.0 g of the above crude (−)-**3** was converted to 6.0 g (100%) of crude (+)-**5** (a residual brown oil). A homogeneous sample of (+)-**5**,[17] $[\alpha]^{25}D$ −176° (*c* 1.32, $CHCl_3$), was obtained by preparative GC (column described above). The NMR spectrum in the presence of Eu(hfbn)$_3$ indicated the sample to be 60% optically pure.

**6,7-Dimethoxy-1,2-dimethyl-2-*exo*-benzonorbornenol (6-OH).** Oxymercuration–demercuration of **5** according to a previously described procedure[12] gave **6**-OH in 93% yield. The crude product (white precipitate) was purified by sublimation (80°, 1 mm) followed by recrystallization from ether: mp 75–76°; NMR ($CCl_4$) $\delta$ 0.8 (s, 3 H), 1.34 (s, 3 H), 1.2–2.2 (m, 5 H), 3.06 (s, 1 H), 3.74 (s, 6 H), 6.62 (s, 2 H).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.58; H, 8.06. Found: C, 72.33; H, 8.00.

The same procedure was used to convert 6 g of the above crude (−)-(**5**) to 5.5 g (85%) of crude (−)-**6**-OH. A homogeneous sample of (−)-**6**-OH),[17] $[\alpha]^{25}D$ −17.6° (*c* 1.5, $CHCl_3$), was obtained by preparative GC (10% FAPP on 45/60 Chromosorb W at 170°). Under these conditions the tertiary alcohol is stable.

**6,7-Dimethoxy-2-methylenebenzonorbornene.** This compound was prepared from **2** by the Wittig reaction using the procedure reported earlier for similar systems.[5,6] The yield of crude product was 85%. The product was purified by two recrystallizations from ether–pentane mixtures followed by sublimation (65°, 1 mm): mp 49–50°; NMR ($CDCl_3$) $\delta$ 3.80 (s, 6 H), 4.66 and 5.05 (2 s, 2 H), 6.80 (s, 2 H).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.78; H, 7.41. Found: C, 77.60; H, 7.62.

**6,7-Dimethoxy-2-methyl-*exo*-2-benzonorbornenol.** This tertiary alcohol (exo isomer of 4) was of interest for developing procedures for preparing tertiary benzonorbornenyl *p*-nitrobenzoates.

Oxymercuration–demercuration of the above dimethoxy-2-methylenebenzonorbornene by the procedure used to convert **5** to **6**-OH gave a product which after recrystallization from ether and sublimation (90°, 1 mm) had mp 83–84°; NMR ($CDCl_3$) $\delta$ 0.96 (s, 3 H), 3.81 (s, 6 H), 6.81 (d, 2 H).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 71.60; H, 7.53.

**6,7-Dimethoxy-2-methyl-*exo*-2-benzonorbornenyl *p*-Nitrobenzoate.** Of several procedures[6] attempted the following gave the highest yields. To a solution of 0.56 g (2.26 mmol) of the above tertiary alcohol in 4 ml of completely dry pyridine was added 0.97 g (5.25 mmol) of freshly recrystallized ($CCl_4$) *p*-nitrobenzoyl chloride. The acid chloride was added in small amounts and after each addition the reaction flask was shaken well at room temperature. The clear orange solution solidified in about 5 min. After 15 min, water was added dropwise with shaking after each addition. After addition of 5 ml of water the reaction mixture was extracted several times with ether and the ether extract was washed with water, aqueous sodium bicarbonate, and again with water. The solvent was removed under reduced pressure and the residual product was placed under high vacuum to remove the pyridine. The yield of crude product was 0.82 g (89%). After recrystallization twice from ether, 0.52 g (57%) of pure tertiary *p*-nitrobenzoate was obtained: mp 146–147°; NMR ($CDCl_3$) $\delta$ 1.35 (s, 3 H), 3.91 (s, 6 H), 8.25 (s, 4 H).

Anal. Calcd for $C_{21}H_{21}NO_6$: C, 65.80; H, 5.48; N, 3.66. Found: C, 65.65; H, 5.57; N, 3.61.

**6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl *p*-Nitrobenzoate (6-OPNB).** This ester was prepared by the above procedure except that the reaction temperature was 55° instead of room temperature and the reaction mixture was stirred instead of shaken. Also, the reaction time at 55° was increased to 27 hr and the product was extracted with benzene.[18] The tertiary ester, **6**-OPNB, was obtained in 65% yield. A small amount of unreacted **6**-OH was separated and recovered by sublimation (100°, 1 mm). The product was purified by column chromatography ($Al_2O_3$ with benzene as eluent) followed by recrystallization from ether–pentane mixtures. The purified nearly colorless **6**-OPNB had mp 165–166°; NMR ($CDCl_3$) $\delta$ 1.27 (s, 3 H), 1.7 (s, 3 H), 1.6–2.8 (m, 4 H), 3.2 (s, 1 H), 3.93 (s, 6 H), 6.86 (s, 2 H), 8.3 (s, 4 H).

Anal. Calcd for $C_{22}H_{23}NO_6$: C, 66.50; H, 5.79; N, 3.53. Found: C, 66.33; H, 5.76; N, 3.56.

By this procedure 5.3 g of the above crude (−)-**6**-OH was converted to (−)-**6**-OPNB which, after purification, had mp 168–169°; $[\alpha]^{25}D$ −85.7° (*c* 1.1, $CHCl_3$). The NMR spectrum in the presence of Eu(hfbc)$_3$ indicated that this material was 65% optically pure.

**(−)-6,7-Dimethoxy-1,2-dimethyl-*exo*-2-benzonorbornenyl Methyl Ether [(−)-6-OMe].** A sample of (−)-**5**, $[\alpha]^{25}D$ −143° (*c* 1.5, $CHCl_3$), was converted to (−)-**6**-OMe, which after purification by preparative GC had mp 64–66°;[17] $[\alpha]^{25}D$ −36.3° (*c* 0.3, $CHCl_3$); NMR ($CDCl_3$) $\delta$ 0.72 (s, 3 H), 1.3–1.7 (m, 2 H), 1.32 (s, 3 H), 2.04–2.3 (m, 2 H), 3.08 (s, 1 H), 3.20 (s, 3 H), 3.74 (d, 6 H), 6.6 (s, 2 H). The NMR spectrum in the presence of Eu(hfbc)$_3$ indicated that this sample was 49% optically pure.

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.00; H, 8.60.

**3-Heptafluorobutyryl-*d*-nopinone (H-hfbn).** *d*-Nopinone, bp 86° (9.5 mm), $[\alpha]^{25}D$ 26.7° (*c* 2.1 $CHCl_3$), was prepared[19] from (−)-$\beta$-pinene, $[\alpha]^{25}D$ −20.4° (neat), in 79% yield. A mixture of 4.6 g (0.118 mol) of sodium amide and 15.56 g (0.110 mol) of *d*-nopinone in 150 ml of dimethoxyethane was refluxed under nitrogen for about 2 hr, after which the reaction mixture was cooled to 0° and 9.1 g (0.039 mol) of heptafluorobutyryl chloride (Pierce Chemical Co.) in 25 ml of dimethoxyethane was added over a 30-min period. The reaction mixture was stirred at 0–5° for an additional 20 min and diluted with 400 ml of ice water. The mixture was acidified with concentrated hydrochloric acid and extracted several times with pentane. The pentane extract was washed with aqueous sodium bicarbonate and water. After drying, the extract was concentrated to 24.3 g of red liquid. Copper chelate purification[9] of the crude $\beta$-diketone followed by distillation gave 10.5 g (78%) of 3-heptafluorobutyryl-*d*-nopinone: bp 84–86° (4 mm); $[\alpha]^{25}D$ 14.7° (*c* 1.1, $CHCl_3$); NMR ($CCl_4$) $\delta$ 0.93 and 1.36 (2 s, 6 H, $CH_3$), 1.2–1.6 (m, 1 H), 2.2–2.4 (m, 1 H), 2.44–2.84 (m, 4 H), 14.9 (s, 1 H, enol H); ir ($CCl_4$) 1670 (C=O), 1630 $cm^{-1}$ (C=C).

**Tris(3-heptafluorobutyryl-*d*-nopinato)europium(III) [Eu(hfbn)$_3$].** This chelate was prepared from the above diketone and europium(III) chloride hexahydrate (99.99%) by the general method reported earlier.[10] As in the cases of Eu(facam)$_3$ and Eu(hfbc)$_3$,[10] Eu(hfbn)$_3$ was obtained as a bright yellow, glassy powder which was dried at 70° under high vacuum for several hours. This product had $[\alpha]^{25}D$ 25.6° (*c* 1.9, $CCl_4$); NMR ($CCl_4$) $\delta$ 1.0–2.0, 3.4 (all resonances broad); ir ($CHCl_3$) 1620 (C=O), 1480 $cm^{-1}$ (C=C).

Anal. Calcd for $C_{39}H_{36}F_{21}O_6Eu$: C, 40.43; H, 3.12. Found: C, 40.67; H, 3.15.

**Determination of Enantiomeric Compositons.** Enantiomeric compositions were determined with a 100-MHz instrument as outlined previously.[10] Pertinent data are summarized in Table I,

**Table I**
**Determination of Enantiomeric Compositions of 6,7-Dimethoxybenzonorbornenyl Derivatives[a]**

| Compd | Reagent | R/S[b] | $\Delta\Delta\delta$, ppm[c] |
|---|---|---|---|
| **2** | Eu(facam)$_3$ | 1.07 | 0.32[e] |
| **4** | Eu(hfbn)$_3$ | 1.04 | 0.22[e] |
| **3** | Eu(hfbn)$_3$ | 1.17 | 0.12[e] |
| **5** | Eu(hfbn)$_3$ | 1.31 | 0.12[d] |
| **6**-OH | Eu(facam)$_3$ | 1.07 | 0.26[e] |
| **6**-OPNB | Eu(hfbc)$_3$ | 1.09 | 0.45[d] |
| **6**-OMe | Eu(hfbc)$_3$ | 1.00 | 0.20[e] |

[a] The solvent was carbon tetrachloride for all determinations. [b] Shift reagent/substrate molar ratio; shift reagent concentration ~0.2 *M*. [c] Separation of low-field methoxyl signal. [d] Separation of high-field methoxyl signal.

which shows the optically active shift reagent which gave the largest nonequivalence for each compound, the shift reagent/substrate molar ratio (S/R), and the set of enantiotopic signals used for the determinations.

**Registry No.**—**1**, 54576-19-1; (±)-**2**, 54576-22-6; (+)-**2**, 54630-83-0; (±)-**3**, 54576-23-7; (−)-**3**, 54712-33-3; (±)-**4**, 54630-84-1; (+)-**4**, 54630-85-2; (±)-4 exo isomer, 54630-86-3; (±)-4 exo isomer *p*-nitrobenzoate, 54576-24-8; (±)-**5**, 54576-25-9; (+)-**5**, 54617-82-2; (−)-**5**, 54630-87-4; (±)-**6**-OH, 54576-26-0; (−)-**6**-OH, 54630-88-5; (±)-**6**-OPNB, 54576-27-1; (−)-**6**-OPNB, 54656-19-8; (−)-**6**-OME, 54576-28-2; 4,5-dimethoxybenzyne, 54632-05-2; cyclopentadiene, 542-92-7; 6,7-dimethoxy-2-methylenebenzonorbornene, 54576-29-3; *p*-nitrobenzoyl chloride, 122-04-3; H-hfbn, 54576-30-6; *d*-nopinone, 24903-95-5; heptafluorobutyryl chloride, 375-16-6; tris(3-heptafluorobutyryl-*d*-nopinato)europium(III), 54576-31-7; europium(III) chloride hexahydrate, 13759-92-7.

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(17) Except for NMR spectra in the presence of optically active shift reagents, optically active samples had the same spectral properties (ir and NMR) as racemic samples.
(18) The 1,2-dimethyl tertiary alcohol, **6**-OH, reacts much slower than the endo (**4**) or exo 2-methyl tertiary alcohols with *p*-nitrobenzoyl chloride.
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