Synthesis of Chiral *O*-Functionalized Isobornyloxy, Menthyloxy and Fenchyloxy Cyclopentadienyl Ligands

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Received 18 January 1996; revised 4 March 1996

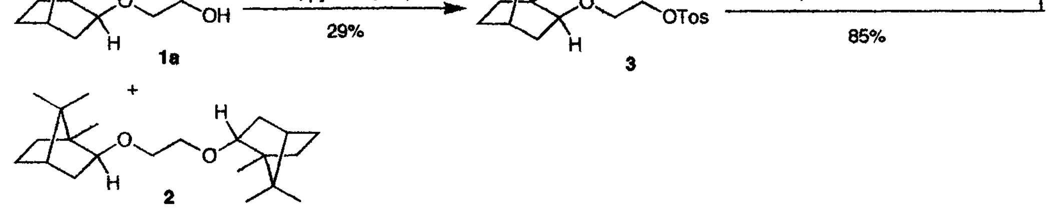
Natural (+)-camphene was used as the starting material for the preparation of an isobornyloxy-substituted cyclopentadienyl ligand in a simple two-step procedure. (−)-Menthol and (+)-fenchol were converted to analogous chiral cyclopentadienyl ligands in a four-step procedure. The new ligands contain an ether linkage suitable for bidentate chelation to a transition metal.

The use of chirally substituted cyclopentadienyl (Cp) ligands in transition metal catalyzed asymmetric conversions becomes more and more attractive.[1] The initial strategy in the development of chiral Cp ligands was the adaption of sterically crowded substituents on the Cp ring. This was hampered by the fact that these substituents tend to be dynamical and bent away from the metal centre. Another strategy is the introduction of a heteroatom onto the Cp ring which, by bidentate coordination, can bring the stereogenic centres closer to the metal, and at the same time create a fixed chiral pocket around the complexed metal. Some scattered reports based on this approach have appeared in literature.[2] We recently revealed the synthesis of a novel chiral *N*-functionalized Cp ligand,[3] and now report on the syntheses of several chiral *O*-functionalized Cp ligands.

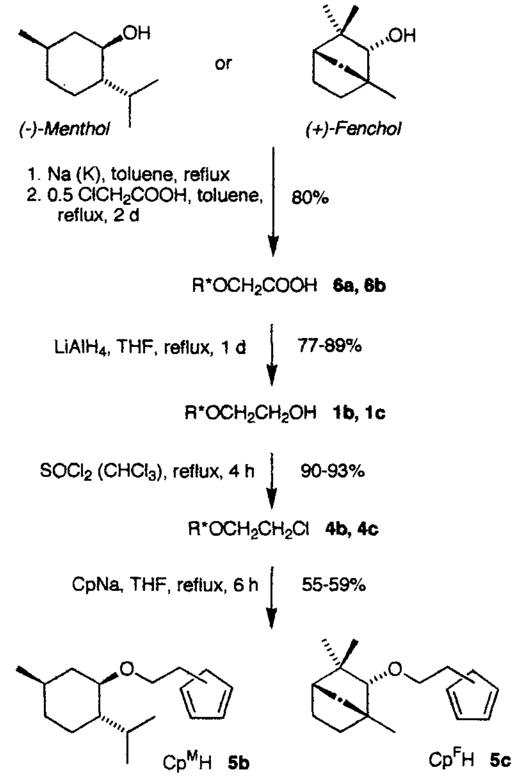
Thus, natural (+)-camphene was reacted with excess glycol in the presence of an acid catalyst. The electrophilic addition of glycol to the chiral olefin is attended by a Wagner–Meerwein rearrangement affording 2-isobornyl oxyethanol (**1a**) in 52 % yield (Scheme 1).[4,5] The alcohol was then converted to the tosylate **3** in 29 % yield. Subsequent reaction with cyclopentadienylsodium (CpNa) afforded 2-(isobornyloxy)ethylcyclopentadiene (Cp^BH, **5a**) as a distillable viscous oil in about 85 % yield.

An even simpler route to **5a** was found using 1-chloro-2-isobornyloxyethane (**4a**) as a precursor. This compound was obtained in excellent yield by an adaption of literature procedures by reacting (+)-camphene with neat 2-chloroethanol in the presence of an acid catalyst.[6] Subsequent reaction with CpNa afforded **5a** in moderate yield. Slightly more than the theoretical amount of CpNa (1.2–1.4 equiv) is required to convert all of the alkyl chloride. The ligand was obtained as a light yellow viscous distillable oil as a 1 : 1 mixture of regioisomers. Although the yield of the reaction of CpNa with the chloro precursor **4a** (50 %) is worse than that with the tosylate precursor **3** (85 %), the overall yield with the former (ca. 45 %) is better than with the latter (ca. 15 %). Because all starting materials for **5a** are readily available, its preparation could be easily scaled up to a multimole amount.

The synthetic pathway, using (+)-camphene as a starting material, is not very suitable for elaborate modifications, and therefore we looked for a more general route for this kind of ligand, using the broader synthetic potential of natural terpene alcohols as starting materials.[7] Accordingly, a four-step procedure for the syntheses of chiral alkoxyethyl cyclopentadienes **5** was developed (Scheme 2). First, the chiral alcohol was converted to the alkoxyacetic acid **6**. The synthetic method for this conversion has been published for menthol,[8] but worked just as well for fenchol and will be suitable probably for many other alcohols too. Reduction of the acid **6** with $LiAlH_4$ in boiling THF gave the 2-alkoxyethanols **1** in virtually quantitative yield. Subsequent reaction with $SOCl_2$ yielded the respective 1-chloro-2-alkoxyethanes **4**,[9] which were then reacted with CpNa affording $Cp^{M(enthol)}H$ (**5b**) and $Cp^{F(enchol)H}$ (**5c**) in ca. 50 % yield. The compounds are obtained as distillable viscous oils as a 1 : 1 mixture of the 1,2- and 1,3-regioisomers.



Scheme 1



Scheme 2

The bidentate ligands Cp^{M}H (**5b**) and Cp^{F}H (**5c**) are structurally similar to the isobornyloxy ligand Cp^{B}H (**5a**) in that all three ligands have an ether linkage in β-position with a large chiral group attached to the oxygen atom. Transition metal complexes using the η^5 coordination of the Cp part may be invoked in (reversible) intramolecular coordination of the ether linkage, bringing the chiral substituent close to the metal centre, and thereby provoke optical inductions during (catalytic) organic transformations mediated by the metal centre. Research in this direction is in progress.[10]

^{1}H and ^{13}C NMR spectra were obained in $CDCl_3$ (δ_H, 7.24; δ_C, 77.0) using a Varian Gemini instrument operating at 300.075 and 75.462 MHz, respectively.[11,12]

2-Isobornyloxyethanol (1a):

A solution of (+)-camphene (68.1 g, 0.500 mol), glycol (124.5 g, 2.01 mol), and $TsOH \cdot H_2O$ (4.5 g, 0.024 mol) in butan-2-one (300 mL) was refluxed for 2 d. Water and Et_2O were added, and the Et_2O layer was separated and washed several times with water. Solvents and other volatiles were removed in vacuo at 70–80 °C. Subsequent distillation 130 °C/2 Torr afforded 51.5 g (52 %) of **1a** as a colourless oil.

Anal. calc. for $C_{12}H_{22}O$ (182.3): C, 72.7; H, 11.1; found: C, 71.4; H, 10.5.

^{1}H NMR: δ = 0.77, 0.86, 0.93 (3 s, 3 H each), $H_{8,9,10}$), 0.95 (m, 2 H), 1.4–1.8 (m, 5 H), 2.1 (1 H, OH), 3.21 (dd, J = 3.4, 7.5 Hz, 1 H, H_2), 3.33 (ddd, J = 3.9, 5.7, 9.5 Hz, 1 H, H_{11}), 3.51 (ddd, J = 3.3, 5.3, 9.5 Hz, 1 H, $H_{11'}$), 3.63 (m, 2 H, H_{12}).

^{13}C NMR: δ = [^1J(C,H) (Hz) between parentheses]: 11.72 (q, 125, C_{10}), 20.14 (q, 125, $C_{8,9}$), 27.18 (t, 131, C_5), 34.35 (t, 131, C_6), 38.34 (t, 130, C_3), 44.98 (d, 140, C_4), 46.33 (C_7), 49.22 (C_1), 61.92 (t, 143, C_{12}), 69.99 (t, 140, C_{11}), 87.43 (d, 150, C_2).

The residue consists of almost pure 1,2-bis(isobornyloxy)ethane (**2**).

^{1}H NMR: δ = 0.77, 0.86, 0.95 (3 s, 6 H each, $H_{8,9,10}$), 0.95 (m, 4 H), 1.4–1.8 (m, 10 H), 3.21 (m, 2 H, H_2), 3.4–3.5 (m, 4 H, $H_{11,11'}$).

^{13}C NMR: δ = 11.85 (C_{10}), 20.26, 20.30 ($C_{8,9}$), 27.39 (C_5), 34.50 (C_6), 38.59 (C_3), 45.14 (C_4), 46.43 (C_7), 49.16 (C_1), 68.91 (C_{11}), 87.30 (C_2).

2-(Isobornyloxy)ethyl Toluenesulfonate (3):

To a cooled solution (−20 °C) of **1a** (39.0 g, 0.197 mol) in anhyd pyridine (150 mL) was added TsCl (75 g, 0.394 mol). The clear reddish solution was stirred overnight at r.t. Water and Et_2O were added, the water layer was separated and extracted with Et_2O. The combined Et_2O extracts were washed with 5 % NaOH. Evaporation of solvent yielded a pale brown oil (31 g), that was washed several times with cold pentane to give 20 g (29 %) of a colourless solid.

^{1}H NMR: δ = 0.75, 0.77, 0.84 (3 s, 3 H each, $H_{8,9,10}$), 0.95 (m, 2 H), 1.4–1.8 (m, 5 H), 2.41 (3 H), 3.12 (dd, J = 3.2, 7.4 Hz, 1 H, H_2), 3.45 (dt, J = 11.3 Hz, 4.8 Hz, 1 H, H_{11}), 3.57 (dt, J = 11.3, 4.8 Hz, 1 H, $H_{11'}$), 4.06 (t, 2 H, J = 4.8 Hz, 2 H, H_{12}), 7.30 (d, J = 8.2 Hz, 2 H), 7.76 (d, J = 8.2 Hz, 2 H).

^{13}C NMR [^1J(C,H) (Hz) between parentheses]: δ = 11.62 (q, 125, C_{10}), 20.05, 20.14 (q, 121, $C_{8,9}$), 21.54 ($ArCH_3$), 27.17 (t, 132, C_5), 34.26 (t, 132, C_6), 38.26 (t, 129, C_3), 44.95 (d, 138, C_4), 46.35 (C_7), 49.20 (C_1), 66.49 (t, 142, C_{12}), 69.62 (t, 150, C_{11}), 87.73 (d, 150, C_2), 127.48, 127.84, 129.71, 144.57 (C_{arom}).

1-Chloro-2-isobornyloxyethane (4a):

A mixture of (+)-camphene (136.3 g, 1.00 mol), 2-chloroethanol (100 mL, 1.50 mol) and $TsOH \cdot H_2O$ (8.2 g, 0.043 mol) was stirred at 60–70 °C for 20 h. The purple-brown solution was cooled and water and Et_2O were added. The Et_2O layer was washed with water several times and dried ($MgSO_4$). Solvent and other volatiles were removed in vacuo at 40–50 °C. Subsequent distillation at 110–120 °C/3 Torr afforded 194.4 g (90 %) of **4a** as colourless oil.

^{1}H NMR: δ = 0.78, 0.87, 0.96 (3 s, 3 H each, $H_{8,9,10}$), 0.95 (m, 2 H), 1.4–1.8 (m, 5 H), 3.21 (dd, J = 3.3, 7.5 Hz, 1 H, H_2), 3.5–3.65 (m, 4 H, $H_{11,12}$).

^{13}C NMR: δ = 11.74 (C_{10}), 20.11, 20.21 ($C_{8,9}$), 27.28 (C_5), 34.58 (C_6), 38.58 (C_3), 43.11 (C_{12}), 45.11 (C_4), 46.43 (C_7), 49.31 (C_1), 69.56 (C_{11}), 87.77 (C_2).

Attempts to distill the product *directly* out of the reaction flask (still containing the acid catalyst) resulted in the reverse reaction with formation of the two starting compounds.

2-(Isobornyloxy)ethylcyclopentadiene (Cp^{B}H, 5a):

A solution of cyclopentadienylsodium was prepared by reacting Na (26.0 g, 1.13 mol) and cyclopentadiene (120 mL, 1.46 mol) in anhyd THF (500 mL) overnight at r.t. under Ar. To this solution was added **4a** (194 g, 0.898 mol) and the resulting suspension was refluxed for 8 h. Water (30 mL) was added and the mixture was evaporated to dryness in vacuo. The residue was extracted with pentane. Removal of solvent yielded 203.2 g of the crude product. Distillation at 200–210 °C/0.1 Torr afforded the pure product as a pale yellow oil; yield: 109.9 g (50 %).

Anal. calc. for $C_{17}H_{26}O$ (246.4): C, 82.9; H, 10.6; found: C, 82.0; H, 10.8.

^{1}H NMR (1:1 mixture of two regioisomers): δ = 0.79, 0.87, 0.95 (3 s, 3 H each, $H_{8,9,10}$), 1.0 (m, 2 H), 1.4–1.8 (m, 5 H), 2.58/2.62 (dt, J = 1.3, 6.9 Hz, 2 H, H_{12}), 2.92 (br s, 2 H, Cp), 3.18/3.19 (dd, J = 3.5, 7.5 Hz, 1 H, H_2), 3.39/3.42, 3.55/3.57 (2 dt, J = 9.1, 6.9 Hz, 2 H, H_{11}), 6.04/6.18 (br s, 1 H, Cp), 6.25/6.37, 6.41/6.46 (2 br d, J = 5.3 Hz, 2 H, Cp).

^{13}C NMR: δ = 11.89 (C_{10}), 20.19, 20.29 ($C_{8,9}$), 27.37 (C_5), 30.82/31.55 (C_{12}), 34.55 (C_6), 38.62 (C_3), 41.26/43.89 (Cp), 45.13 (C_4), 46.39 (C_7), 49.18 (C_1), 68.75/69.31 (C_{11}), 87.16 (C_2), 127.07/127.30/130.80/132.36/133.23/135.08/144.35/146.89 (Cp).

In order to avoid extensive Diels–Alder dimerization all Cp derivatives should be stored at temperatures below −20 °C.

Using **3** as the starting material a 85 % yield of **5a** was obtained.

Menthyloxyacetic Acid (6a):

This compound was prepared according to Ref. 8.

^{1}H NMR: $\delta = 0.75$, 0.87, 0.89 (3d, $J = 6.8$, 6.6, 5.9 Hz, 3 H each, $H_{7,9,10}$), 0.7–1.0 (m, 3 H), 1.28 (m, 2 H), 1.61 (m, 2 H), 2.02 (m, 1 H), 2.19 (m, 1 H, H_4), 3.17 (dt, $J = 4.1$, 10.6 Hz, 1 H, H_3), 4.06 (d, $J = 16.7$ Hz, 1 H, H_{11}), 4.17 (d, $J = 16.7$ Hz, 1 H, $H_{11'}$), 8.9 (br s, 1 H, OH).

^{13}C NMR: $\delta = 16.12$ (C_9), 20.88 (C_{10}), 22.16 (C_7), 23.16 (C_5), 25.59 (C_8), 31.44 (C_1), 34.26 (C_6), 39.85 (C_2), 47.91 (C_4), 65.42 (C_{11}), 80.56 (C_3), 174.57 (C_{12}).

2-Menthyloxyethanol (1b); Typical Procedure:

A mixture of **6a** (27.6 g, 0.129 mol) and $LiAlH_4$ (10.5 g, 0.276 mol) in THF (200 mL) was refluxed overnight. Then, water (30 mL) was cautiously added until a white suspension was formed. The THF solution was filtered and evaporated to dryness under reduced pressure affording crude **1b** as a pale yellow oil in 89% yield (22.9 g).

^{1}H NMR: $\delta = 0.75$, 0.86, 0.88 (3d, $J = 6.9$, 6.7, 6.0 Hz, 3 H each, $H_{7,9,10}$), 0.7–1.4 (m, 5 H), 1.60 (m, 2 H), 2.06 (m, 1 H), 2.15 (m, 1 H, H_4), 3.05 (dt, $J = 4.1$, 10.5 Hz, 1 H, H_3), 3.38 (m, 1 H, $H_{11,12}$), 3.67 (m, 3 H, $H_{11,12}$).

^{13}C NMR: $\delta = 16.18$ (C_9), 20.89 (C_{10}), 22.24 (C_7), 23.33 (C_5), 25.71 (C_8), 31.48 (C_1), 34.49 (C_6), 40.42 (C_2), 48.23 (C_4), 62.20 (C_{12}), 69.43 (C_{11}), 79.52 (C_3).

1-Chloro-2-menthyloxyethane (4b); Typical Procedure:

A solution of **1b** (14.0 g, 70 mmol) and $SOCl_2$ (15 mL, 1.5 equiv) in $CHCl_3$ (30 mL) was refluxed for 4 h. Evaporation of volatiles afforded 14.3 g (93%) of the crude product as a brownish oil. The compound may be distilled for further purification at 110 °C/0.1 Torr as a colourless oil, but this was not necessary for the next step.

^{1}H NMR: 0.75, 0.87, 0.89 (3 d, $J = 7.0$, 7.0, 6.6 Hz, 3 H each, $H_{7,9,10}$), 0.7–1.4 (m, 5 H), 1.61 (m, 2 H), 2.04 (m, 1 H), 2.19 (m, 1 H, H_4), 3.06 (dt, $J = 4.1$, 10.5 Hz, 1 H, H_3), 3.56 (m, 3 H, $H_{11,12}$), 3.81 (m, 1 H, $H_{11,12}$).

^{13}C NMR: 16.34 (C_9), 20.85 (C_{10}), 22.25 (C_7), 23.48 (C_5), 25.62 (C_8), 31.54 (C_1), 34.52 (C_6), 40.50 (C_2), 43.22 (C_{12}), 48.23 (C_4), 68.71 (C_{11}), 79.95 (C_3).

2-(Menthyloxy)ethylcyclopentadiene (Cp^MH, 5b); Typical Procedure:

A solution of cyclopentadienylsodium was prepared by reacting Na (7.8 g, 0.34 mol) and cyclopentadiene (38 mL, 0.46 mol) in anhyd THF (200 mL) overnight at r.t. under Ar. To this solution was added **4b** (52.4 g, 0.240 mol). The resulting intense purple mixture was refluxed for 6 h. Water (10 mL) was added and the mixture was evaporated to dryness in vacuo. The residue was extracted with pentane. The dark brown pentane extracts were concentrated and fractionally distilled at low pressure. At 190–200 °C/0.1 Torr, the product distilled as a pale yellow viscous oil (34.95 g, 59%). It should be stored at temperatures below −20 °C.

^{1}H NMR (1:1 mixture of regioisomers): $\delta = 0.72/0.73$ (2d, $J = 6.9$ Hz), 0.86 (d, $J = 7.2$ Hz), 0.89 (d, $J = 6.6$ Hz) (9 H all, $H_{7,9,10}$), 0.7–1.0 (m, 3 H), 1.19 (m, 1 H), 1.31 (m, 1 H), 1.58 (m, 2 H), 2.08 (m, 1 H), 2.18 (m, 1 H, H_4), 2.64 (m, 2 H, H_{12}), 2.89/2.92 (br s, 2 H, Cp), 3.01 (dt, $J = 4.1$, 10.5 Hz, 1 H, H_3), 3.43 (m, 1 H, H_{11}), 3.77 (m, 1 H, $H_{11'}$), 6.05/6.19 (br s, 1 H, Cp), 6.24/6.38, 6.40/6.44 (2 br d, $J = 5.3$ Hz, 2 H, Cp).

^{13}C NMR: $\delta = 16.26$ (C_9), 20.93 (C_{10}), 22.33 (C_7), 23.39 (C_5), 25.54 (C_8), 29.68/30.86 (C_{12}), 31.55 (C_1), 34.59 (C_6), 40.51 (C_2), 41.30/43.63 (Cp), 48.23 (C_4), 67.81/68.33 (C_{11}), 79.26/79.32 (C_3), 127.09/127.34/130.76/132.36/134.69/134.72/143.77/146.26 (Cp).

Fenchyloxyacetic Acid (6b):

A solution of potassium fencholate was generated by refluxing a mixture of fenchol (100 g, 0.648 mol) and K (25.4 g, 0.65 mol) in KOH-dried toluene (250 mL) for 2 h under Ar. To the cooled solution was slowly added a warm solution of monochloroacetic acid (24.49 g, 0.259 mol) in toluene (500 mL). The thick suspension that formed immediately was thoroughly stirred and refluxed for 48 h. After completion of the reaction, the mixture was extracted with water (3 × 250 mL). The combined water extracts were acidified with 30% HCl whereupon the fenchyloxyacetic acid formed floated on the water surface. The acid was extracted with toluene (3 × 100 mL). Removal of solvent under reduced pressure afforded a white residue of crude **6b** (43.3 g, 79%), which was used for the subsequent step. The product may be purified by distillation.

Anal. calc. for $C_{12}H_{20}O_3$ (212.3): C, 67.9; H, 9.4; found: C, 68.1; H, 9.8.

^{1}H NMR: $\delta = 0.92$, 1.03, 1.12 (3 s, 3 H each, $H_{8,9,10}$), 0.8–1.1 (m, 2 H), 1.43 (m, 2 H), 1.66 (m, 3 H), 3.03 (s, 1 H, H_2), 4.04 (d, $J = 16.5$ Hz, 1 H, H_{11}), 4.16 (d, $J = 16.5$ Hz, 1 H), 10.05 (br s, OH).

^{13}C NMR: $\delta = 19.96$ (C_{10}), 20.54 (C_9), 25.82 (C_5), 25.98 (C_6), 31.45 (C_8), 39.56 (C_3), 41.37 (C_7), 48.53 (C_4), 49.23 (C_1), 68.64 (C_{11}), 94.82 (C_2), 173.88 (C_{12}).

2-Fenchyloxyethanol (1c):

Compound **6b** was reduced with $LiAlH_4$ in THF as described for the preparation of **1b** yield: 77%; bp 75–83 °C/0.1 Torr.

Anal. calc. for $C_{12}H_{22}O_2$ (182.3): C, 72.7; H, 11.1; found: C, 72.8; H, 10.4.

^{1}H NMR: $\delta = 0.86$, 0.98, 1.05 (3 s, 3 H each, $H_{7,9,10}$), 0.8–1.1 (m, 2 H), 1.38 (m, 2 H), 1.63 (m, 3 H), 2.20 (s, 1 H, OH), 2.87 (s, 1 H, H_2), 3.45 (m, 1 H, $H_{11\ 12}$), 3.64 (m, 3 H, $H_{11,12}$).

^{13}C NMR: $\delta = 19.95$ (C_{10}), 20.55 (C_9), 25.84 (C_5), 26.06 (C_6), 31.59 (C_8), 39.43 (C_3), 41.30 (C_7), 48.61 (C_4), 49.11 (C_1), 62.10 (C_{12}), 72.83 (C_{11}), 93.41 (C_2).

1-Chloro-2-fenchyloxyethane (4c):

2-Fenchyloxyethanol **(1c)** was reacted to give **4c** as described for the preparation of **4b** except that the reaction was done in neat $SOCl_2$; yield: 90%; bp 100–110 °C/1 Torr.

Anal. calc. for $C_{12}H_{21}ClO$ (216.8): C, 66.4; H, 9.7; found: C, 65.3; H, 10.1.

^{1}H NMR: $\delta = 0.87$, 1.00, 1.07 (3 s, 3 H each, $H_{8,9,10}$), 0.8–1.1 (m, 2 H), 1.37 (m, 2 H), 1.64 (m, 3 H), 2.89 (s, 1 H, H_2), 3.55 (m, 3 H, $H_{11,12}$), 3.73 (m, 1 H, $H_{11,12}$).

^{13}C NMR: $\delta = 19.91$ (C_{10}), 20.64 (C_9), 25.85 (C_6), 26.08 (C_5), 31.62 (C_8), 39.55 (C_3), 41.33 (C_7), 42.86 (C_{12}), 48.66 (C_4), 49.21 (C_1), 71.92 (C_{11}), 93.91 (C_2).

2-(Fenchyloxy)ethylcyclopentadiene (Cp^FH, 5c):

Compound **4c** was converted to **5c** as described for the preparation of **5b**; yield: 55%; bp 170–180 °C/0.1 Torr.

Anal. calc. for $C_{17}H_{26}O$ (246.4): C, 82.9; , H 10.9; found: C, 82.7; H, 10.7.

^{1}H NMR (1:1 mixture of regioisomers): $\delta = 0.89$, 1.02, 1.08 (3 s, 3 H each, $H_{8,9,10}$), 0.85–1.15 (m, 2 H), 1.3–1.5 (m, 2 H), 1.6–1.8 (m, 3 H), 2.62 (m, 2 H, H_{12}), 2.88/2.94 (2 s, 3 H, H_2, Cp), 3.52 (m, 1 H, H_{11}), 3.65 (m, 1 H, $H_{11'}$), 6.06/6.20 (br s, 1 H, Cp), 6.26/6.39, 6.43/6.48 (2 br d, $J = 5$ Hz, 2 H, Cp).

^{13}C NMR: $\delta = 19.98/20.03$ (C_{10}), 20.60 (C_9), 25.99 (C_6), 26.17 (C_5), 30.87/31.59 (C_{12}), 31.71 (C_8), 39.46 (C_3), 41.27/43.92 (Cp), 41.42 (C_7), 48.77 (C_4), 49.12 (C_1), 71.41/71.96 (C_{11}), 93.26/93.31 (C_2), 127.13/127.41/130.81/132.36/133.28/135.06/144.10/146.60 (Cp).

Financial aid from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. Prof. Dr. Karl-Heinz Thiele is thanked for his generous support and interest.

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(5) Byproduct of this reaction is the interesting, C_2-symmetric compound 1,2-bis(isobornyloxy)ethane **(2)**, which might find its use as a chiral *O,O′*-bidentate ligand.

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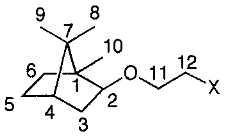
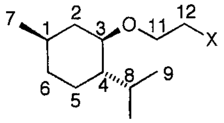
(11) Assignment of ^{13}C NMR signals, cf.: Bohlmann, F.; Zeisberg, R.; Klein, E. *Org. Magn. Res.* **1975**, *7*, 426.

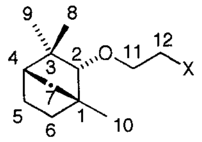
(12) Numbering system:



Isobornyloxy



Menthyloxy



Fenchyloxy