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Rev

# Supporting Information

## Catalytic Asymmetric Epoxidation of α,β-Unsaturated Ketones Promoted by Lanthanoid Complexes

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**General:** Enones **3** and **9** were recrystallized from ethanol and petroleum ether, respectively. Enones **5**, **11**, **13** and **15** were distilled under reduced pressure. Enone **7** was synthesized from 2-hydroxychalcone.

Anhydrous TBHP in toluene was prepared as follows: To a 70% TBHP solution in $H_2O$ (35 mL) was added toluene (30 mL) and the solution was swirled. The aqueous layer was separated and the organic layer was dried over anhydrous $MgSO_4$ twice, then stored at room temperature over activated 4A molecular sieves.

Anhydrous CMHP in toluene was prepared by adding the commercially available CMHP (70%, 25 mL) slowly and with agitation to 80 mL of 25% NaOH in water, keeping the temperature below 15 ℃. The resulting crystals were filtered off, washed twice with petroleum ether (25 mL), then stirred with petroleum ether (50 mL) 30 min. After filtering off of the crystals, they were suspended in 30 mL of water and the *p*H was adjusted to 7.5 by addition of 4 M HCl. The free CMHP was extracted into two 20 mL portions of petroleum ether, dried over anhydrous $MgSO_4$, and solvent evaporated under vacuum at room temperature. The residue was dissolved in toluene and then stored at room temperature over activated 4A molecular sieves.

All reactions were performed under an argon atmosphere. THF was distilled from sodium benzophenone ketyl.

### General procedure for the catalytic asymmetric epoxidation with La-(*R*)-BINOL catalyst

### Synthesis of *trans*-(2*S*, 3*R*)-epoxy-1,3-diphenylpropan-1-one (4)

To a suspension of MS 4A (1.0 g) in THF (25 mL) was added (*R*)-BINOL in THF (0.1 M, 2.5 mL, 0.25 mmol) and then $La(O^iPr)_3$ in THF (0.2 M, 1.25 mL, 0.25 mmol) at room temperature. After stirring at room temperature for 30 min, *trans*-chalcone (**3**)(1.04 g, 5.0 mmol) was added and the resulting mixture was stirred for an additional 5 min at the same temperature. To this solution was added CMHP in toluene (ca. 3.5 M, 2.1 mL, 7.5 mmol) in one portion. After stirring for 6 h at room temperature, the reaction mixture was treated with saturated $NH_4Cl$ aq (3 mL) and extracted with EtOAc (25 mL x 3). The combined organic extracts were washed with

brine, dried ($Na_2SO_4$), and concentrated to give a residue. Purification of this by flash chromatography ($SiO_2$, AcOEt/hexane = 1: 30) gave the *trans*-(2*S*,3*R*)-epoxy-1,3-diphenylpropan-1-one (**4**) (1.04 g, 93 %) in 83% ee as a colorless oil.

**General procedure for the catalytic asymmetric epoxidation with La-(*R*)-3-hydroxymethyl-BINOL catalyst**

To a suspension of MS 4A(100 mg) in THF (2.6 mL) were added (*R*)-3-hydroxymethyl-BINOL in THF (0.1 M, 188 μL, 0.0188 mmol) and then $La(O^iPr)_3$ in THF (0.2 M, 75 μL, 0.015 mmol) at 0 ℃. After being stirred at room temperature for 60 min, *trans*-chalcone (**3**)(62.4 mg, 0.3 mmol) was added and the resulting mixture was stirred for an additional 10 min at the same temperature. To this solution was added CMHP in toluene (ca. 3.5 M, 130 μL, 0.45 mmol) in one portion. After being stirred for 7 h at room temperature, the reaction mixture was treated with saturated $NH_4Cl$ aq (1.0 mL). The usual workup gave **4** (62.5 mg, 93 %) in 91% ee as a colorless oil.
IR (neat) 1688, 1230 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 4.07 (d, *J* = 2.0 Hz, 1 H), 4.29 (d, *J* = 2.0 Hz, 1 H), 7.30 - 7.70 (m, 8 H), 8.19 (m, 2 H); $^{13}$C-NMR ($CDCl_3$) δ 59.3, 60.9, 125.7, 128.2, 128.7, 128.8, 128.8, 129.0, 133.9, 135.4, 193.0; MS *m/z* 224 ($M^+$). Anal. calcd for $C_{15}H_{12}O_2$: C, 80,34; H, 5.39; Found: C, 80,32; H, 5.31 $[\alpha]_D^{25}$ +182.2° (*c* 1.14, $CHCl_3$) (91% ee). Enantiomeric excess of **4** was determined by chiral stationary phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH-hexane = 2:98, flow rate 1.0 ml/min, 16.2 min (2*S*,3*R*) isomer and 18.7 min (2*R*,3*S*) isomer); detection at 254 nm. The absolute configuration was determined by comparing the measured optical rotation with the reported one, see: Marsman, B.; Wynberg, H. *J. Org. Chem.44*, **1979**, 2312-2314.

**Synthesis of *trans*-(2*S*, 3*R*)-epoxy-4-methyl-1-phenylpentan-1-one (6)**

43.4 mg of **6** (95 %) was obtained from **5** (41.8 mg, 0.24 mmol), according to the general procedure for the synthesis of **4** by La-(*R*)-3-hydroxymethyl-BINOL catalyst (rt, 7 h).
Colorless oil; IR (neat) 1691, 1230 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.07 (d, *J* = 6.9 Hz, 3 H), 1.10 (d, *J* = 6.9 Hz, 3 H), 1.78 (sept, *J* = 6.9 Hz, 1 H), 2.95 (dd, *J* = 2.3, 6.6 Hz, 1 H), 4.08 (d, *J* = 2.3 Hz, 1 H), 7.50 (m, 2 H), 7.60 (m, 1 H), 8.02 (m, 2 H); $^{13}$C-NMR ($CDCl_3$) δ 18.1, 18.8, 30.4, 56.3, 64.9, 128.1, 128.7, 133.6, 135.4, 194.6; MS *m/z* 190 ($M^+$). $[\alpha]_D^{25}$ -22.8° (*c* 1.47, $CHCl_3$) (94% ee). Enantiomeric excess of **6** was determined by chiral stationary phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH-hexane = 2:98, flow rate 1.0 ml/min, 8.2 min (2*S*,3*R*) isomer and 10.2 min (2*R*,3*S*) isomer ); detection at 254 nm. The absolute configuration was determined by comparing the measured optical rotation with the reported one after converted into β-

hydroxyketone. Conversion into β-hydroxyketone, see: Marsman, B.; Wynberg, H. *J. Org. Chem.*, 44, **1979**, 2312-2314. Optical rotation, see: Ramachandran, P.V.; Xu, W-C.; Brown, H. C. *Tetrahedron* **1996**, *37*, 4911-4914.

**Synthesis of *trans*-(2*S*, 3*R*)-epoxy-3-phenyl-1-(2-methoxymethyloxy phenyl)propan-1-one (8)**

48.3 mg of **8** (85 %) was obtained from **7** (53.6 mg, 0.2 mmol), according to the general procedure for the synthesis of **4** by La-(*R*)-BINOL catalyst (rt, 20 h).
White solid; mp 77 ℃; IR (nujol) 1635, 1265 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 3.09 (s, 3 H), 4.02 (d, *J* = 2.0 Hz, 1H), 4.30 (d, *J* = 2.0 Hz, 1 H), 4.83 (d, *J* = 7.0 Hz, 1 H), 4.93 (d, *J* = 6.9 Hz, 1 H), 7.10 (m, 2 H), 7.37 (m, 5 H), 7.48 (dt, *J* = 2.0, 9.0 Hz, 1 H), 7.81 (dd, *J* = 1.7, 7.6 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) δ 56.2, 59.8, 64.9, 94.4, 114.4, 121.9, 125.7, 126.5, 128.6, 128.8, 130.5, 134.7, 136.4, 157.2, 194.7; MS *m/z* 284 ($M^+$). Anal. calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67; Found: C,71.68; H, 5.53. $[\alpha]_D^{25}$ +120.5 °(*c* 1.03, $CHCl_3$) (85% ee). Enantiomeric excess of **8** was determined by chiral stationary phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH-hexane = 1:9, flow rate 1.0 ml/min, 15.2 min (2*S*,3*R*) isomer and 18.9 min (2*R*,3*S*) isomer); detection at 254 nm. The absolute configuration was determined by comparing the measured optical rotation with the reported one, see: Augustyn, J. A. N.; Bezuidenhoudt, B. C. B.; Swanepoel, A.; Ferreira, D. *Tetrahedron* **1990**, *46*, 4429-4442.

**General procedure for the catalytic asymmetric epoxidation with Yb-(*R*)-BINOL catalyst**

**Synthesis of *trans*-(3*S*, 4*R*)-epoxy-4-phenylbutan-2-one (10)**

To a suspension of MS 4A (100 mg) in THF (2.0 mL) was added (*R*)-BINOL in THF (0.1 M, 150 μL, 0.015 mmol) and then $Yb(O^iPr)_3$ in THF (0.1 M, 150 μL, 0,015 mmol) at room temperature. After being stirred at 40 ℃ for 60 min and cooling to room temperature, *trans*-benzalacetone (**9**) (44 mg, 0.3 mmol) was added and the resulting mixture was stirred for an additional 5 min at the same temperature. To this solution was added a toluene solution of TBHP (ca. 3 M, 150μL, 0,45 mmol) in one portion. After being stirred for 9 h at room temperature, the reaction mixture was treated with saturated $NH_4Cl$ aq (1.0 mL) and extracted with EtOAc (10 mL x 3). The combined organic extracts were washed with brine, dried ($Na_2SO_4$), and concentrated to give a residue. Purification by flash chromatography ($SiO_2$, $CH_2Cl_2$) gave the *trans*-(3*S*,4*R*)-epoxy-4-phenylbutan-2-one (**10**)(46 mg, 94 %) in 89% ee as a colorless oil.

**General procedure for the catalytic asymmetric epoxidation with Yb-(*R*)-3-hydroxymethyl-BINOL catalyst**

To a suspension of MS 4A(100 mg) in THF (2.5 mL) were added (*R*)-3-hydroxymethyl BINOL in THF (0.1 M, 188 μL, 0.0188 mmol) and then $Yb(O^iPr)_3$ in THF (0.1 M, 150 μL, 0.015 mmol) at 0 ℃. After being stirred at 40 ℃ for 60 min and cooling to room temperature, *trans*-benzalacetone (**9**) (44 mg, 0.3 mmol) was added and the resulting mixture was stirred for an additional 10 min at the same temperature. To this solution was added a toluene solution of TBHP (ca. 3 M, 150 μL, 0.45 mmol) in one portion. After being stirred for 96 h at room temperature, the reaction mixture was treated with saturated $NH_4Cl$ aq (1.0 mL). The usual workup gave **10** (40.3 mg, 83 %) in 94% ee as a colorless oil.

IR (neat) 1710, 1249 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2.17 (s, 3 H), 3.48 (d, $J$ = 2.0 Hz, 1 H), 4.00 (d, $J$ = 2.0 Hz, 1 H), 7.27 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 24.8, 57.7, 63.4, 125.7, 128.7, 129.0, 135.0, 204.1; MS *m/z* 162 ($M^+$). $[\alpha]_D^{25}$ +96.5° (*c* 1.0, $CHCl_3$) (94% ee).

Enantiomeric excess of **10** was determined by chiral stationary phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH-hexane = 2:98, flow rate 1.25 ml/min, 9.8 min (2*R*,3*S*) isomer and 12.6 min (2*S*,3*R*) isomer); detection at 254 nm. The absolute configuration was determined by comparing the measured optical rotation with the reported one after converted into β-hydroxyketone, see: Awano, K.; Yanai, T.; Watanabe, I.; Takagi, Y.; Kitahara, T.; Mori, K. *Biosci. Biotech. Biochem.* **1995**, *59*, 1251-1254.

**Synthesis of *trans*-(4*S*, 5*R*)-epoxy-2-methyl-5-phenylpentan-3-one (12)**

15.8 mg of **12** (55 %) was obtained from **11** (26.1 mg, 0.15 mmol), according to the general procedure for the synthesis of **10** by Yb-(*R*)-3-hydroxymethyl-BINOL catalyst (rt, 159 h).

Colorless oil; IR (neat) 1720, 1237 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.16 (d, $J$ = 6.9 Hz, 3 H), 1.17 (d, $J$ = 6.9 Hz, 3 H), 2.82 (sept, $J$ = 6.9 Hz, 1 H), 3.60 (d, $J$ = 2.0 Hz, 1 H), 3.92 (d, $J$ = 2.0 Hz, 1 H), 7.33 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 18.0, 18.7, 37.6, 59.1, 62.6, 126.3, 129.4, 129.6, 136.0, 209.3; MS *m/z* 190 ($M^+$). $[\alpha]_D^{25}$ +144.8° (*c* 1.0, $CHCl_3$) (88% ee). Enantiomeric excess of **12** was determined by chiral stationary phase HPLC analysis (DAICEL CHIRALPAK AS, *i*-PrOH-hexane = 2:98, flow rate 1.0 ml/min, 8.9 min (4*S*,5*R*) isomer and 12.6 min (4*R*,5*S*) isomer; detection at 254 nm. The absolute configuration was determined by Mosher method after converted into β-hydroxyketone.

**Synthesis of *trans*-(3*S*, 4*R*)-epoxy-6-phenylhexan-2-one (14)**

25.9 mg of **14** (91 %) was obtained from **13** (26.1 mg, 0.15 mmol), according to the general procedure for the synthesis of **10** by Yb-(*R*)-3-hydroxymethyl-BINOL catalyst (rt, 118 h).

Colorless oil; IR (neat) 1709, 1248 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 1.95 (dt, $J$ = 5.6, 7.6 Hz, 2 H), 2.02 (s, 3 H), 2.80 (m, 2 H), 3.08 (dt, $J$ = 2.0, 5.6 Hz, 1 H), 3.17 (d, $J$ = 2.0 Hz, 1

H), 7.25 (m, 5 H); $^{13}C$ NMR ($CDCl_3$) δ 24.5, 31.9, 33.4, 57.4, 59.9, 126.3, 128.3, 128.6, 140.4, 205.6; MS *m/z* 190 ($M^+$). Anal. calcd for $C_{12}H_{14}O_2$: C, 75.76 ; H, 7.42; Found: C, 75.48; H, 7.60. $[\alpha]_D^{26}$ -21.9° (*c* 1.24, $CHCl_3$) (88% ee). Enantiomeric excess of **16** was determined by chiral stationary phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH-hexane = 2:98, flow rate 1.0 ml/min, 8.9 min (3*R*,4*S*) isomer and 11.5 min (3*S*,4*R*) isomer); detection at 254 nm. The absolute configuration was determined by comparing the measured optical rotation with the reported one after converted into β-hydroxyketone. see; Narasaka, K.; Miwa, T.; Hayashi, H.; Ohta, M. *Chem. Lett.* **1984**, 1399-1402.

**Synthesis of *trans*-(3*S*, 4*R*)-epoxynonan-2-one (16)**

26.6 mg of **16** (71 %) was obtained from **15** (33.7 mg, 0.24 mmol), according to the general procedure for the synthesis of **10** by Yb-(*R*)-3-hydroxymethyl-BINOL catalyst (rt, 67 h).

Colorless oil; IR(neat) 1711 $cm^{-1}$; $^1H$-NMR ($CDCl_3$) δ 0.89 (m, 3 H), 1.20 - 1.75 (m, 8 H), 2.06 (s, 3 H), 3.07 (dt, *J* = 2.0, 5.0 Hz, 1 H), 3.18 (d, *J* = 2.0 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) δ 14.5, 23.1, 24.9, 26.1, 32.0, 32.3, 58.7, 60.5, 206.7; MS *m/z* 156 ($M^+$).; $[\alpha]_D^{25}$ -38.7° (*c* 0.75, $CHCl_3$) (91% ee). Enantiomeric excess of **16** was determined by chiral stationary phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH-hexane = 1:100, flow rate 0.4 ml/min, 17.2 min (3*R*,4*S*) isomer and 19.5 min (3*S*,4*R*) isomer); detection at 280 nm. The absolute configuration was determined by Mosher method after converted into β-hydroxyketone.

**Synthesis of (*R*)-3-hydroxymethyl-BINOL (2)**

For the synthesis of racemic 3-hydroxymethyl-BINOL, see: Cram, D. J.; Helgeson, R. C.; Koga, K.; Kyba, E. P.; Madan, K.; Sousa, L.; Siegel, M. G.; Moreau, P.; Gokel, G. W.; Timko, J. M.; Sogah, D. Y. *J. Org. Chem.* **1978**, *43*, 2758-2772. Li, J.; Li, W.; Li, Y.; Li, Y.; Yang, S. *Org. Prep. Proced. Int.* **1995**, *27*, 685-690.

**(*R*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene**

(*R*)-BINOL (3.62 g, 12.6 mmol) in 30mL of DMF was added to a stirred suspension of NaH (60% dispersion in mineral oil; 3.54 g, 88.5 mmol) in 30 mL of DMF at 0 ℃. After stirring for 20 min, MOMCl (3.80 ml, 50.6 mmol) was added to the reaction mixture and the mixture was allowed to warm to rt. Water was added to the reaction mixture after 40 min, and the resulting mixture was extracted with ether. The combined extracts were washed with water (4 times), sat.$NaHCO_3$, and brine, and dried over $Na_2SO_4$. The solvent was removed under reduced pressure at rt. The crude

product was dried under vacuum at rt for 4h and used without further purification. y. quant. (colorless solid)

**(*R*)-3-formyl-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene**

To a solution of (*R*)-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene (2.77 g, 7.4 mmol) in 90 mL of THF was added 1.57 N *t*-BuLi in pentane (10.4 mL, 16.3 mmol) dropwise at -78 ℃. After stirring for 1 h, DMF (740 μL, 9.62 mmol) was added dropwise, after 1.5 h, additional DMF (285μL, 3.7 mmol) was added to the reaction mixture. The mixture was allowed to warm to rt slowly, quenched with sat. $NH_4Cl$ after stirring for 9 h (total reaction time), and extracted with AcOEt. The combined extracts were washed with water and brine, and dried over $Na_2SO_4$. The solvent was removed under reduced pressure at rt. Purification by flash chromatography ($SiO_2$, hexane / AcOEt = 12 : 1 ~ 5 : 1) gave the (*R*)-3-formyl-2,2'-bis(methoxmethyloxy)-1,1'-binaphthalene in 53% yield (1.57 g) as a yellow viscous oil. 31% (851 mg) of the starting material was also recovered.

IR (neat) 1690, 1241, 1153, 1048, 1013, 754 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 3.00 (s, 3 H), 3.16 (s, 3 H), 4.63 (d, $J$ = 6.2 Hz, 1 H), 4.75 (d, $J$ = 6.2 Hz, 1 H), 5.04 (d, $J$ = 7.0 Hz, 1 H), 5.14 (d, $J$ = 7.0 Hz, 1 H), 7.12 - 7.49 (m, 6 H), 7.61 (d, $J$ = 9.2 Hz, 1 H), 7.89 (br-d, $J$ = 8.0 Hz, 1 H), 7.96 - 8.07 (m, 2 H), 8.57 (s, 1 H), 10. 59 (s, 1 H); $^{13}$C NMR ($CDCl_3$) δ 55.98, 57. 11, 94.88, 100.14, 116.33, 119.44, 124.30, 125.16, 125.88, 125.97, 126.79, 126.92, 128.01, 129.00, 129.00, 129.65, 130.15, 130.15, 130.28, 131.00, 133.73, 136.98, 152. 88, 153.82, 191.18; MS *m/z* 402 ($M^+$), 296, 269, 45 (bp); HRMS calcd for $C_{25}H_{22}O_5$ ($M^+$) 402.1467, found ($M^+$) 402.1479; $[\alpha]_D^{25}$ +74.2° (*c* 1.28, $CHCl_3$)

**(*R*)-3-hydroxymethyl-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene**

$NaBH_4$ (139 mg, 3.67 mmol) was added to a solution of (*R*)-3-formyl-2,2'-bis(methoxmethyloxy)-1,1'-binaphthalene (1.477 g, 3.67 mmol) in MeOH (36 mL) at 0 ℃. After stirring for 15 min at 0 ℃, water was added to the reaction mixture. After being stirred for 30 min, the solvent was removed under reduced pressure at rt. To the mixture were added sat.$NH_4Cl$ and AcOEt, and the AcOEt extracts were washed with brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure at rt. Purification by flash chromatography ($SiO_2$, hexane / acetone = 5 : 1 ~ 4 : 1) gave (*R*)-3-hydroxymethyl-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene in 98% yield (1.46 g) as a colorless viscous oil.

IR (neat) 3442, 1240, 1150, 1033, 1012, 751 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 3.15 (s, 3 H), 3.25 (s, 3 H), 3.44 (dd, $J$ = 7.0, 7.0 Hz, 1 H), 4.47 (d, $J$ = 6.0 Hz, 1 H), 4.67 (d, $J$ = 6.0 Hz, 1 H), 4.89 (dd, $J$ = 7.0, 12.5 Hz, 1 H), 4.93 (dd, $J$ = 7.0, 12.5 Hz, 1 H), 5.03

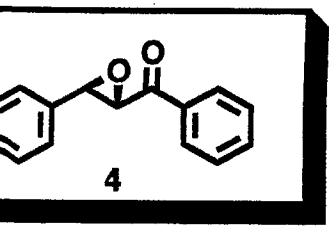
(d, $J$ = 7.0 Hz, 1 H), 5.11 (d, $J$ = 7.0 Hz, 1 H), 7.11 - 7.44 (m, 6 H), 7.59 (d, $J$ = 9.1 Hz, 1 H), 7.85 - 7.92 (m, 2 H), 7.97 (s, 1 H), 7.98 (d, $J$ = 9.1 Hz, 1 H); $^{13}$C-NMR ($CDCl_3$) δ 55.90, 56.98, 61.98, 94.81, 99.25, 116.41, 120.40, 124.19, 125.12, 125.28, 125.43, 125.59, 126.18, 126.79, 127.91, 127.96, 129.00, 129.63, 129.97, 131.00, 133.66, 133.73, 134.29, 152.69, 153.06; MS *m/z* 404 ($M^+$), 298, 84 (bp); HRMS calcd for $C_{25}H_{24}O_5$ ($M^+$) 404.1624, found ($M^+$) 404.1634; $[\alpha]_D^{24}$ +65.3° (*c* 0.79, $CHCl_3$)

**(*R*)-3-hydroxymethyl-1,1'-bi-2-naphthol (2)**

To a solution of (*R*)-3-hydroxymethyl-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene (1.46 g, 3.61 mmol) in 15 mL of THF was added 15 mL of *c*. HCl at 0 ℃. After stirring for 30 min the reaction mixture was extracted with AcOEt (2 times). The combined extracts were washed with water (2 times), sat.$NaHCO_3$ (2 times), and brine, and dried over $Na_2SO_4$. Purification by flash chromatography ($SiO_2$, $CH_2Cl_2$ / MeOH = 50 : 1 ~ 40 : 1) gave (*R*)-3-hydroxymethyl-1,1'-bi-2-naphthol in 96% yield (1.09 g) as a colorless amorphous solid.

IR ($CHCl_3$) 3528, 3372 $cm^{-1}$; $^1$H-NMR ($CDCl_3$) δ 2.47 (br-t, $J$ = 6.0 Hz, 1 H), 4.99 (br-d, $J$ = 6.0 Hz, 2 H), 5.10 (br-s, 1 H), 5.83 (br-s, 1 H), 7.10 - 7.17 (m, 2 H), 7.25 - 7.42 (m, 4 H), 7.38 (d, $J$ = 9.0 Hz, 1 H), 7.85 - 7.95 (m, 3 H), 7.97 (d, $J$ = 9.0 Hz , 1 H); $^{13}$C-NMR ($CDCl_3$) δ 62.88, 111.21, 111.86, 117.79, 123.94, 124.22, 124.26, 124.35, 127.35, 127.35, 128.34, 128.39, 128.66, 129.09, 129.10, 129.40, 131.25, 133.14, 133.42, 151.37, 152.58; MS *m/z* 316 ($M^+$), 298 (bp), 269, 253; HRMS calcd for $C_{21}H_{16}O_3$ ($M^+$) 316.1099, found ($M^+$) 316.1099; $[\alpha]_D^{25}$ +14.9° (*c* 0.57, $CHCl_3$)

$^1$H NMR ($CDCl_3$)



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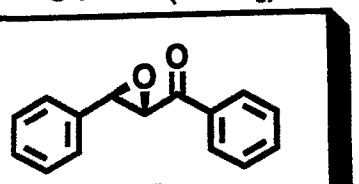

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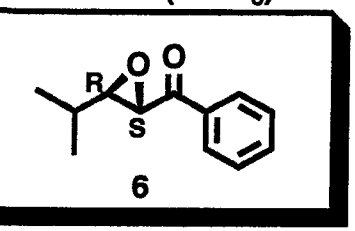


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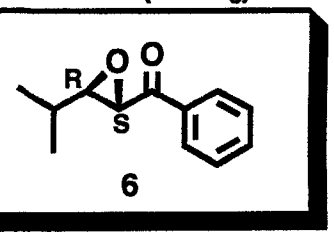


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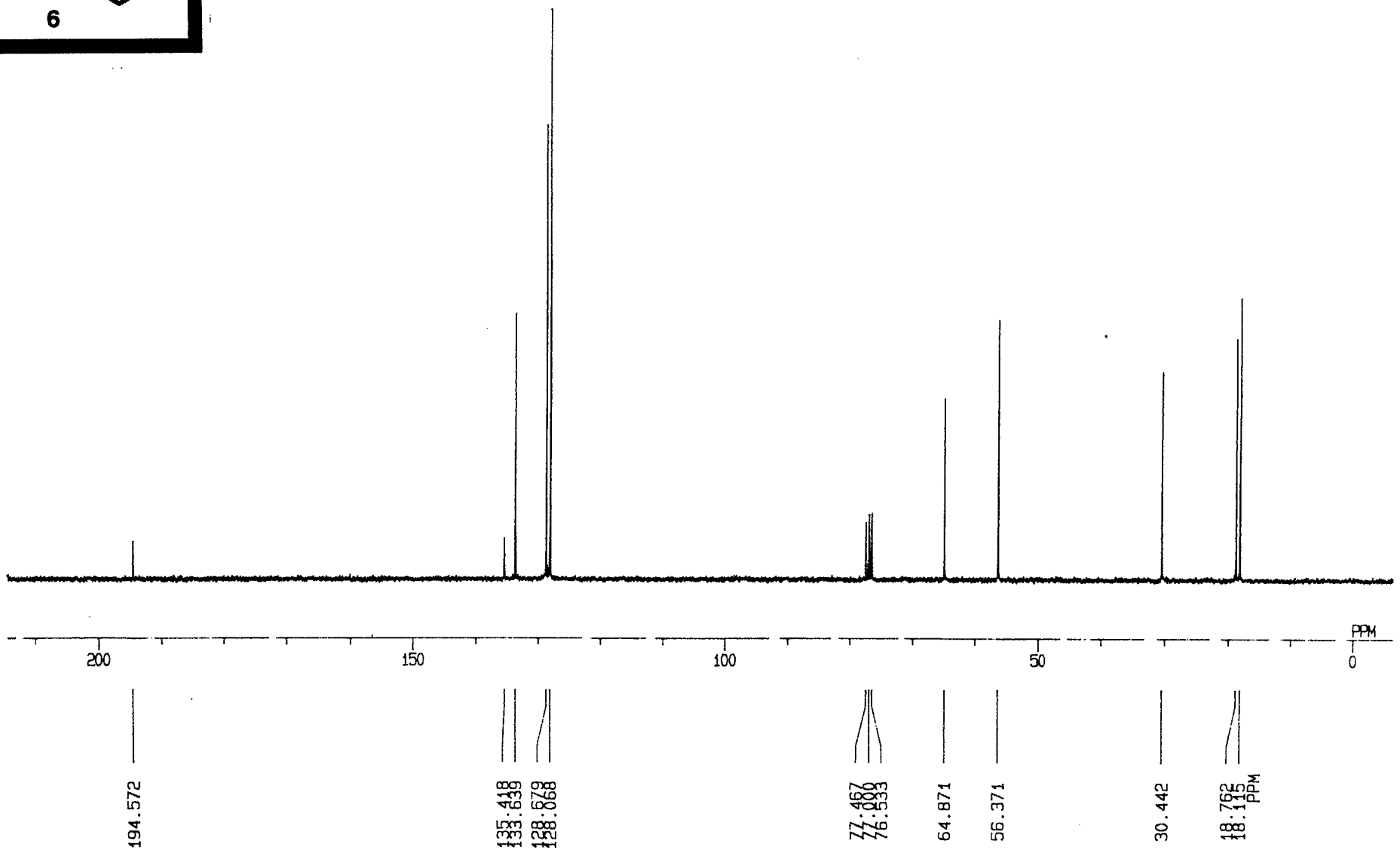
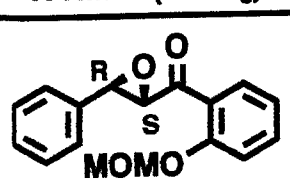
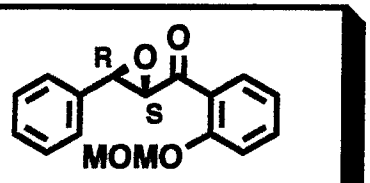


$^1$H NMR ($CDCl_3$)



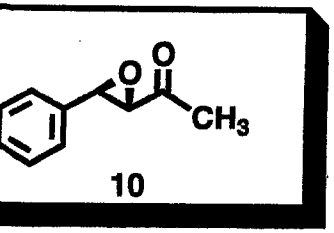

8

$^{13}C$ NMR ($CDCl_3$)



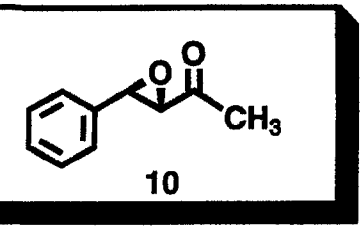

8

$^1$H NMR ($CDCl_3$)




10

$^{13}C$ NMR ($CDCl_3$)




10

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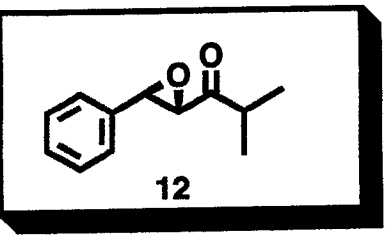
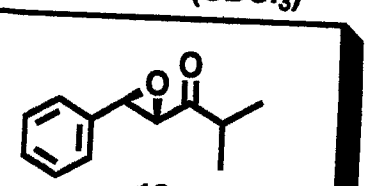
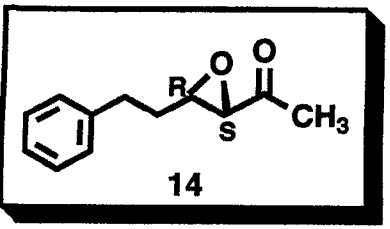


$^{13}C$ NMR ($CDCl_3$)



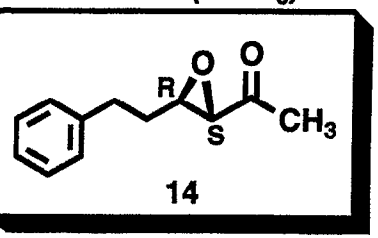
12

$^1$H NMR ($CDCl_3$)



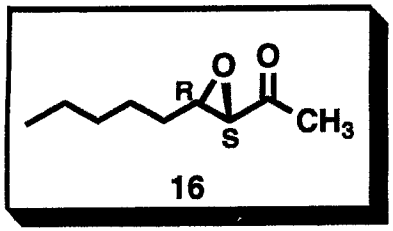

14

$^{13}C$ NMR ($CDCl_3$)



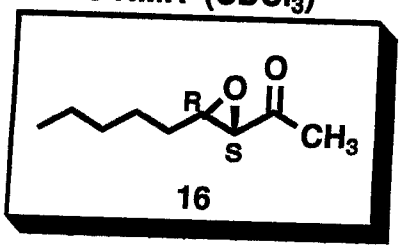

14

$^1$H NMR ($CDCl_3$)

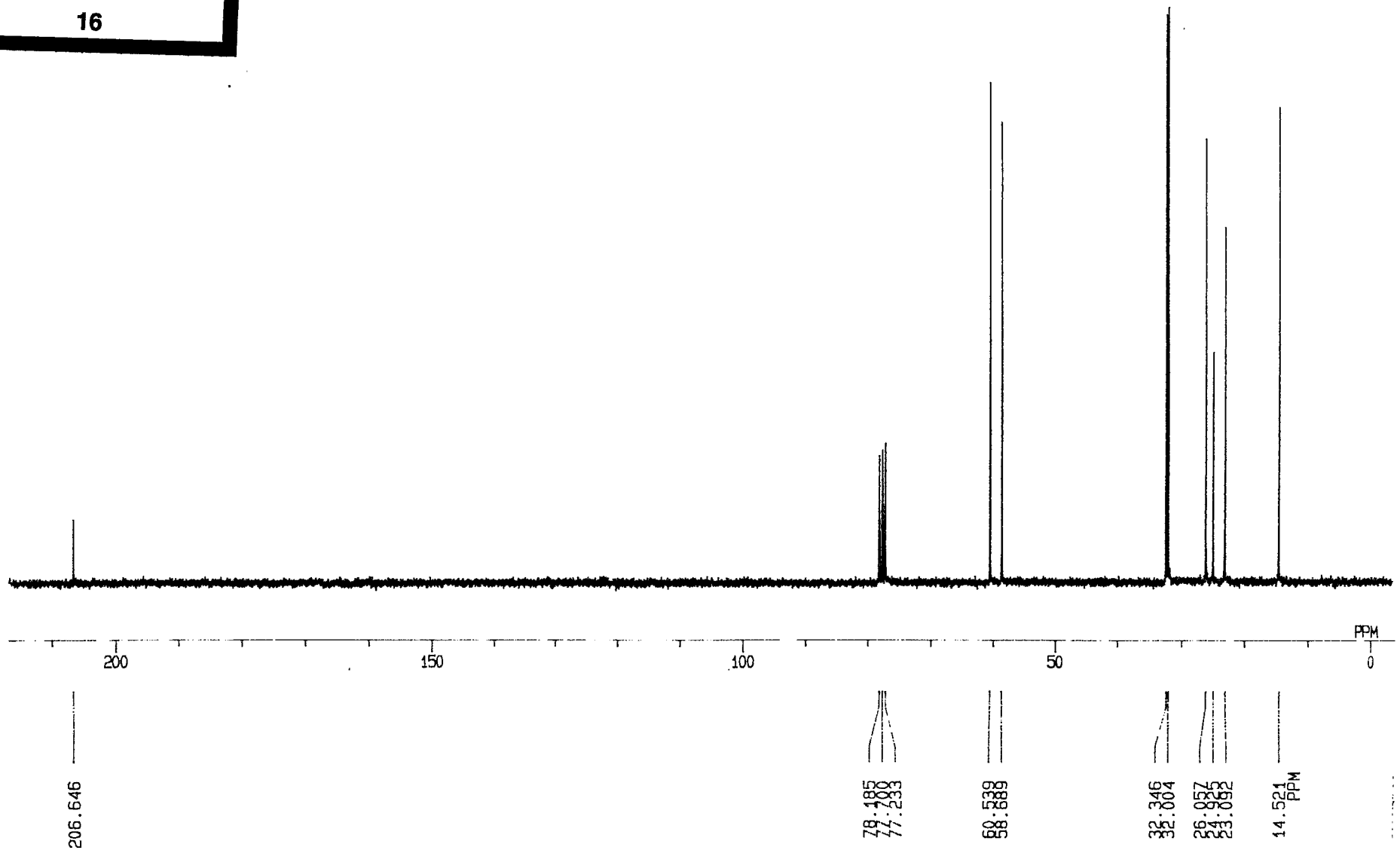


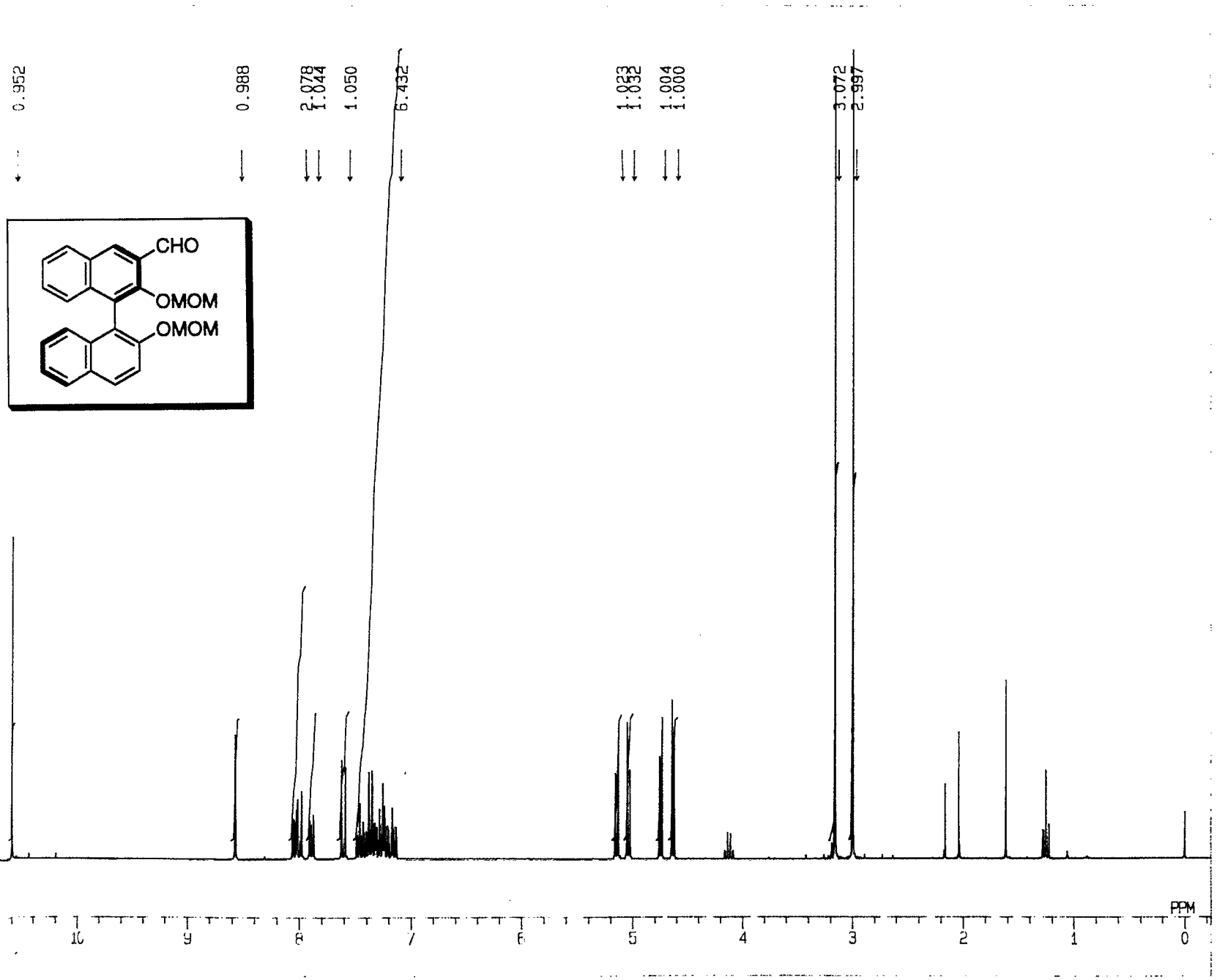

16

$^{13}C$ NMR ($CDCl_3$)




16

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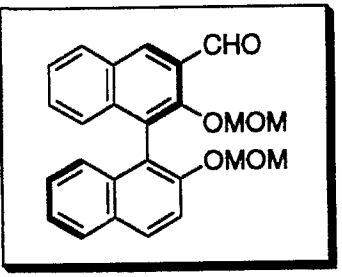
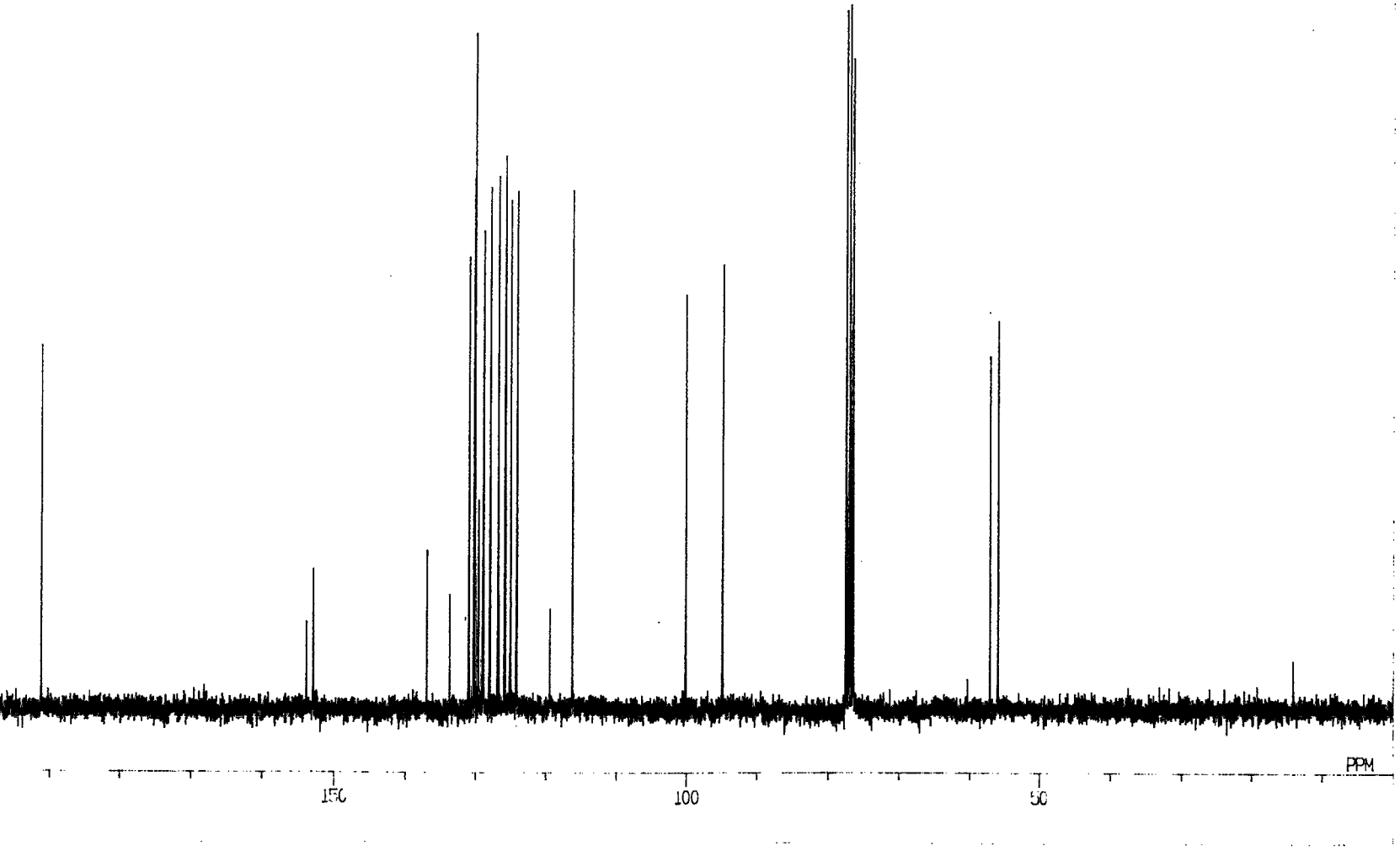
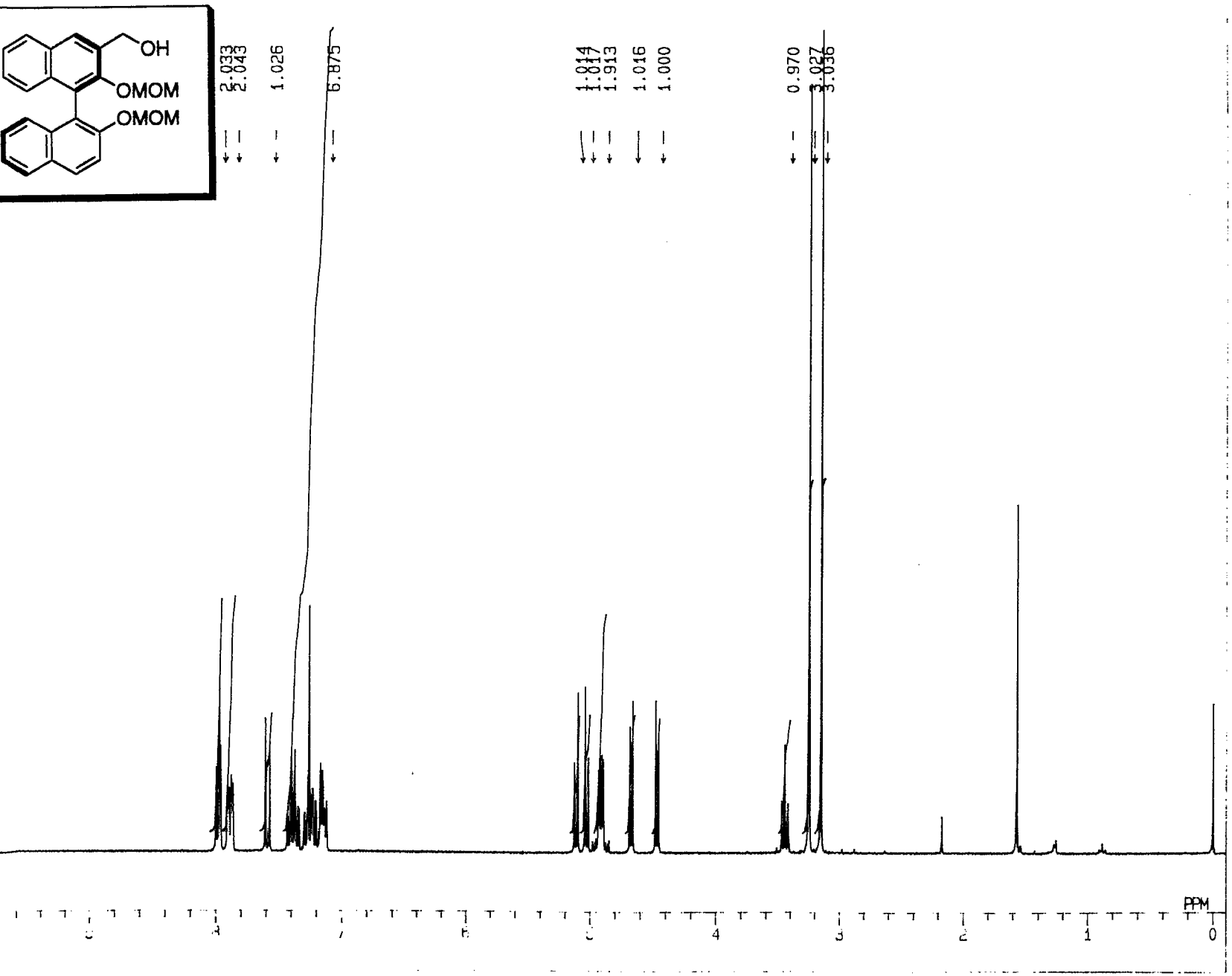
0.988
2.078
1.044
1.050
6.432
1.023
1.032
1.004
1.000
3.072
2.997
CHO
OMOM
OMOM
PPM
10
9
8
7
6
5
4
3
2
1
0


CHO
OMOM
OMOM


PPM
150
100
50


OH
OMOM
OMOM
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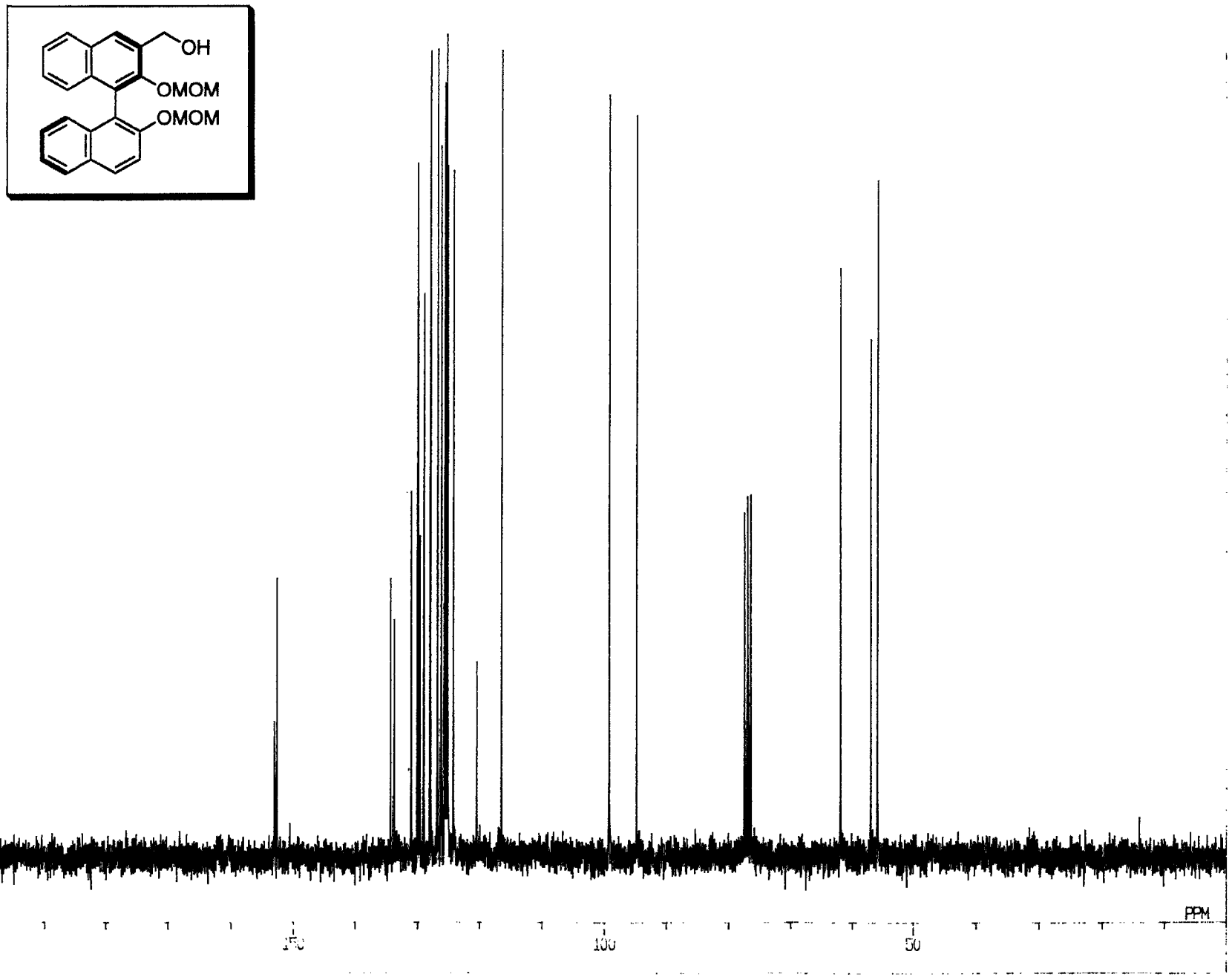
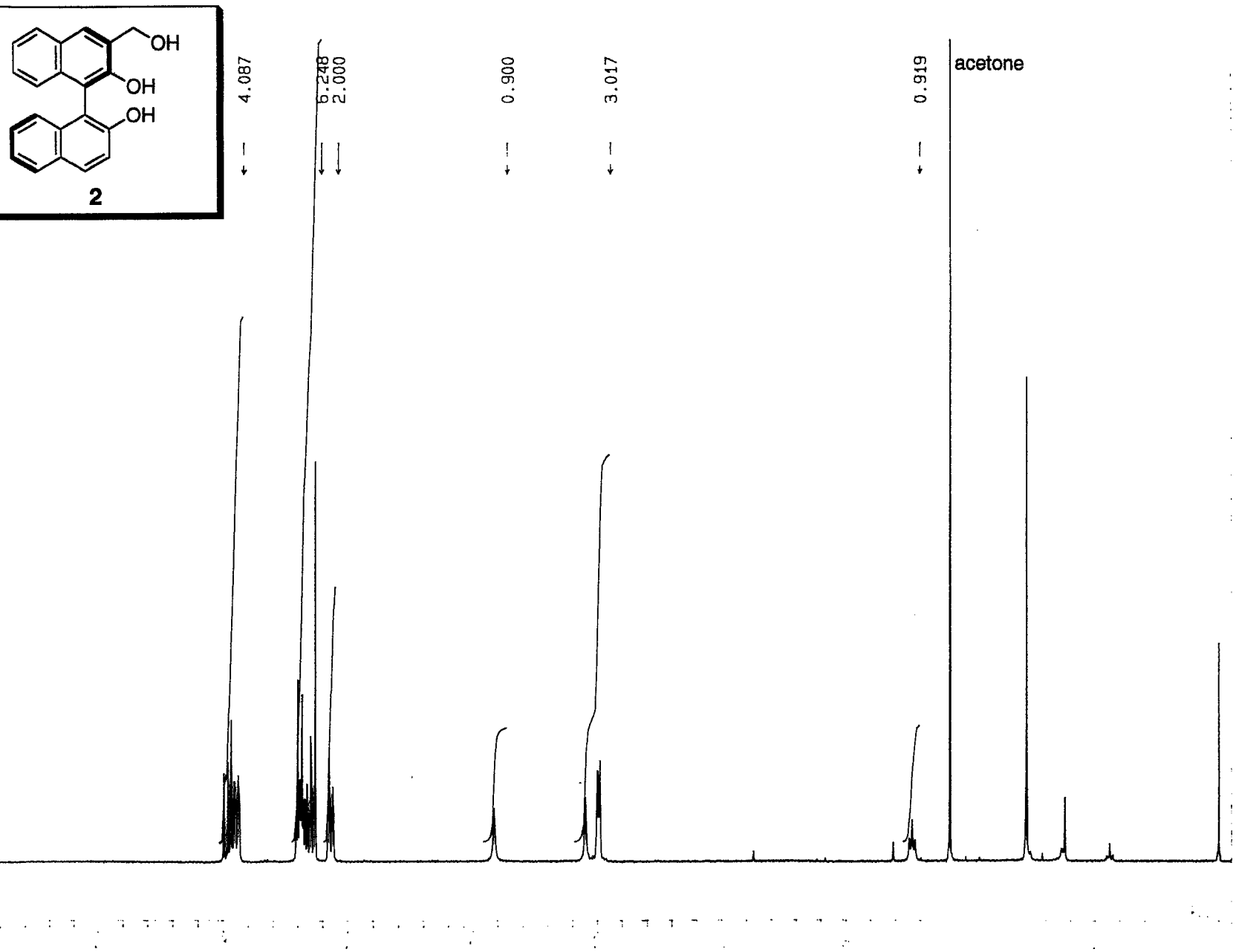
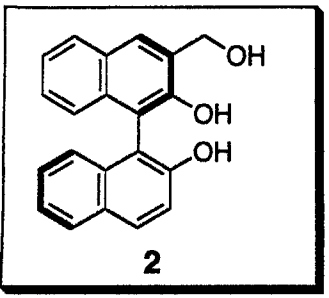
2.043
1.026
6.875
1.014
1.017
1.913
1.016
1.000
0.970
3.027
3.036
PPM
7
6
4
3
2
1
0


OH
OMOM
OMOM
PPM
150
100
50


OH
OH
OH
2
4.087
6.248
2.000
0.900
3.017
0.919
acetone




**2**