Supporting Information Available

Procedure for the preparation of (*S*)-(-)-[(-)-menthyloxy](4-methoxy-1-naphthyl)methylphenylsilane (*S*)-6. 4-Bromo-1-methoxynaphthalne was prepared according to the literature[1]. This compound was converted to methoxy(4-methoxy-1-naphthyl)methylphenylsilane *via* Grignard reaction with dimehoxymethylphenylsilane at 80°C for 15hr. The crude product was purified by distillation under reduced pressure (161-172°C/0.13mmHg, 88% yield). Methoxy(4-methoxy-1-naphthyl)methylphenylsilane (93.09 g, 256 mmol) was converted to diastereomeric [(-)-menthyloxy](4-methoxy-1-naphthyl)methylphenylsilnae (173-189°C/0.053mmHg, 78% yield) similarly to the reported method[2]. The diastereomeric mixture (86.76 g) was dissolved in pentane (350 mL) and chilled over night at –78°C, and formed crystalline were collected. Four times recrystallization from pentane gave (*S*)-(-)-[(-)-menthyloxy](4-methoxy-1-naphthyl)methylphenylsilane (36.50 g), and its optical purity was determined >99%d.e. by ^{1}H NMR and HPLC (CHIRALCEL OD®, *n*-hexane as an eluent, 0.4mL/min, 254nm): m.p. 112.2-112.8 °C; $[\alpha]^{22}_D$ = – 61.2 (*c*=1.00, cyclohexane); ^{1}H NMR (500MHz, $CDCl_3$) δ 0.47 and 0.79 (2d, *J*=7.0Hz, 6H), 0.75 (s, 3H), 0.81 (d, *J*=5.0Hz, 3H), 0.80-0.87 (m, 2H), 1.07-1.14 (m, 1H), 1.19-1.28 (m, 2H), 1.53-1.58 (m, 2H), 1.82-1.87 (m, 1H), 2.22-2.28 (m, 1H), 3.48-3.54 (m, 1H), 4.03 (s, 3H), 6.85 (d, *J*=7.5Hz, 1H), 7.30-7.36 (m, 4H), 7.39-7.42 (m, 1H), 7.59 (d, *J*=7.5Hz, 2H), 7.78 (d, *J*=7.5Hz, 1H), 7.99 (d, *J*=8.0Hz, 1H), 8.28 (d, *J*=9.0Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$) δ – 0.62, 15.3, 21.3, 22.3, 22.7, 25.1, 31.6, 34.5, 45.4, 50.3, 55.5, 73.5, 103.3, 122.4, 124.9, 126.87, 126.07, 126.3, 127.9, 128.9 129.5, 134.4, 135.9, 138.2, 138.6, 157.8; IR (KBr, cm^{-1}) 3071, 3046, 3012, 2954, 2916, 2882, 2866, 2842, 1588, 1423, 1128; EI-MS (m/e) 432 (M^+), 417 ([M-Me]$^+$), 405 ([M-OMe]$^+$), 277 ([M-NpOMe]$^+$), 158 (NpOMe$^+$).

Procedure for the preparation of (1*S*,3*S*)-1-(4-methoxy-1-naphthyl)-1,3-dimethyl-3-(1-naphthyl)-1,3-diphenyldisiloxane (1*S*,3*S*)-8. (*S*)-**6** (5.63 g, 13 mmol) was converted to (*S*)-potassium (4-methoxy-1-naphthyl)methylphenylsilanolate **7** in xylene (15 mL) *via* reaction with excess KOH (7.28 g, 130 mmol). To a mixture of (*R*)-methyl(1-naphthyl)phenylchlorosilane (2.79 g, 10 mmol) in xylene (15 mL), a solution of (*S*)-**7** in xylene (25 mL) was added dropwise during 3.0hr at 0°C. The reaction mixture was stirred at r.t. for 17hr. After the filtration, the filtrate was extracted with

Et_2O and washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent afforded a crude product, which was purified by silica gel column chromatography with 5 : 1 ~ 3 : 1 *n*-hexane : $CHCl_3$ as an eluent (2.62 g, 49% yield): m.p. 145.6-150.7 °C; $[\alpha]^{24}_D$ = – 3.8 (*c*=1.008, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$) δ 0.64 (s, 3H), 0.66 (s, 3H), 4.00 (s, 3H), 6.73 (d, *J*=7.7Hz, 1H), 7.16-7.23 (m, 2H), 7.23-7.41 (m, 9H), 7.49-7.52 (m, 4H), 7.66 (d, *J*=7.7Hz, 1H), 7.75 (d, *J*=9.0Hz, 1H), 7.81 (d, *J*=8.2Hz, 1H), 7.86-7.92 (m, 2H), 7.97 (d, *J*=8.5Hz, 1H), 8.28 (d, *J*=8.0Hz, 1H); ^{13}C NMR (75MHz, $CDCl_3$) δ 0.53, 0.59, 55.4, 103.2, 122.4, 124.9, 125.1, 125.5, 125.8, 125.9, 126.2, 126.4, 127.90, 127.91, 128.0, 128.7, 129.1, 129.6, 129.7, 130.6, 133.5, 134.2, 134.9 (overlap), 135.4, 135.7, 136.8, 137.9, 138.5, 138.8, 157.6; IR (KBr, cm^{-1}) 3068, 3052, 3013, 2991, 2953, 2839, 1587, 1507, 1428, 1114, 1028; EI-MS (m/e) 540 (M^+), 447 ([M-Me-Ph]$^+$), 397 ([M-Me-Np]$^+$), 367([M-Me-MeONp]$^+$), 224 ([M-2Me-Np-MeONp]$^+$).

(1) Konishi, H.; Aritomi, K.; Okano, T.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1989,** *62,* 591.

(2) Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964,** *86,* 3271.