Electronic Supporting Information for

"Stereoselective self-assembly of C_3-symmetric Ti(IV) amine triphenolate complexes"

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General remarks. Dry solvents were purchased from Fluka. Where 'degassed' solvents or solutions are noted, degassing was carried out by three freeze-pump-thaw cycles. Chemicals were purchased from Aldrich, Fluka or Acros and used without further purification. Ligand **1a** was synthesized as reported in literature.[1] If not mentioned, all reactions were carried out under nitrogen and the glassware was oven-dried prior to use. Molecular sieves (3 Å and 4 Å) were heated (160 °C) under vacuum (0.4 mbar) for 16 h. Flash chromatography (FC): silica gel 60 (40 µm), P.H. Stehlin A. G. T.L.C.: Merck SIL G/UV_{254}; detection by UV/VIS or by treatment with Ce-Mo-staining reagent made from $Ce(SO_4)_2$ (4.0 g), $H_3PMo_{12}0_{40}$ (8.0 g) and H_2SO_4 (80.0 g) in 320 ml water. Optical rotations were measured on a Perkin-Elmer 241 polarimeter, 1 dm cell, c in g/100ml. CD spectra were recorded on a Jasco J-715 instrument. IR spectra were recorded on a Perkin-Elmer FT-IR 1650. ^1H and $^{13}C\{^1H\}$ NMR spectra (referenced to tetramethylsilane or residual solvent peak) were recorded at 301 K on Bruker AC-250, 300, 400 or 500 MHz instruments. MS: ESI-MS experiments were carried out in positive mode on an Agilent Technologies LC/MSD Trap SL AGILENT instrument, mobile phase acetonitrile/formic acid 01-1%.. HRMS (ESI-TOF) were performed in an Applied Biosystems ESI-TOF Mariner™ Biospectrometry™ Workstation, acetonitrile/formic acid 0.1% as mobile phase with internal standards. In all cases, isotope patterns were in agreement with the theoretical ones.

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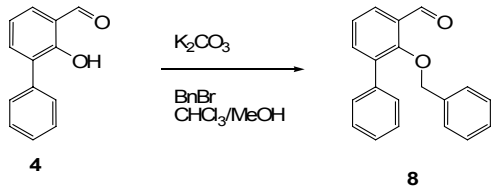
[1] L. J. Prins, M. Mba, A. Kolarović, G. Licini, *Tetrahedron Lett.* **2006**, *47*, 2735-2738.



4 8

2-Benzyloxy-biphenyl-3-carbaldehyde (8): A mixture of K_2CO_3 (9.6 g, 69.5 mmol, 4.4 eq.), 2-hydroxybiphenyl-3-carbaldehyde (**4**) (3.17 g, 16.0 mmol) and benzyl bromide (2.12 ml, 17.8 mmol) in CH_3CN (285 ml) was refluxed for 18 h. The mixture was filtered through Celite washed with ethyl acetate and the filtrate was concentrated under reduce pressure. The resulting yellow oil was purified by flash chromatography (petroleum ether/ ethyl acetate 10:1). Compound **1** was obtained as a white solid (2.04 g, 7.1 mmol, 87%).

Mp: 99 – 101 °C.

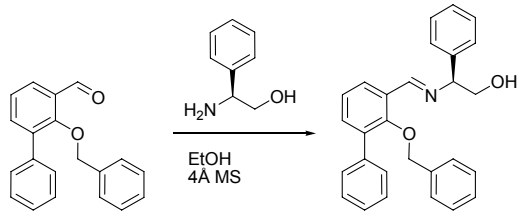
IR: (ν, KBr) 3344; 3061; 3032; 2878; 1953; 1901; 1878; 1804; 1683; 1583; 1573; 1497; 1453; 1433; 1373; 1298; 1274; 1245; 1220; 1205; 1173; 1072; 1026; 963; 918; 868; 803; 769; 743; 695 cm^{-1}.

^{1}H-NMR: (500 MHz, $CDCl_3$) δ 4.56 (2 H, *s*); 7.06 – 7.09 (2 H, *m*); 7.27 – 7.32 (4 H, *m*); 7.42 – 7.51 (3 H, *m*); 7.64 – 7.66 (3 H, *m*); 7.84 (1 H, *dd*, *J* = 7.8, 1.8); 10.35 (1 H, *s*).

^{13}C{^{1}H}-NMR: (125 MHz, $CDCl_3$) δ 77.1 (*C*H_2); 124.7 (*C*H); 127.4 (*C*H); 127.9 (*C*H); 128.49 (*C*H); 128.53 (2x*C*H); 128.6 (2x*C*H); 128.7 (2x*C*H); 129.2 (2x*C*H); 130.2 (*C*); 135.5 (*C*); 136.4 (*C*); 137.2 (*C*); 137.3 (*C*H); 159.2 (*C*); 190.3 (*C*H).

MS (ESI): 306.3 $[M + NH_4]^+$.

HR-MS (ESI): calcd for $C_{20}H_{17}O_2$: 303.1254; found 303.1252.



8 (*S*)-5

(–)-(*S*)-2-{[1-(2-Benzyloxybipheny-3-yl)-meth-(*E*)-ylidene]-amino}-2-phenyl-ethanol ((–)-(*S*)-5). A solution of (*S*)-(+)-2-amino-2-phenylethanol (303 mg, 2.21 mmol) and 2-methoxybenzaldehyde (8) (637 mg, 1 eq., 2.21 mmol) in ethanol (5 ml) was refluxed for 30

min in the presence of activated 4 Å molecular sieve. The hot reaction mixture was filtered over Celite and then cooled to r.t.. The product crystallized upon standing over night. The brownish crystals were filtered and dried *in vacuo* to give 798 mg of the imine 5 (1.95 mmol, 88%).

Mp: 97 – 99 °C.

$[\alpha]_D^{20}$: -55.6 (c = 0.4 in CH_2Cl_2).

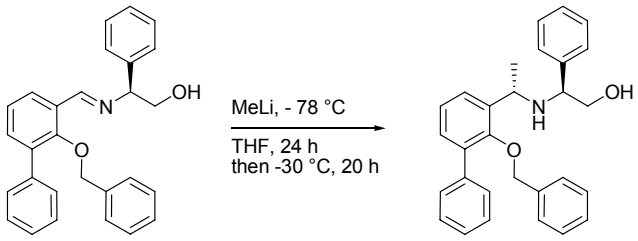
IR: (ν, KBr) 3339 (broad, OH); 3061; 3030; 2961; 2927; 2868; 1950; 1876; 1808; 1663; 1601; 1581; 1497; 1453; 1429; 1375; 1307; 1256; 1201; 1173; 1156; 1072; 1026; 981; 911; 865; 803; 761; 734; 698 cm^{-1}.

^{1}H-NMR: (500 MHz, $CDCl_3$) δ 3.90 (1 H, *dd*, *J* = 11.1, 4.6); 3.96 (1 H, *dd*, *J* = 11.1, 8.2); 4.38 – 4.49 (3 H, *m*); 6.97 – 7.01 (2 H, *m*); 7.23 – 7.32 (3 H, *m*); 7.36 – 7.50 (10 H, *m*); 7.62 – 7.64 (2 H, *m*); 8.11 (1H, *dd*, *J* = 7.75, 1.85); 8.74 (1 H, *s*).

^{13}C{^{1}H}-NMR: (125 MHz, $CDCl_3$) δ 67.7 (*C*H_2); 75.6 (*C*H); 76.1 (*C*H); 124.6 (*C*H); 126.88 (*C*H); 127.4 (*C*H); 127.48 (*C*H); 127.52 (2x*C*H); 128.2 (*C*H); 128.35 (2x*C*H); 128.42 (2x*C*H); 128.57 (2x*C*H); 128.63 (2x*C*H); 129.3 (2x*C*H); 130.0 (*C*); 133.8 (*C*H); 135.8 (*C*); 136.1 (*C*); 137.9 (*C*); 140.7 (*C*); 156.3 (*C*); 159.1 (*C*H).

MS (ESI): 408.4 $[M + H]^+$

HR-MS (ESI): calcd for $C_{28}H_{26}NO_2$: 408.1963; found 408.1965.



(*S*)-**5** (*S,S*)-**6**

(+)-(*S*)-2-[(*S*)-1-(2-Benzyloxybiphenyl-3-yl)-ethylamino]-2-phenylethanol ((+)-(*S,S*)-6). Methyl-lithium (4.3 ml of 1.5 M in Et_2O, 4 eq., 6.4 mmol) was added dropwise to a magnetically stirred solution of (*S*)-**5** (637 mg, 1.61 mmol) in dry, degassed THF (30 ml) at -78°C under N_2. This mixture was stirred for 24 h at -78 °C. It was then brought to -30 °C over a 4 h period and stirring was continued for an additional 20 h. The reaction was quenched at -30 °C by the addition of sat. aq. NH_4Cl and was allowed to warm to 20 °C. The organic layer was separated. After evaporation of the solvent the residue was taken up in Et_2O (20 ml), and washed with sat. aq. $NaHCO_3$ (3 x 10 ml). The combined organic layers were

dried over Na_2SO_4 and concentrated *in vacuo* to give an orange oil. Purification by flash chromatography (CH_2Cl_2/MeOH/Et_3N 98:1:1) gave amine **3** as a pale yellow oil. The other diastereoisomer could not be detected by ^{1}H-NMR (de >95%).

$[\alpha]_D^{20}$: +45.0 (c = 0.1 in CH_2Cl_2).

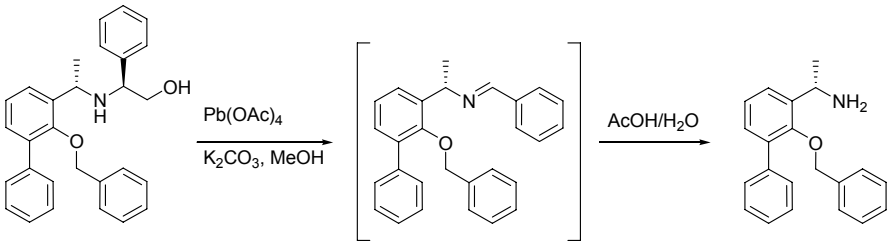
IR: (ν, KBr) 3557; 3326; 3062; 3030; 2965; 2928; 2867; 1951; 1881; 1806; 1714; 1655; 1601; 1584; 1497; 1454; 1430; 1376; 1328; 1309; 1255; 1201; 1071; 1027; 980; 914; 865; 803; 760; 734; 699 cm^{-1}.

^{1}H-NMR: (500 MHz, $CDCl_3$) δ 1.37 (3 H, *d*, *J* = 6.5); 3.56 (1 H, *dd*, *J* = 10.7, 7.9); 3.75 (1 H, *dd*, *J* = 10.7, 4.7); 3.91 (1 H, *dd*, *J* = 7.9, 4.7); 4.17 (1 H, *d*, *J* = 10.4); 4.22 (1 H, *d*, *J* = 10.4); 4.31 (1 H, *q*, *J* = 6.6); 6.77 – 6.80 (2 H, *m*); 7.18 – 7.44 (14 H, *m*); 7.57 – 7.60 (2 H, *m*).

^{13}C{^{1}H}-NMR: (125 MHz, $CDCl_3$) δ 22.3 (*C*H_3); 48.6 (*C*H); 61.6 (*C*H); 66.0 (*C*H_2); 75.0 (*C*H_2); 124.7 (*C*H); 126.4 (*C*H); 127.15 (2x*C*H); 127.23 (*C*H); 127.5 (*C*H); 127.8 (*C*H); 128.1 (2x*C*H); 128.2 (2x*C*H); 128.3 (2x*C*H); 128.6 (2x*C*H); 129.2 (2x*C*H); 129.9 (*C*H); 135.3 (*C*); 135.8 (*C*); 136.7 (*C*); 138.7 (*C*); 139.3 (*C*); 140.9 (*C*); 153.2 (*C*H).

MS (ESI): 424.3 $[M + H]^+$.

HRMS: calcd for $C_{29}H_{30}NO_2$: 424.2276; found 424.2278.



(*S*,*S*)-**6** (S)-**7**

(+)-(*S*)-1-(2-Benzyloxybiphenyl-3-yl)-ethylamine ((+)-(*S*)-7): A 250 ml flask was charged with anhydrous K_2CO_3 (124.5 mg, 6 eq., 0.9 mmol) and methanol (0.3 ml). The resulting white suspension was cooled to 0 °C with an ice bath. A solution of (*S*,*S*)-**6** (63 mg, 0.15 mmol) in CH_2Cl_2 (0.6 ml) and a solution of $Pb(OAc)_4$ (78.6 mg, 1.2 eq., 0.18 mmol) in CH_2Cl_2 (0.6 ml) were simultaneously added dropwise over a 12 min period. After 10 min, the reaction was hydrolysed with sat. aq. Na_2CO_3 (0.5 ml). The mixture was filtered through Celite and washed with CH_2Cl_2 and sat. aq. Na_2CO_3. The combined aqueous phases were extracted with CH_2Cl_2. The combined organic layers were dried over K_2CO_3 and the solvents were removed *in vacuo*.

The crude imine was taken up in THF (1 ml) and hydrolysed with an aq. AcOH solution (30%, 1 ml) for 20 h at 20 °C. The mixture was concentrated under vacuum and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with an aq. AcOH solution (30%). The combined aqueous layers were cooled to 0 °C, brought to pH 14 by addition of NaOH (6 N) and extracted with Et_2O. The combined organic layers were dried (K_2CO_3) and concentrated. The crude amine was dissolved in Et_2O and a commercial solution of HCl in Et_2O (0.5 M) was added until no more precipitation was observed. The precipitate was filtered and washed with cold hexane and dried to afford the ammonium salt **7·HCl** (30.6 mg, 0.10 mmol, 60%). A sample was crystallized from cyclohexane/ethyl acetate (4:1). The enantiomeric purity of the free amine was determined by chiral HPLC (Chiralcel OD-H, hexane/2-propanol 97:3, 1 ml/min: 10.0 min (minor, *R*), 13.2 min (major, *S*): ee 95%.

Mp: 118 – 121 °C.

$[\alpha]_D^{20}$: +22.7 (c = 1.9 in CH_2Cl_2).

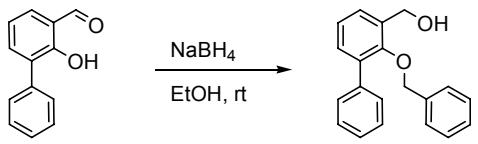
IR: (ν, KBr) 3024 (broad); 2873; 1981; 1943; 1881; 1803; 1603; 1520; 1598; 1455; 1432; 1367; 1266; 1202; 1112; 1070; 973; 917; 865; 804; 757; 696 cm^{-1}.

^{1}H-NMR: (300 MHz, CD_3OD) δ 1.47 (3 H, *d*, *J* = 6.9); 4.41 (1 H, *d*, *J* = 10.8); 4.54 (1 H, *d*, *J* = 10.9); 4.70 (1 H, *q*, *J* = 7.0); 7.1 – 7.2 (2 H, *m*); 7.2 – 7.6 (9 H, *m*); 7.66 (2 H, *bd, J* = 6.8).

^{13}C{^{1}H}- NMR: (100 MHz, CD_3OD) δ 19.7 (*C*H_3); 46.3 (*C*H); 76.5 (*C*H_2); 123.8 (*C*H); 126.3 (*C*H); 126.4 (*C*H); 129.0 (*C* and *C*H); 129.6 (*C* and *C*H); 129.7 (*C*H); 129.8 (4x*C*H); 130.2 (2x*C*H); 133.2 (*C*); 133.5 (*C*H); 139.5 (*C*); 154.8 (*C*).

MS (ESI): 304.4 $[M + H]^+$.

HRMS (ESI): calculated for $C_{21}H_{22}NO$: 304.1701 found 304.1703.



8 **9**

1-(2-Benzyloxybiphenyl-3-yl)-methanol (9). Aldehyde **8** (500 g, 1.73 mmol) was dissolved in ethanol (10 ml) and $NaBH_4$ (78.7 mg, 2.08 mmol) was added. The resulting mixture was stirred at r.t. for 2.5 hr. (TLC EA/p. ether = 1/4), concentrated to dryness, taken in Et_2O (20 ml) and washed with 10% NaOH (20 ml). The layers were separated and the aqueous one extracted with Et_2O (2 x 20 ml). The combined organic phases were washed with brine, dried

over $MgSO_4$ and concentrated. Compound **9** was obtained as a white solid that was used without further purifications.

Mp: 69 -70 °C.

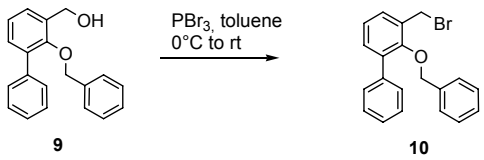
IR: (ν, KBr) 3509, 3052, 3028, 2940, 2884, 1454, 1433, 1204, 1004, 982, 804, 766, 749, 696 cm^{-1}.

^{1}H-NMR: (250 MHz, $CDCl_3$) δ 4.55 (2 H, *s*), 4.78 (2 H, *s*), 7.20 – 7.55 (*m,* 11 H), 7.74 (*d*, 2 H, *J* = 7.2).

^{13}C{^{1}H}-NMR: (62.9 MHz, $CDCl_3$) δ 62.1 (CH_2), 75.4 (CH_2), 124.8 (*C*H), 127.6 (*C*H), 128.5 (*C*H), 128.6 (*C*H), 128.7 (2x*C*H), 128.8 (*C*H), 129.4 (*C*H), 131.1 (*CH*), 135.0 (*C*), 135.4 (*C*), 136.9 (*C*), 138.6 (*C*), 154.5 (*C*).

MS (ESI): 291.1 $[M + H]^+$, 313.2 $[M + Na]^+$, 329.1 $[M + K]^+$.

HRMS (ESI): calcd for $C_{20}H_{19}O_2$: 291.1380; found 291.1383.



9 **10**

1-(2-Benzyloxybiphenyl-3-yl)-methylbromide (10). To a solution of alcohol 1-(2-Benzyloxybiphenyl-3-yl)-methanol (300 mg, 1.03 mmol) in dry toluene (5 ml) at 0 ºC and under N_2 atmosphere, was added dropwise a solution of. PBr_3 (110 µl, 1.13 mmol) in toluene (2 ml). The mixture was stirred at 0 °C for 20 minutes, then allowed to r.t. and stirred for another 30 minutes. The solution was diluted with ice water (5 ml) and stirred vigorously for 2-3 minutes; then diluted with $CHCl_3$. The organic phase was separated, washed with brine (10 ml), dried over $MgSO_4$ and concentrated. The crude was purified by column chromatography (petroleum ether / AcOEt 9:1) to give compound **10** as a white solid (85 % two steps).

Mp: 84-85 °C.

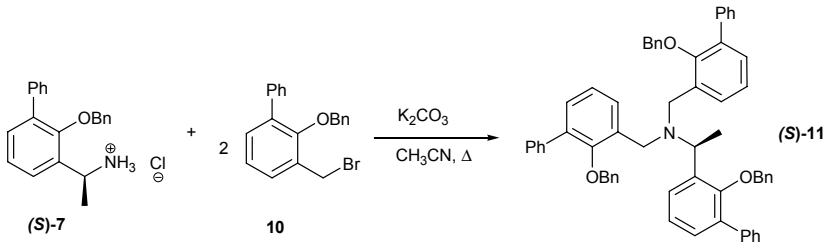
IR: (ν, KBr) 3430, 3050, 3027, 2951, 2880, 1454, 1375, 1219, 1072, 1066, 976, 913, 766, 695 cm^{-1}.

^{1}H-NMR: (250 MHz, $CDCl_3$) δ 4.55 (2 H, *s*) 4.63 (2 H, *s*), 7.16 – 7.45 (11 H, *m*), 7.62 (2 H, *d, J* = 6.9).

^{13}C{^{1}H}-NMR: (75 MHz, $CDCl_3$) δ 27.5 (*C*H_2), 73.5 (*C*H_2), 123.5 (*C*H), 126.4 (*C*H), 127.0 (*C*H), 127.2 (*C*H), 127.3 (*C*H), 127.4 (*C*H), 128.0 (*C*H), 129.3 (*C*H), 130.8 (*C*H), 130.9 (*C*), 134.6 (*C*), 135.5 (*C*), 137.0 (*C*), 153.3 (*C*).

MS (ESI): 353.1 $[M + H]^+$.

HR-MS (ESI): calcd for $C_{20}H_{18}OBr$: 353.0536; found 353.0538.



***tri-O*-Benzyl protected-(*S*)-1b.** A mixture of (*S*)-**7** (70 mg, 0.205 mmol), 1-(2-Benzyloxybiphenyl-3-yl)-methylbromide (160 mg, 0.453 mmol, 2.2 eq.) and K_2CO_3 (142 mg, 1.03 mmol) in dry MeCN (4 ml) was refluxed for 24h. The mixture was filtered over celite washing with AcOEt (5 ml), concentrated and purified by column chromatography (petroleum ether /AcOEt /Et_3N 50:5:1) to give the *tri-O*-benzyl protected-(*S*)-**11** as a colourless oil. (90%).

$[\alpha]_D^{20}$: +68.1 (c = 0.1 in CH_2Cl_2).

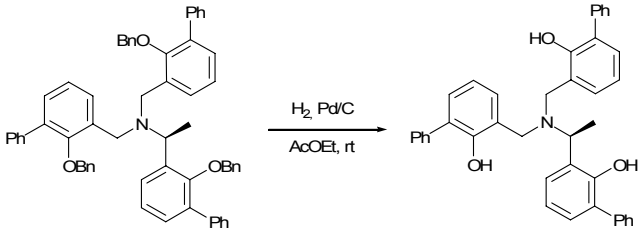
IR: (ν, KBr) 3060, 3030, 2921, 2861, 1592, 1495, 1469, 1452, 1382, 1271, 1243, 1211, 1172, 909, 867, 735, 697 cm^{-1}.

^{1}H-NMR: (300MHz, $CDCl_3$) δ 1.39 (3 H, *d*, *J* = 7.0), 3.82 (2 H, *d, J* =15.6), 3.89 (2 H, *d*, *J* = 15.6), 4.13 (2 H, *s*), 4.15 (2 H, *d*, *J* =10.5), 4.27 (2 H, *d*, *J* = 10.5 Hz), 4.54 (1 H, quintet, *J* = 7.0), 6.58 (2 H, *d*, *J* = 7.6), 6.90 – 6.94 (4 H, *m*), 7.02 – 7.40 (24 H, *m*), 7.47 – 7.68 (7 H, *m*), 7.78 – 7.81 (2 H, m).

^{13}C{^{1}H}-NMR: (75 MHz, $CDCl_3$) δ 19.3 (*C*H_3), 49.0 (2x*C*H_2), 52.5 (*C*H), 74.2 (2x*C*H_2), 75.2 (*C*H_2), 123.8 (2x*C*H), 124.1 (2x*C*H), 125.1 (*C*H), 126.8 (2x*C*H), 127.5 (*C*H), 127.6 (4x*C*H), 127.8 (2x*C*H), 127.97 (4x*C*H), 128.03 (2x*C*H), 128.1 (2x*C*H), 128.2 (4x*C*H) , 128.4 (2x*C*H), 128.8 (2x*C*H), 128.9 (2x*C*H), 129.2 (4x*C*H), 129.3 (2x*C*H), 129.4 (*C*H), 134.6 (2x*C*), 134.7 (2x*C*), 135.4 (*C*), 135.8 (*C*), 136.3 (*C*), 136.9 (2x*C*), 138.7 (2x*C*), 138.8 (*C*), 154.0 (*C*); 154.5 (2x*C*) .

MS (ESI): 848.7 $[M + H]^+$.

HR-MS (ESI): calcd for $C_{61}H_{54}NO_3$: 848.4098; found 848.4097.



(S)-1b

Ligand (*S*)-1b The *O*-benzyl protected-(*S*)-**11** (170 mg, 0.2 mmol) was dissolved in ethyl acetate (15 ml) and 10% Pd/C (25 mg) was added. The mixture was stirred under H_2-atmosphere for 2h. The mixture was filtered through Celite and concentrated under vacuum. Purification by preparative TLC (petroleum ether/AcOEt = 9:1) gave the pure ligand (*S*)-**1b** as a colorless oil (85 %).

$[\alpha]_D^{20}$: -17.0 (c = 0.1 in CH_2Cl_2).

IR: (ν, KBr) 3422, 3056, 3033, 2972, 2926, 1608, 1590, 1497, 1460, 1431, 1382, 1222, 1082, 827, 755, 699 cm^{-1}.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ 7.52-7.46 (2H, m), 7.44 – 7.30 (13H, m), 7.25 – 7.15 (2H, m), 7.11 – 7.05 (4H, m), 6.90 (1H, t, *J* = 7.6 Hz), 6.80 (2H, t, *J* = 7.6 Hz), 4.53 (1H, q, *J* = 6.7 Hz), 3.90 (6H, s), 1.62 (3H, d, *J* = 6.7 Hz).

^{13}C{^{1}H}-NMR: (75 MHz, $CDCl_3$) δ 19.4 (*C*H_3), 50.2 (2x*C*H_2), 55.0 (*C*H), 120.1 (2x*C*H), 123.5 (*C*), 125.3 (2x*C*), 125.4 (*C*H), 127.1 (*C*H), 127.3 (2x*C*H), 128.2 (2x*C*), 128.5 (2x*C*H), 128.6 (2x*C*H), 128.7 (4x*C*H), 128.8 (*C*), 128.9 (*C*H), 129.0 (6x*C*H), 129.6 (*C*H), 130.3 (2x*C*H), 136.9 (2x*C*), 137.2 (*C*), 152.0 (*C*), 152.5 (2x*C*).

MS (ESI): 578.1 $[M + H]^+$.

HR-MS (ESI): calcd for $C_{40}H_{36}NO_3$: 578.2690; found 578.2693.

Synthesis of Ti(IV) complexes.

Complexes **2** were prepared in a glovebox by mixing homogeneous solutions of the corresponding ligands **1** (0.10 M) and Ti(O*i*-Pr)$_4$ (0.18 M) in dry $CDCl_3$ in a 1:1 ratio to a final concentration 0.01 M of the complex. Bright yellow solutions were obtained which were used without further purifications and without removing the three equivalents of *i*-PrOH released from the metal precursor. In all cases resonances relative to free *iso*-propanol released in the reaction were present in the NMR spectra: ^{1}H-NMR (300 MHz, $CDCl_3$): 4.04 (1H, *hept*, *J* = 6.1 Hz), 1.22 (6H, *d*, *J* = 6.1 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 64.5 (*C*H),

25.1 (CH_3). In the case of complex **2a** (R=H) addition of water allows the complete formation of complex **3**, which crystallizes out of the solution. Filtration and washing with cold benzene allows the recovery of complex **3** as a yellow crystalline compound (87%).

Complex 2a.

^{1}H NMR: (300 MHz, $CDCl_3$) δ 1.02 (6 H, *d*, *J* = 6.0), 3.62 (6 H, *bs*), 4.64 (1 H, hept, *J* = 6.0), 6.91 (3 H, *m*), 7.10 (3 H, *m*), 7.25 – 7.41 (12 H, *m*), 7.64 – 7.68 (6 H, *m*).

Complex (*S*)**-2b.**

^{1}H NMR: (300 MHz, $CDCl_3$) δ 0.96 (3 H, *d*, *J* = 6.0), 0.98 (3 H, *d*, *J* = 6.0), 1.62 (3 H, *d*, *J* = 6.6), 3.40 (2 H, *m*), 3.75 (1 H, *d*, *J* = 13.5), 3.90 (1 H, *d*, *J* = 14.1), 4.17 (1 H, *q*, *J* = 6.6), 4.58 (1H, *hept*, *J* = 6.0), 6.87 – 7.00 (4 H, *m*), 7.07 – 7.17 (2 H, *m*), 7.25 – 7.41 (12 H, *m*), 7.62 – 7.69 (6 H, *m*).

µ-oxo complex 3.

Mp > 300 °C.

IR: 3433, 3054, 2882, 1585, 1455, 1424, 1269, 1240, 1065, 874, 753, 694.

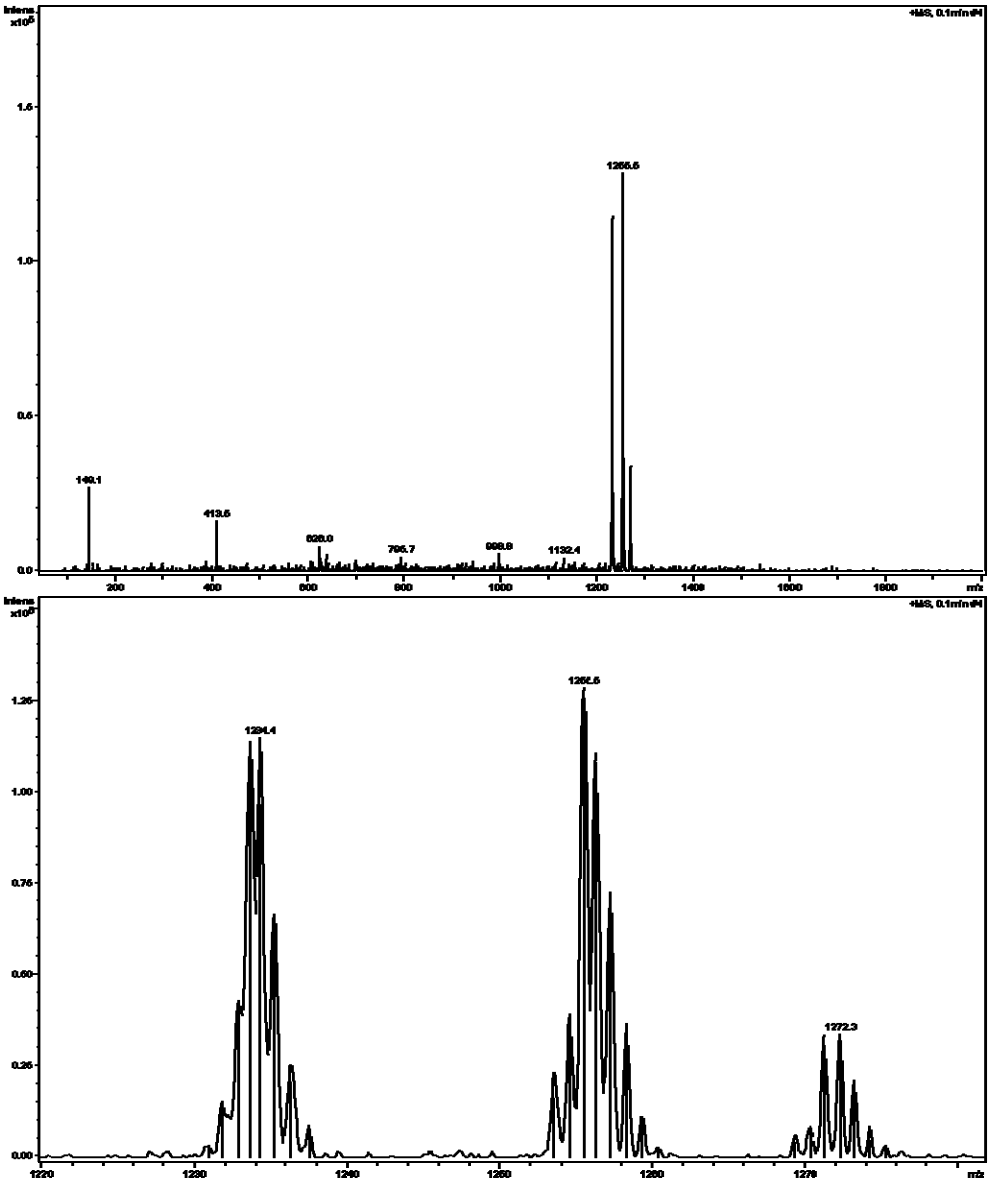
^{1}H NMR: (300 MHz, $CDCl_3$) δ 3.28 (6 H, *d*, *J* = 13.9), 4.36 (6 H, *d*, *J* = 13.9 Hz), 6.23 (6 H, *t*, *J* = 7.3), 6.58 (12 H, *t*, *J* = 7.4), 6.68 (12 H, *d*, *J* = 7.4), 6.96 (6 H, *t*, J = 7.4), 7.19 – 7.26 (12 H, *m*).

^{13}C{^{1}H}-NMR: (75 MHz, DMSO) δ 60.8 (6xCH_2), 118.6 (6x*C*), 126.5 (6x*C*H), 127.0 (6x*C*H), 127.1(6x*C*H), 127.8 (12x*C*H), 129.2 (12x*C*H), 129.4 (6x*C*), 129.8 (6x*C*H), 139.4 (6x*C*), 160.0 (6x*C*).

MS (ESI): 1233. 4 $[M + H]^+$; 1255. 5 $[M + Na]^+$; 1271.3 $[M + K]^+$.

HRMS: calcd for $C_{78}H_{61}N_2O_7Ti_2$: 1233;3451 found 1233.3454.

ESI-MS of 3. 1μM solution in acetonitrile, acetonitrile + 0.1 % HCOOH as mobile phase



CD spectra.

Recorded in CH_2Cl_2. (*S*)-**1b** 0.00052M, (*S*)-**2b** 0.000347 M.