

**Supporting Information**

**Titanium Isopropoxide Complexes of a Series of Sterically Demanding Aryloxo Based  $[N_2O_2]^{2-}$  Ligands as Precatalysts for Ethylene Polymerization**

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Reliance Industries Limited

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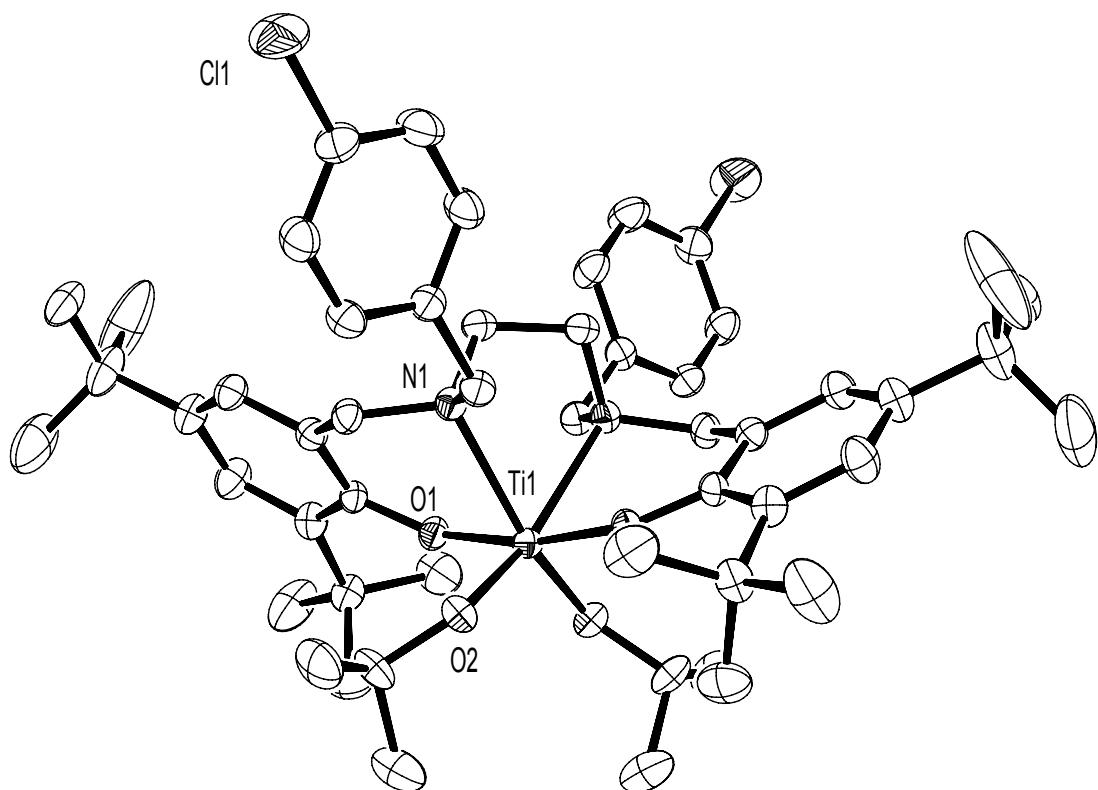
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Washington DC 20059, USA.

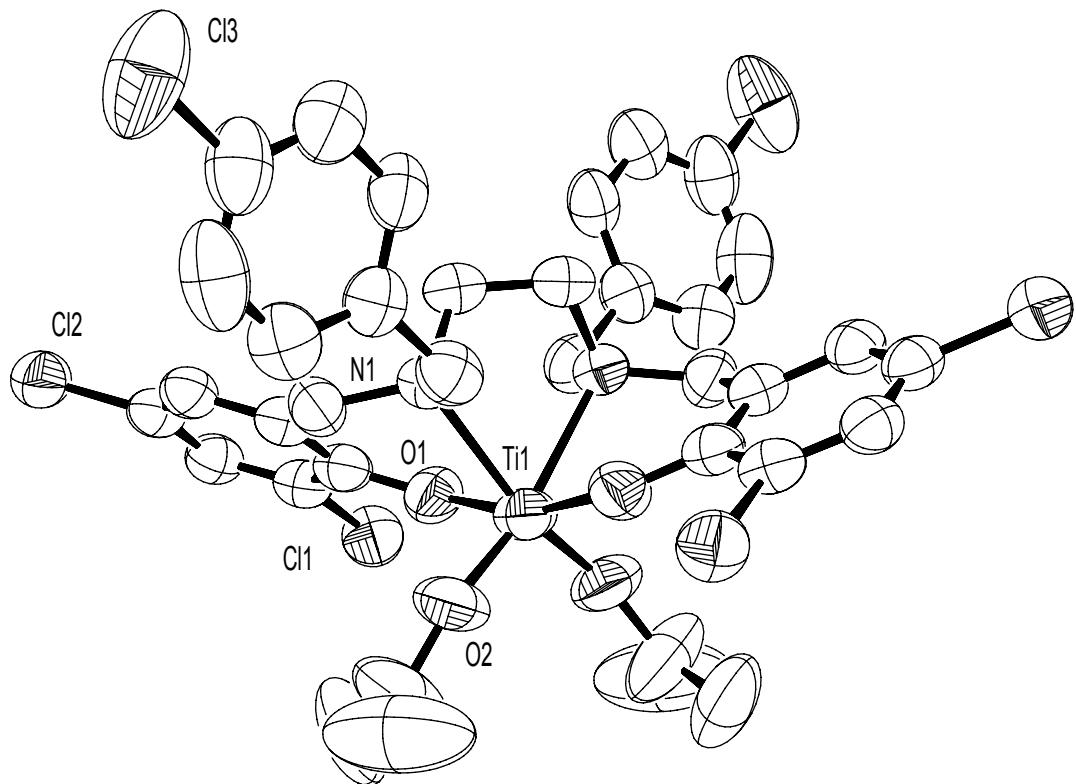
Supplementary Material (ESI) for Dalton Transactions  
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Email: [pghosh@chem.iitb.ac.in](mailto:pghosh@chem.iitb.ac.in)

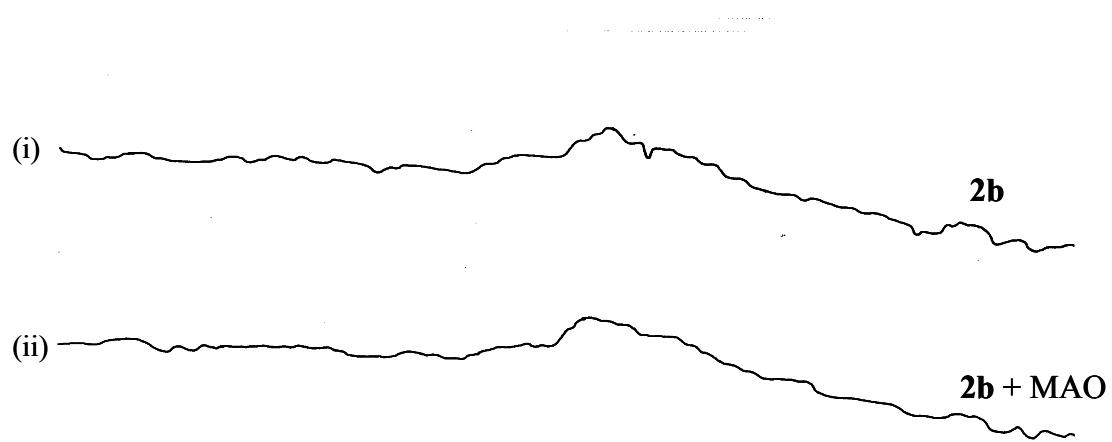
Fax: +91-22-2572-3480



**Figure S1.** ORTEP view of the solid state structure of **5b**. The thermal ellipsoids are shown in 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are given: Ti1-O1 1.887(2), Ti1-O2 1.823(2), Ti1-N1 2.401(3), O1-Ti1-O2 91.37(10), O1-Ti1-N1 90.86(10), O2-Ti1-N1 89.36(10).



**Figure S2.** ORTEP view of the solid state structure of **6b**. The thermal ellipsoids are shown in 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) are given: Ti1-O1 1.909(4), Ti1-O2 1.767(4), Ti1-N1 2.354(4), O1-Ti1-O2 96.81(19), O2-Ti1-N1 164.39(17), O1-Ti1-N1 85.56(16).



**Figure S3.** ESR spectrum (i) of the complex **2b** and (ii) of the complex **2b** when activated by MAO and both recorded at 77 K.

```

MP-8-19-7

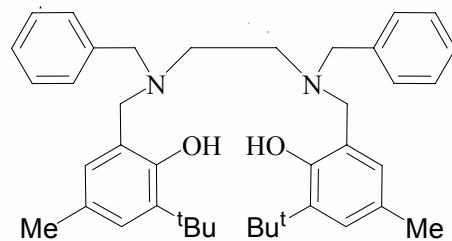
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  date Nov 20 2007  temp   not used
  solvent C6C13    gain   not used
  file ./export/home/~/gain
quest1/2007/NOVEMB~  hst   not used
ER/20-Nov/PG-MP-8-~ pw90   0.008
                           19-2.fid alfa  8.500
                           19-2.fid alfa  20.000

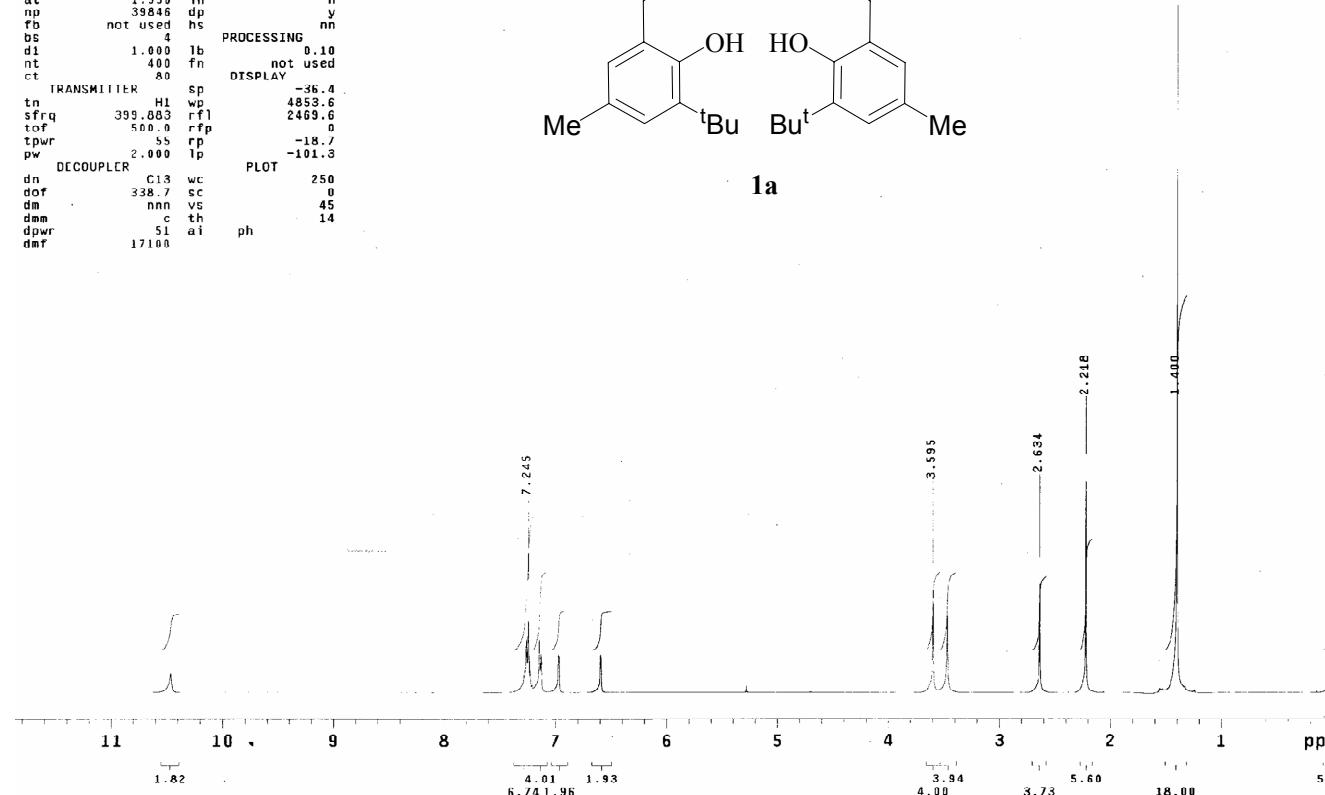
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  at         1.393 in   n
  np       39846 dp   y
  rb      not used hs   nn
  ds           4
  bt        1.000 lb   0.10
  nt         400 fn   not used
  ct            0
  tr      not used
  tdisplay          DISPLAY
  tn          H1 wp   -36.4
  sfrq     399.883 r1f  4853.6
  tof       500.0 rfp  2469.6
  tpwr      55 rp   -18.7
  pw       2.000 lp   -101.3

      TRANSMITTER          PLOT
  dn        G13 wc   250
  do       338.7 sc   0
  dm       nnn vs   45
  dmm      c th   14
  dpwr      51 ai   ph
  dmf      17100

```



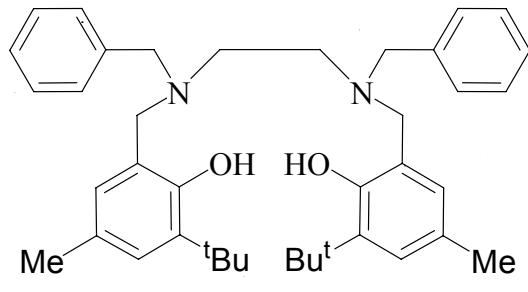
1a



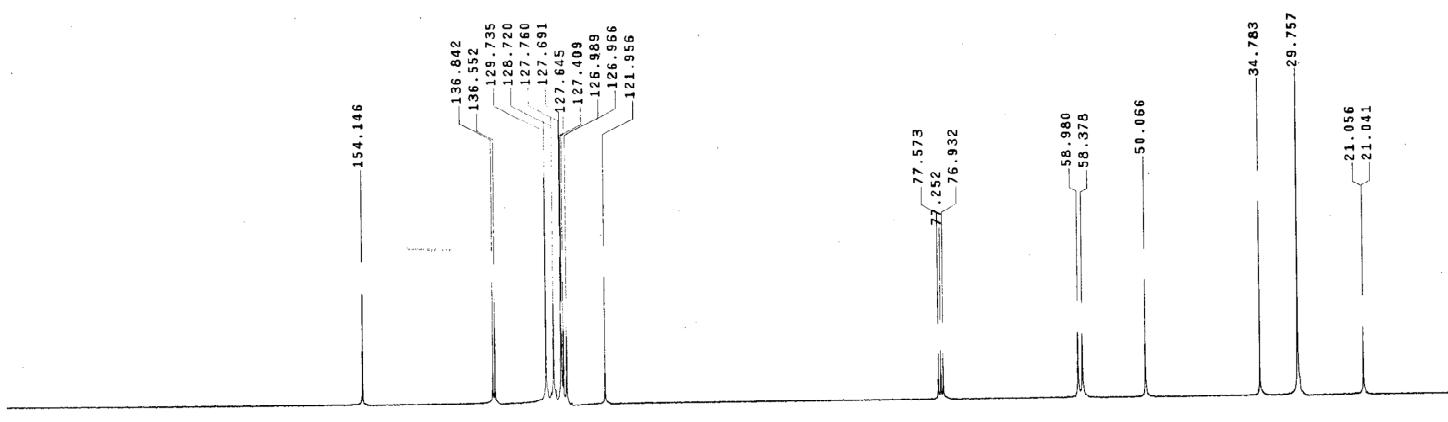
**Figure S4.**  $^1\text{H}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ .

```

MP-12-186-13C
exp4 CARBON
SAMPLE          SPECIAL
date Nov 5 2008 temp not used
solvent   CDCl3 gain not used
file /export/home/~/spin not used
pg1/MANAS/2008/Nov~ hst 0.008
08/5-Nov/PG-MP-12~~ pw90 14.000
186-13C.fid alfa 20.000
ACQUISITION      FLAGS
sw 25125.6 il n
at 1.199 in n
np 60270 dp y
fb 13800 hs nn
bs 4 PROCESSING
dl 1.000 lb 1.00
nt 20000 fn not used
ct 2084 DISPLAY
TRANSMITTER      SP -146.4
tn C13 wp 20403.7
sfrq 100.561 rfp 9268.3
t0f 1554.3 rfp 7768.5
tpwrr 56 rp 138.5
pw 7.000 lp -309.3
DECOUPLER        PLOT
dn H1 wc 250
dof 0 sc 0
dm vvy vs 34
dmm w th 7
dpwr 41 ai ph
dmf 11900
    
```

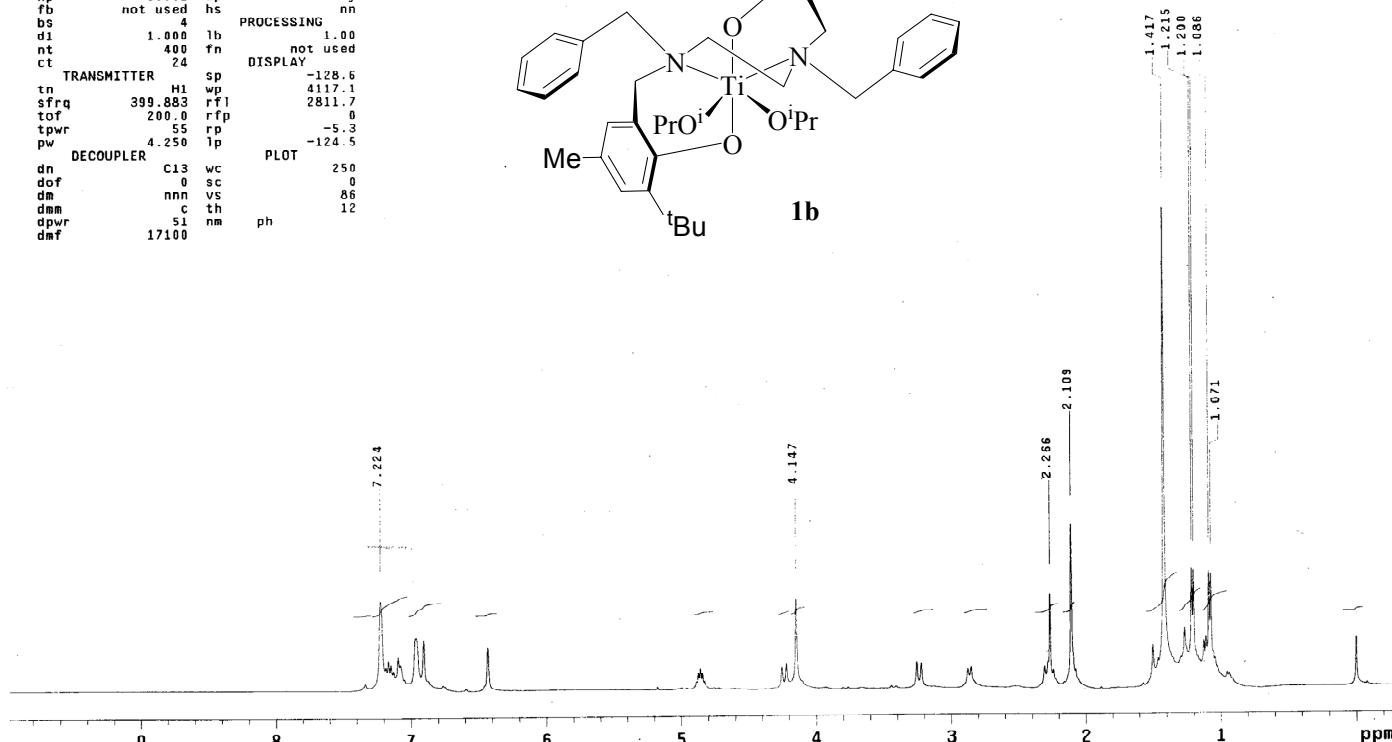
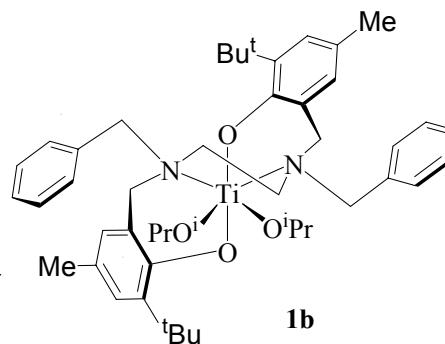


**1a**



**Figure S5.**  $^{13}\text{C}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ .

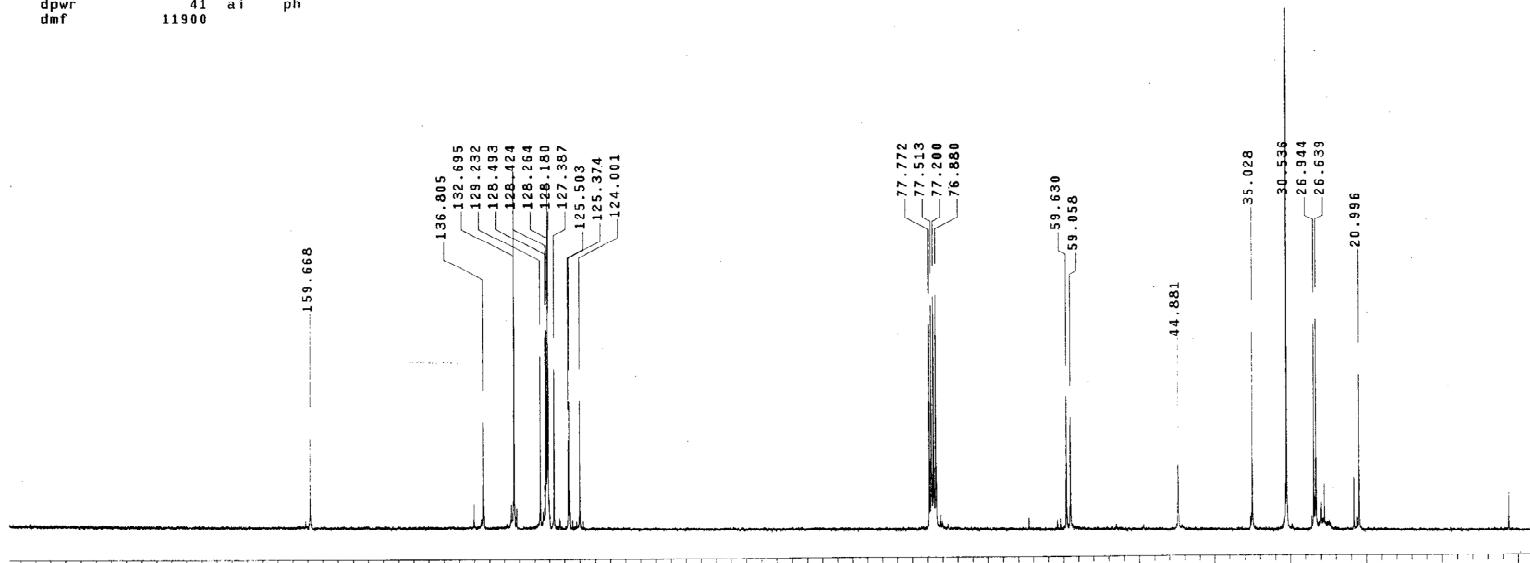
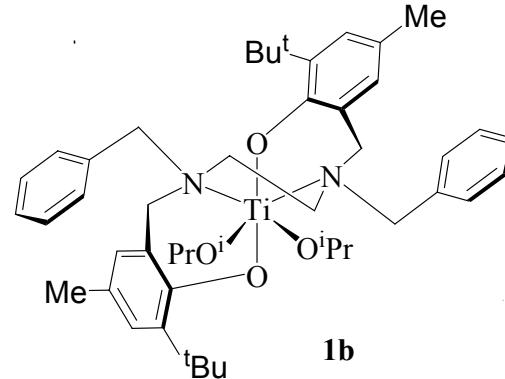
MP-8-216-1  
exp4 PROTON  
SAMPLE SPECIAL  
date Dec 22 2007 temp not used  
solvent CDCl<sub>3</sub> gain not used  
file /export/home/~ spin not used  
pgl/MANAS/2007/Dec- hst 0.008  
07/22-dec/PG-MP-8~~ pw90 8.500  
216-1.tid alfa 20.000  
ACQUISITION FLAGS  
sw 10010.0 il n  
at 1.993 in n  
np 39902 dp y  
fb not used hs nn  
bs 4 PROCESSING  
di 1.000 lb 1.00  
nt 400 fn not used  
ct 24 DISPLAY  
TRANSMITTER sp -128.6  
tn H1 wp 4117.1  
sfrq 399.883 rfp 2811.7  
tof 200.0 rfp 0  
tpwr 55 rp -5.3  
pw 4.250 lp -124.5  
DECOUPLER PLOT  
dn C13 wc 250  
dof 0 sc 0  
dm nnn vs 86  
dmm c th 12  
dpvr 51 nm ph  
dmf 17100



**Figure S6.** <sup>1</sup>H NMR spectrum of **1b** in CDCl<sub>3</sub>.

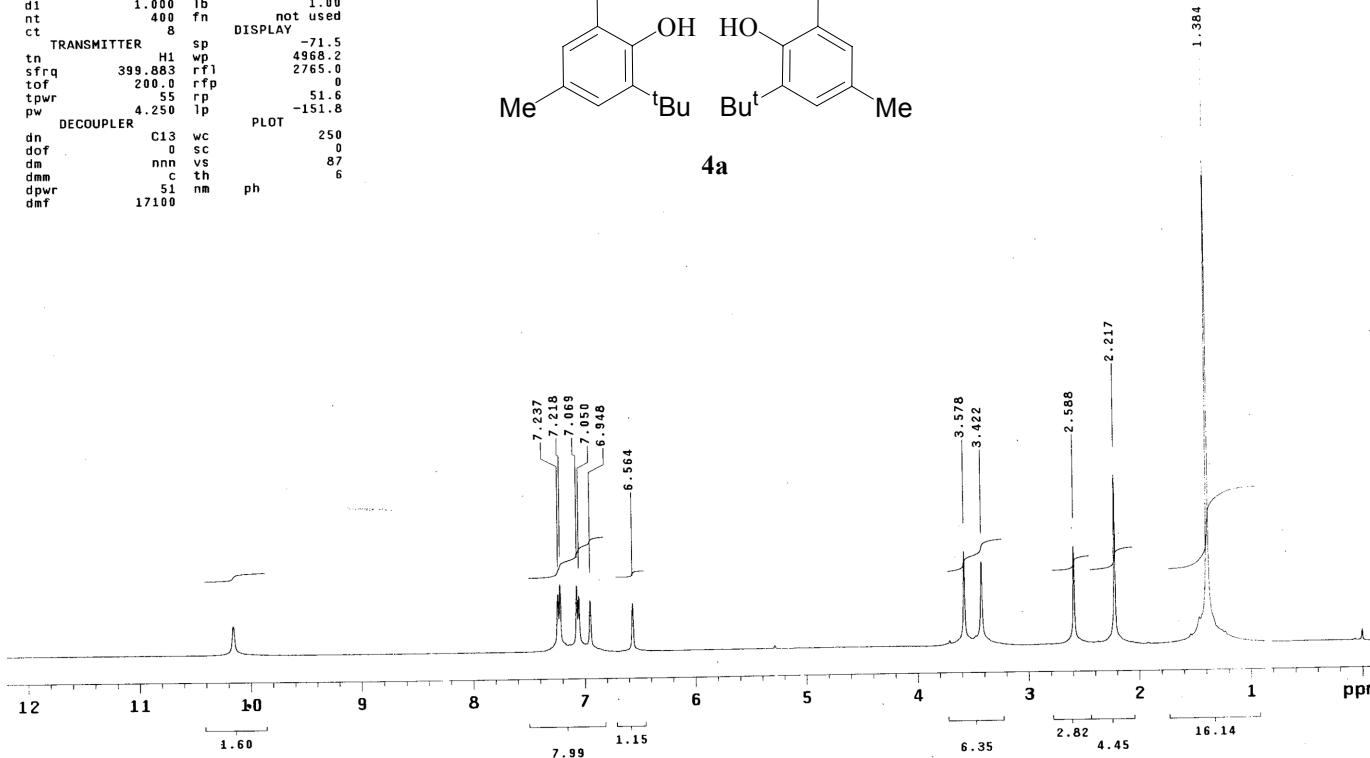
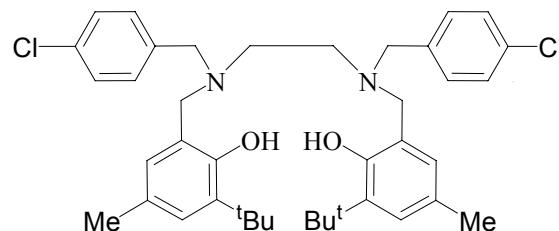
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MP-B-216-13C
exp4 CARBON
SAMPLE          SPECIAL
date Dec 23 2007 temp not used
solvent CDCl3 gain not used
file /export/home/~/spin not used
pg1/MANAS/2007/Dec~ hst 0.008
07/23-dec/PG-MP-B-- pw90 14.000
216-13C.fid alfa 20.000
ACQUISITION FLAGS
sw 25125.6 il n
at 1.199 in
np 60270 dp y
fb 13800 hs nn
bs 4 PROCESSING
di 1.000 lb 1.00
nt 20000 fn not used
ct 7004 DISPLAY
TRANSMITTER sp -356.4
tn Cl3 wp 20416.0
sfreq 100.561 rfl 9249.9
t0f 1554.3 rfp 7762.5
tpwr 56 rp -31.1
pw 7.000 lp -313.6
DECOUPLER PLOT
dn H1 wc 250
dof 0 sc 0
dm vvv vs 83
dmm w th 10
dpwr 41 ai ph
dmf 11900
    
```



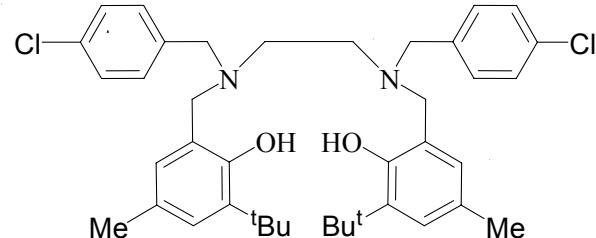
**Figure S7.**  $^{13}\text{C}$  NMR spectrum of **1b** in  $\text{CDCl}_3$ .

ARR-2-108-1  
exp4 PROTON  
SAMPLE SPECIAL  
date Oct 25 2008 temp not used  
solvent CDCl<sub>3</sub> gain not used  
file /export/home/~/spin not used  
pg1 RAJSEKHKAR/2008~ hst 0.008  
/Oct08/25-oct/PG-A~ pw90 8.500  
RR-2-108-1.fid alfa 20.000  
ACQUISITION FLAGS  
sw 10010.0 il n  
at 1.993 in n  
np 39902 dp y  
fb not used hs nn  
bs 4 PROCESSING  
d1 1.000 1b 1.00  
nt 400 fn not used  
ct 8 DISPLAY  
TRANSMITTER sp -71.5  
tn H1 wp 4988.2  
sfrq 399.883 rf1 2765.0  
tof 200.0 rfp 0  
tpwr 55 rp 51.6  
pw 4.250 lp -151.8  
DECOUPLER PLOT  
dn C13 wc 250  
dof 0 sc 0  
dm nnn vs 87  
dmm c th 6  
dpwr 51 nm ph  
dmf 17100

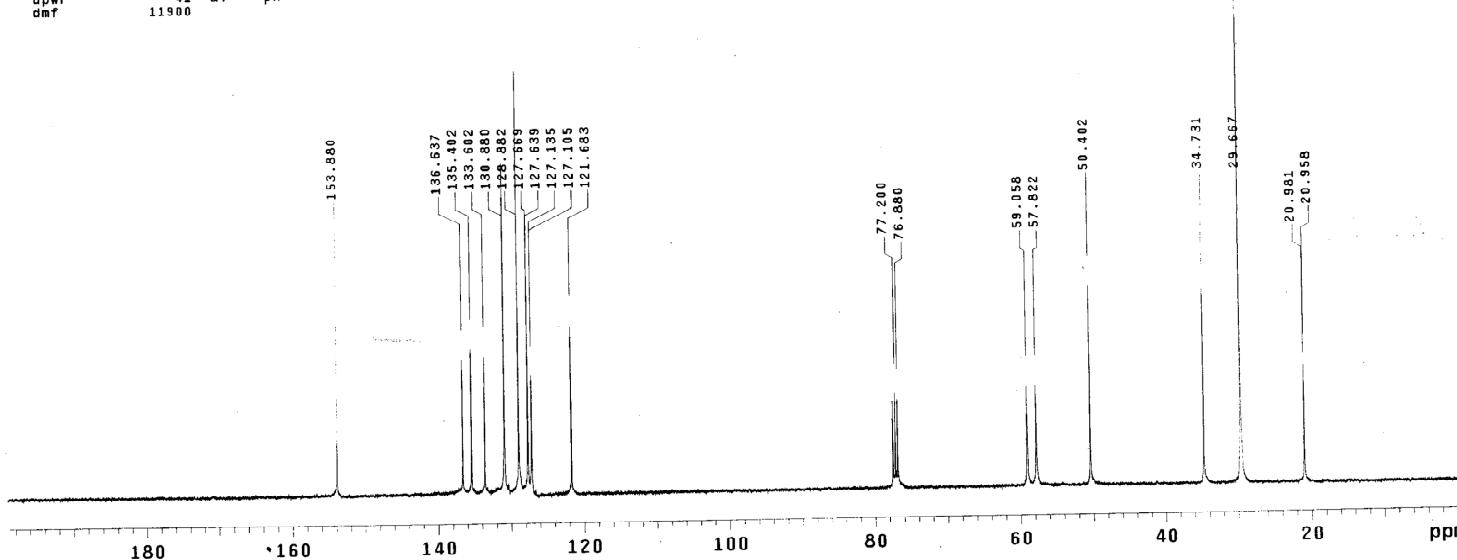


**Figure S8.** <sup>1</sup>H NMR spectrum of **4a** in CDCl<sub>3</sub>.

```
ARR-2-134-2-13C
exp4 CARBON
SAMPLE          SPECIAL
date Nov 4 2008 temp not used
solvent CDCl3 gain not used
file /export/home/~ spin not used
pg1/RAJSEKHAR/2008- hst 0.008
/Nov08/4-nov/PG-AR~ pw90 14.000
/Nov08/4-nov/PG-AR~ pw90 20.000
R-2-134-C13.fid alfa
ACQUISITION FLAGS
sw 25125.6 i1 n
at 1.199 in n
np 60270 dp y
fb 13800 hs nn
bs 4 PROCESSING
d1 1.000 1b 1.00
nt 20000 fn not used
ct 1312 DISPLAY
TRANSMITTER sp -180.8
tn C13 wp 20205.1
sfrq 100.561 rfp 9258.3
tof 1554.3 rfp 7762.5
tpwr 56 rp 129.3
pw 7.000 lp -303.6
PLOT
DECOUPLER dn H1 wc 250
dof 0 sc 0
dm vvv vs 79
dmm w th 15
dpwr 41 ai ph
dmf 11900
```



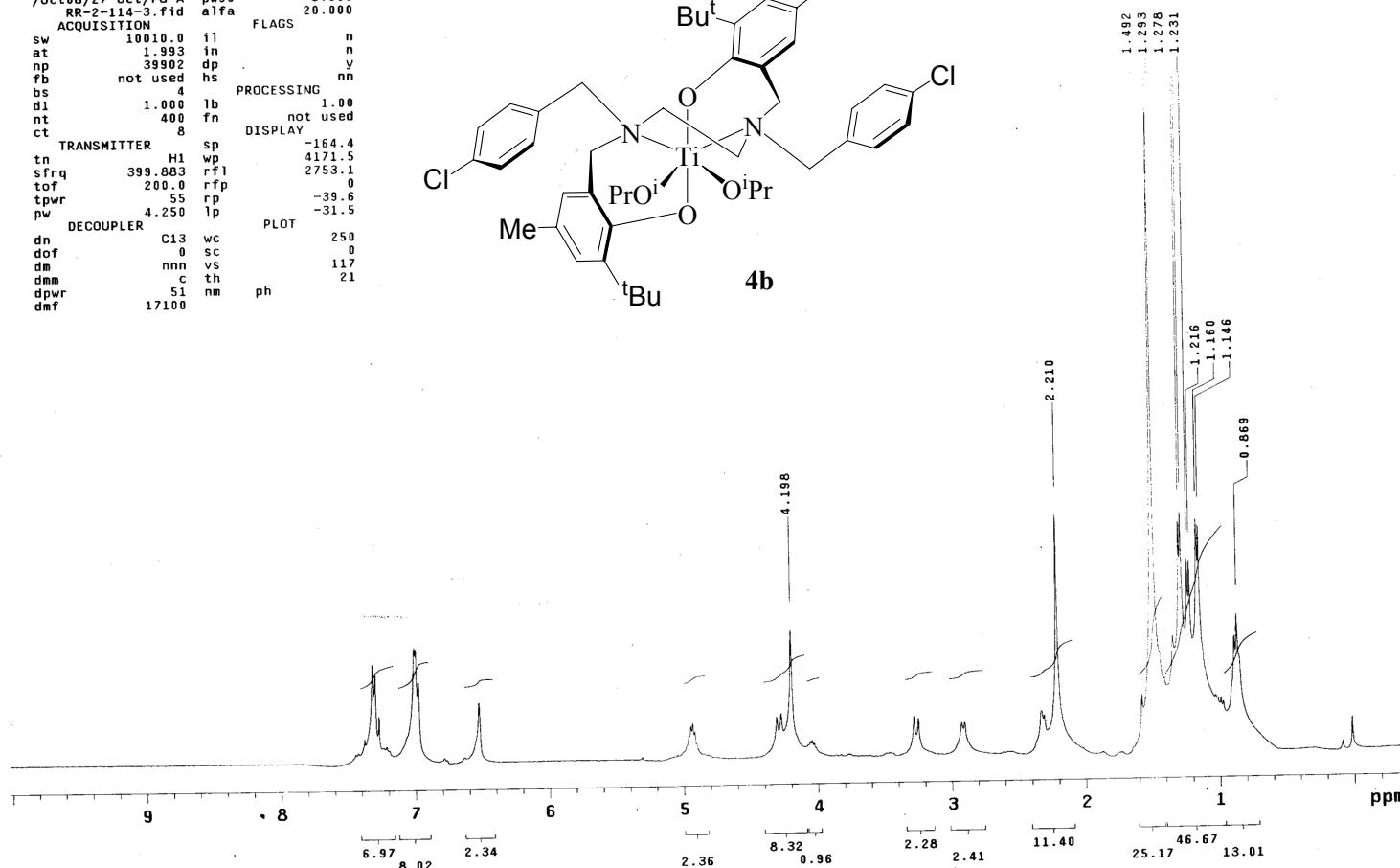
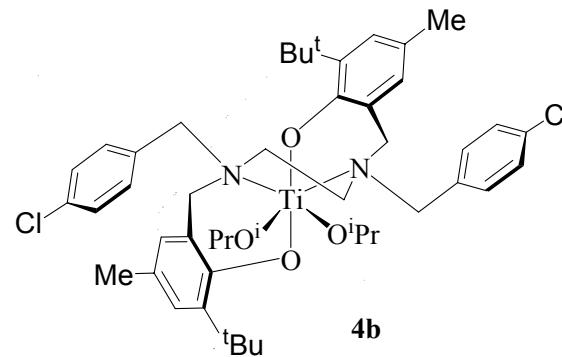
**4a**



**Figure S9.**  $^{13}\text{C}$  NMR spectrum of **4a** in  $\text{CDCl}_3$ .

```

ARR-2-114-3
exp4 PROTON
SAMPLE          SPECIAL
date  Oct 27 2008 temp  not used
solvent  CDCl3 gain  not used
file /export/home/~ spin  not used
pg1/RAJSEKHAR/2008-/hst  0.008
/0ct08/27-Oct/PG-A- pw90  8.500
RR-2-114-3.fid alfa  20.000
ACQUISITION   FLAGS
sw      10010.0  il  n
at      1.993  in  n
np      39902  dp  y
fb      not used hs  nn
bs      4  PROCESSING
d1      1.000  1b  1.00
nt      400  fn  not used
ct      8  DISPLAY
TRANSMITTER   sp  -164.4
tn      H1  wp  4171.5
sfrq    399.883 rfp  2753.1
t0f     200.0 rfp  0
tpwr    55  rp  -39.6
pw      4.250  lp  -31.5
DECOUPLER    C13  wc  250
dn      0  sc  0
dot     nnn vs  117
dm      c th  21
dmm     51 nm  ph
dpwr   17100
        PLOT
        17100
    
```



**Figure S10.**  $^1\text{H}$  NMR spectrum of **4b** in  $\text{CDCl}_3$ .

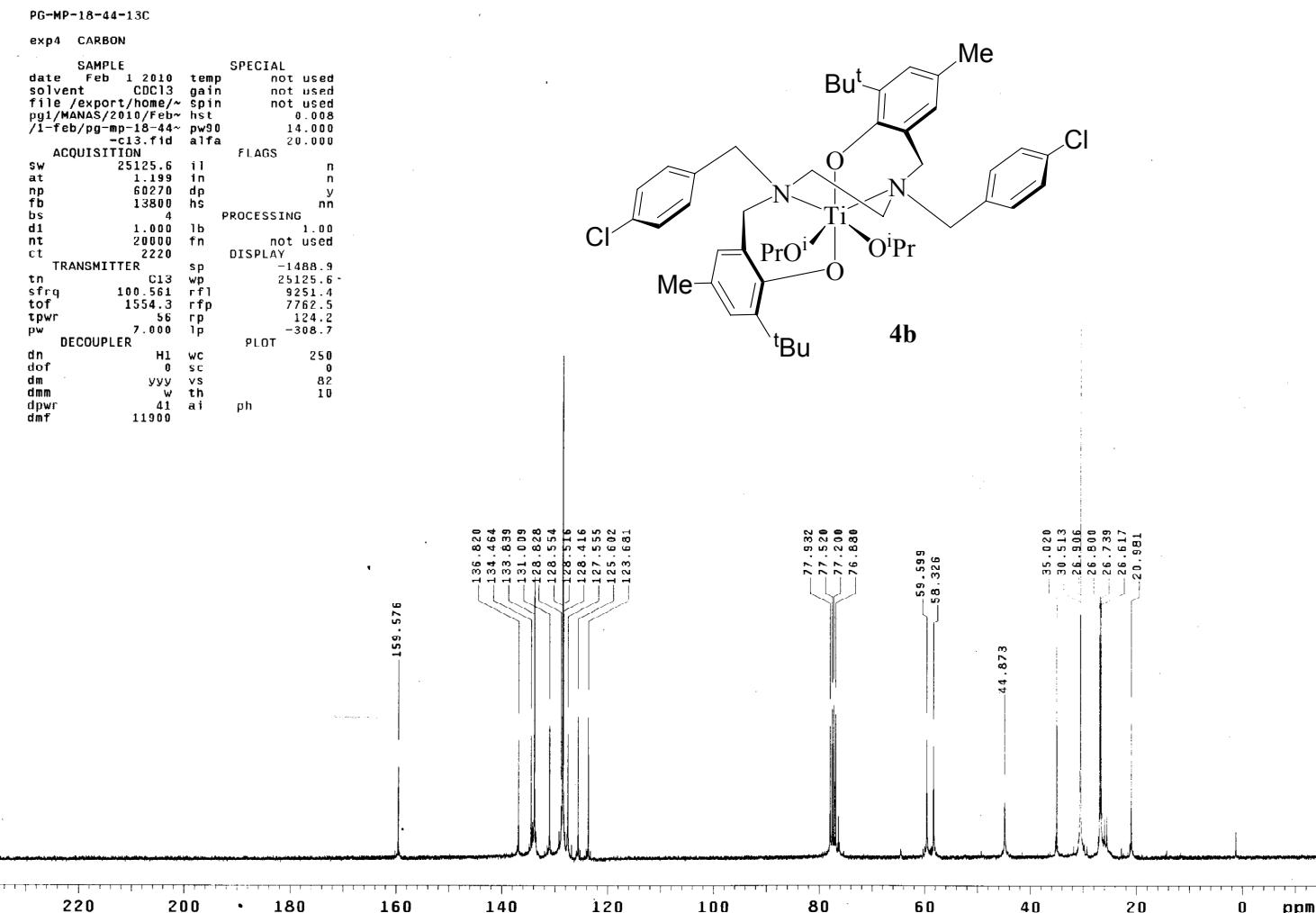


Figure S11. <sup>13</sup>C NMR spectrum of 4b in CDCl<sub>3</sub>.

```

ARR-2-112-1

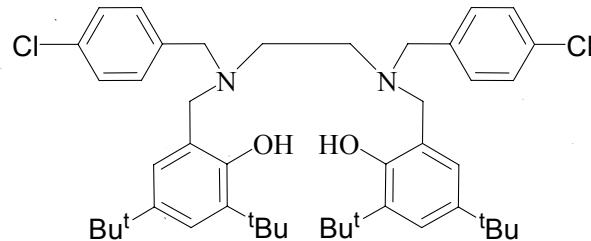
exp4 PROTON

        SAMPLE           SPECIAL
date Oct 25 2008 temp not used
solvent CDCL3 gain not used
file /export/home/~ spin not used
pg1/RAJSEKHA/2008 hst 0.008
/UCTO8/25-25/PG-A~ pw90 8.500
          RR-2-112-1.fid alfa 20.000

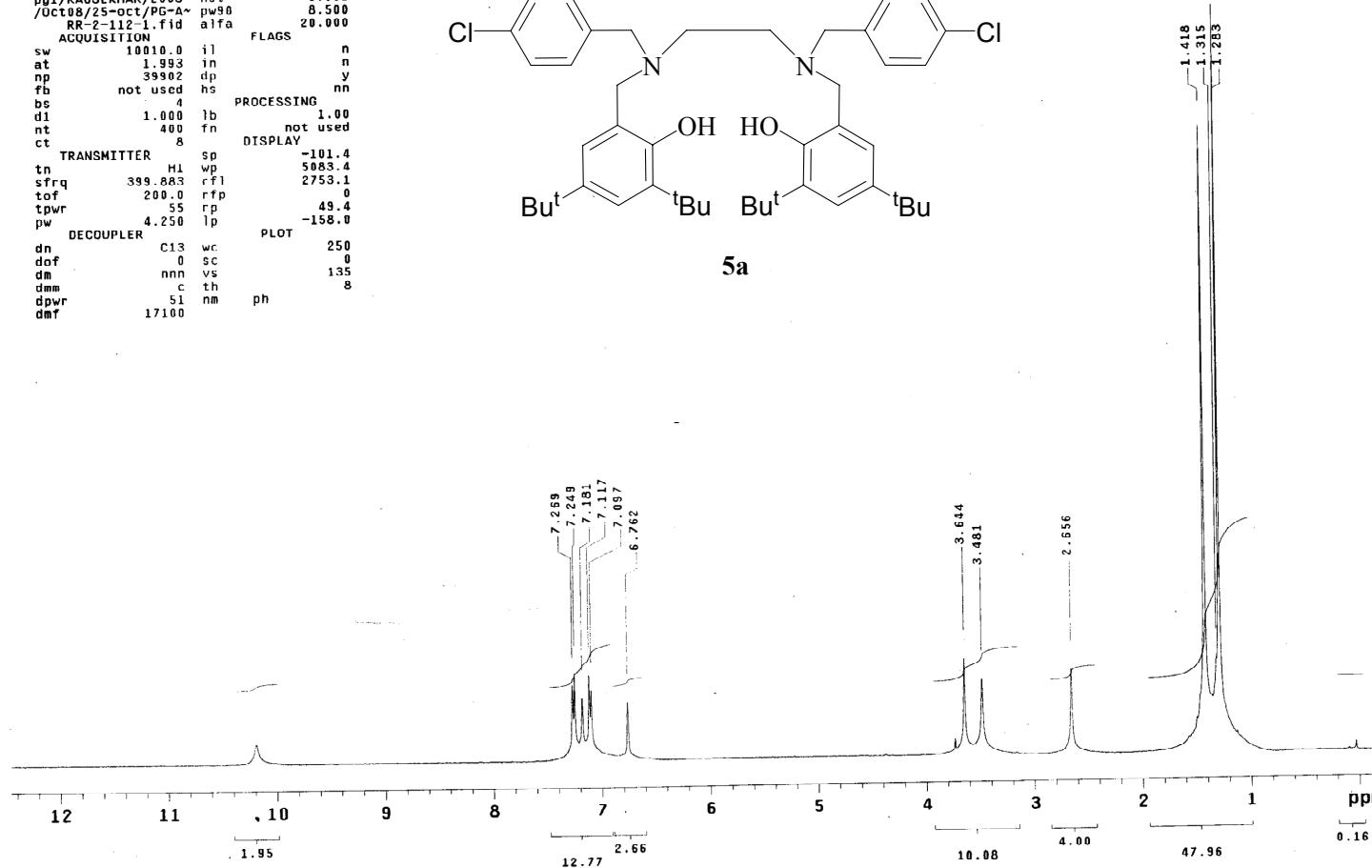
ACQUISITION           FLAGS
sw          1001.00 il   n
at          1.993 in   y
np          39902 dp   y
fb          not used hs   nn
bs          4      r   PROCESSING
dt          1.000 lb   1.000
nt          400 fn   not used
ct          8      s   DISPLAY

        TRANSMITTER
tn          H1 wp   -101.4
sfrq        399.883 rf1  5083.4
tof         200.0 rfp  2753.1
tpwr        55   rp   49.4
pw          4.250 lp   -158.0

        DECOUPLER
dn          C13 wc   250
dof         0 sc   0
dm          nnn vs   135
dmm         c th   8
dpwr        51 nm   ph
dmf        17100
```

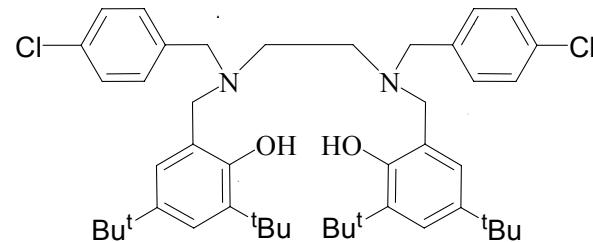


5a



**Figure S12.**  $^1\text{H}$  NMR spectrum of **5a** in  $\text{CDCl}_3$ .

MP-18-43-13C  
exp7 CARBON  
SAMPLE DATE Jan 31 2010 TEMP not used  
SOLVENT CDCl<sub>3</sub> GAIN not used  
FILE /export/home/~ SPIN not used  
PG1/MANAS/2000/JAN~ HST 0.008  
/31-Jan/mp-18-43-1~ PW90 14.000  
30 FID ALFA 20.000  
ACQUISITION FLAGS  
SW 25125.6 t1 n  
AT 1.199 in n  
NP 60270 DP n  
TB 13800 HS Y  
BS 14 PROCESSING nn  
DI 1.000 LB 1.00  
RT 20000 FN 1.00  
CT 340 DISPLAY  
TRANSMITTER SP -173.9  
TN C13 VP 20468.6  
SFRQ 100.561 RFL 9256.8  
TOF 1554.3 RFP 7762.5  
TPWR .56 RP 77.1  
PW 7.000 LP -349.8  
DECOPULER PLOT  
DN H1 WC 250  
DOF 0 SC 0  
DIM VVY VS 62  
DMM W TH 6  
DPWR 41 AI PH  
DMF 11900



5a

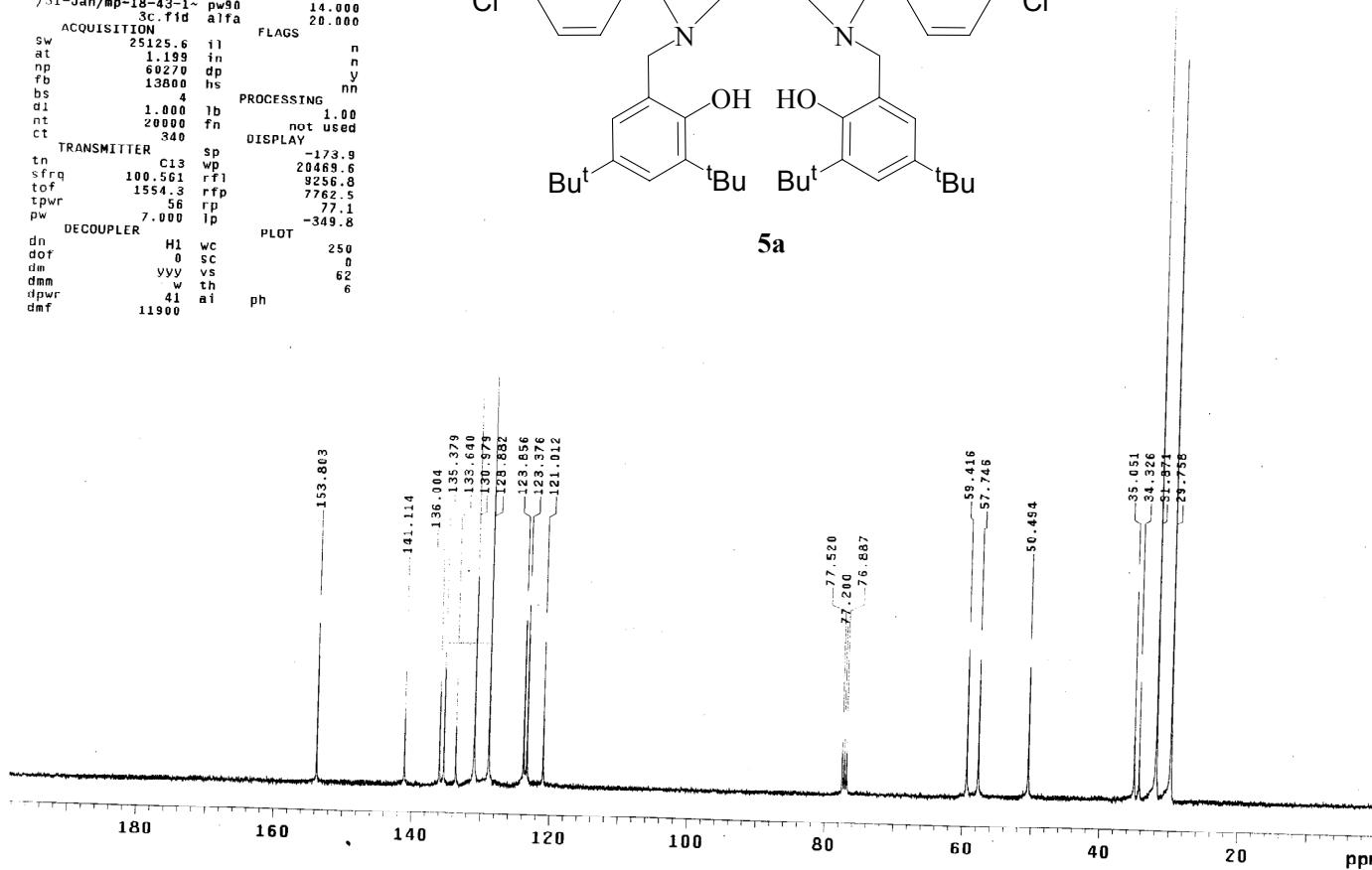


Figure S13. <sup>13</sup>C NMR spectrum of 5a in CDCl<sub>3</sub>.

```

ARR-2-117-1

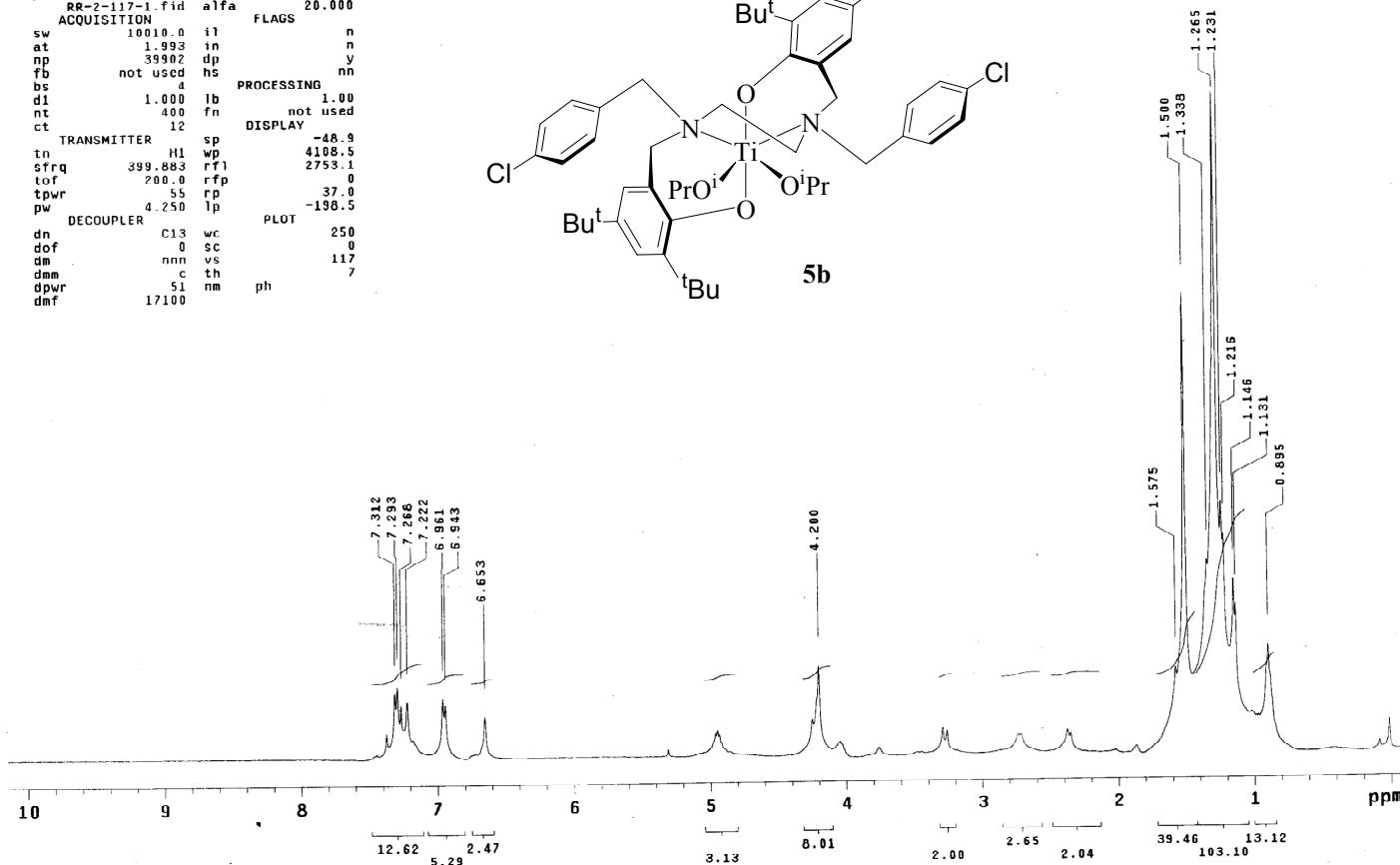
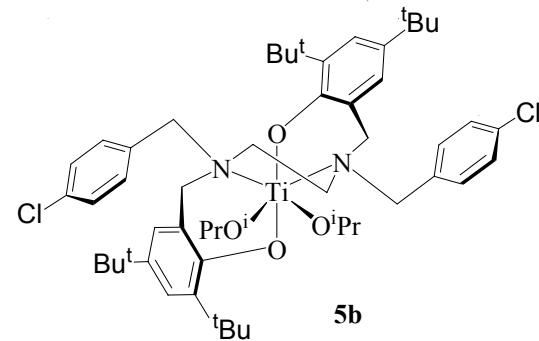
exp4 PROTON

          SAMPLE           SPECIAL
date   Oct 27 2008  temp    not used
solvent      C6C13  gain    not used
file /export/home/~/spin  not used
pg1/RAJSEKHAR/2004.hst  0.008
/OCT08/27-Oct/PG-A-     pw90   8.500
RR-2-117-1.fid  alfa  20.000

          ACQUISITION        FLAGS
sw      10010.0 il      n
at      1.993 in      n
np      39902 dp      y
fb      not used hs      nn
bs      4          PROCESSING
d1      1.000 lb      1.00
nt      400       not used
nr      12          DISPLAY
          TRANSMITTER        SP      -48.9
tn      H1 wp      4108.5
sfreq   399.883 rf1      2753.1
tfrq   200.0 rfp      0
tpwr   55 rp      37.0
pw      4.250 lp      -198.5

          DECOUPLER          PLOT
dn      C13 wc      250
dof     0 sc      0
dm      nnn vs      117
dmm    c th      7
dpwr   51 nm      ph
dmf    17100

```



**Figure S14.**  $^1\text{H}$  NMR spectrum of **5b** in  $\text{CDCl}_3$ .

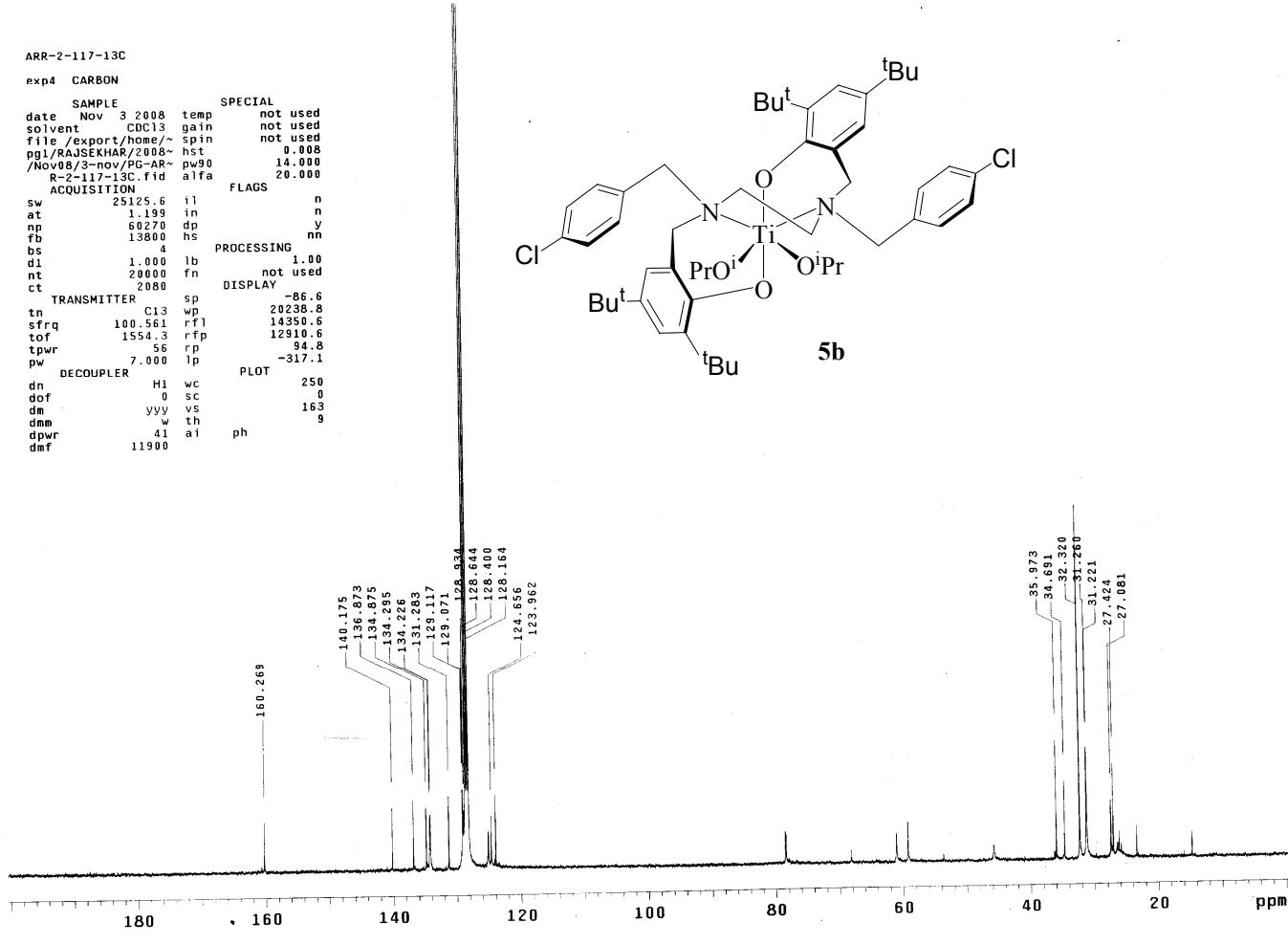
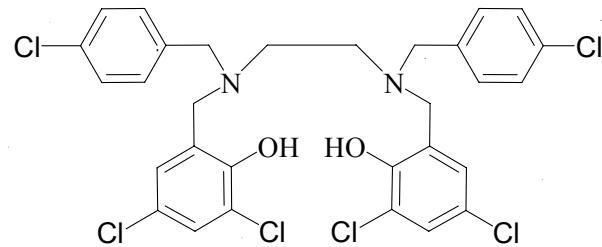


Figure S15. <sup>13</sup>C NMR spectrum of **5b** in C<sub>6</sub>D<sub>6</sub>.

ARR-2-123-1  
exp4 PROTON  
SAMPLE SPECIAL  
date Oct 30 2008 temp not used  
solvent CDCl<sub>3</sub> gain not used  
file /export/home/- spin not used  
pg1/RAJSEKHAR/2008- hst 0.008  
/Oct08/30-Oct/PG-A- pw90 8.500  
RR-2-123-1.fid alfa 20.000  
ACQUISITION FLAGS  
sw 10010.0 il n  
at 1.093 in n  
np 39902 dp y  
fb not used hs nn  
bs not used 4  
PROCESSING  
di 1.000 lb 1.00  
nt 400 fn not used  
ct 8 DISPLAY  
TRANSMITTER sp -237.7  
tn H1 wp 5261.8  
sfrq 399.883 rfi 2753.1  
tor 200.0 rfp 0  
tpwr 55 rp 45.3  
pw 4.250 lp -147.5  
DECOUPLER PLOT  
dn C13 wc 250  
dof 0 sc 0  
dm nnn vs 58  
dmm c th 17  
dpwr 51 nm ph  
dmf 17100



6a

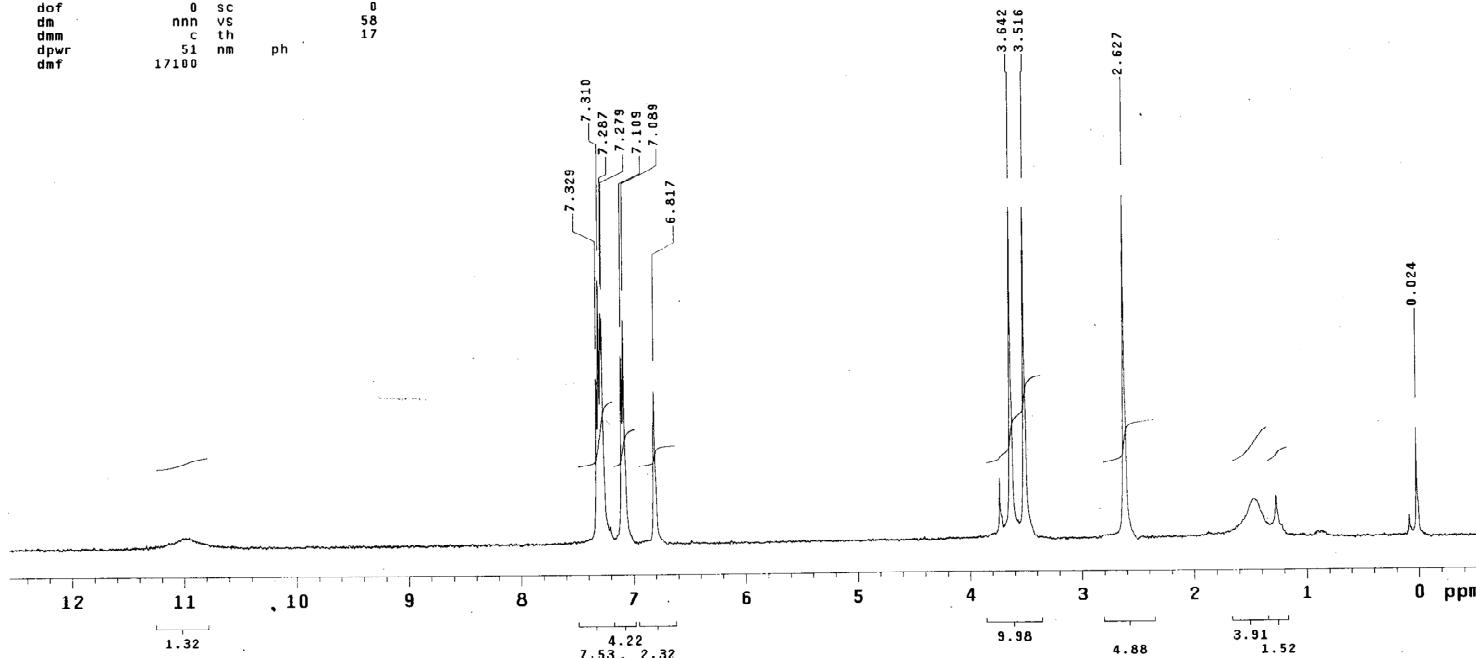
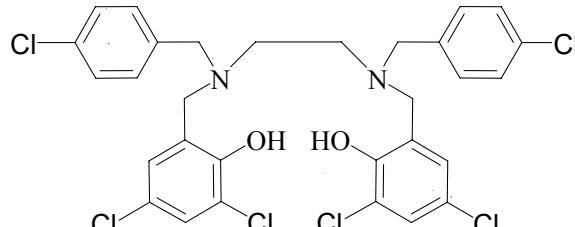


Figure S16. <sup>1</sup>H NMR spectrum of 6a in CDCl<sub>3</sub>.

ARR-2-123-2-13C  
exp4 CARBON  
SAMPLE SPECIAL  
date Aug 6 2004 temp not used  
solvent CDCl<sub>3</sub> gain not used  
file /export/home/~ spin not used  
guest/vnmrsys/data= hst 0.008  
/guest\_2004-08-06/~ pw90 14.000  
CARBON\_01.fid alfa 24.000  
ACQUISITION FLAGS  
sw 25125.6 i1 n  
at 1.199 in n  
np 60270 dp y  
fb 13800 hs nn  
bs 64 PROCESSING  
d1 1.000 lb 1.00  
nt 16 fn not used  
ct 16 DISPLAY  
TRANSMITTER sp -397.4  
tn C13 wp 21047.0  
sfreq 100.561 rfp 1502.3  
tot 1554.3 rfp 0  
tpwr 56 rp 148.7  
pw 7.000 1p -319.2  
DECOUPLER PLOT  
dn H1 wc 250  
dof 0 sc 0  
dm yyy vs 37  
dmm w th 6  
dpwr 41 ai no ph  
dmf 11900



6a

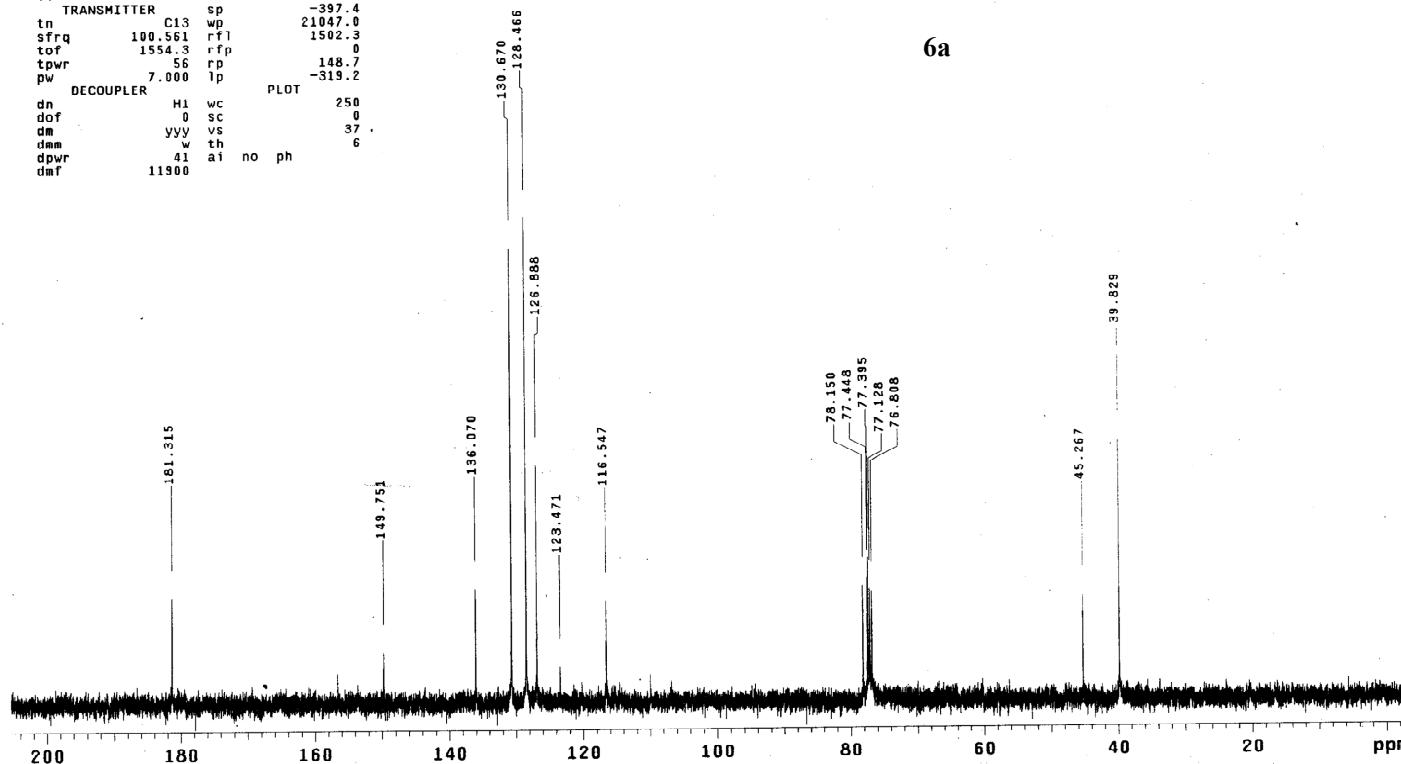
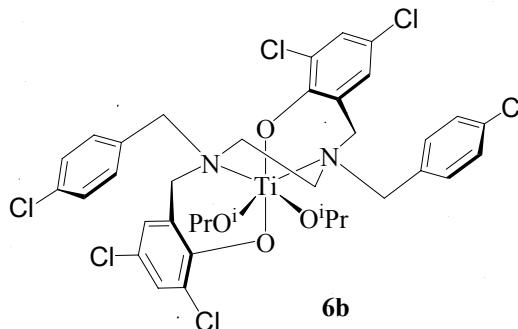


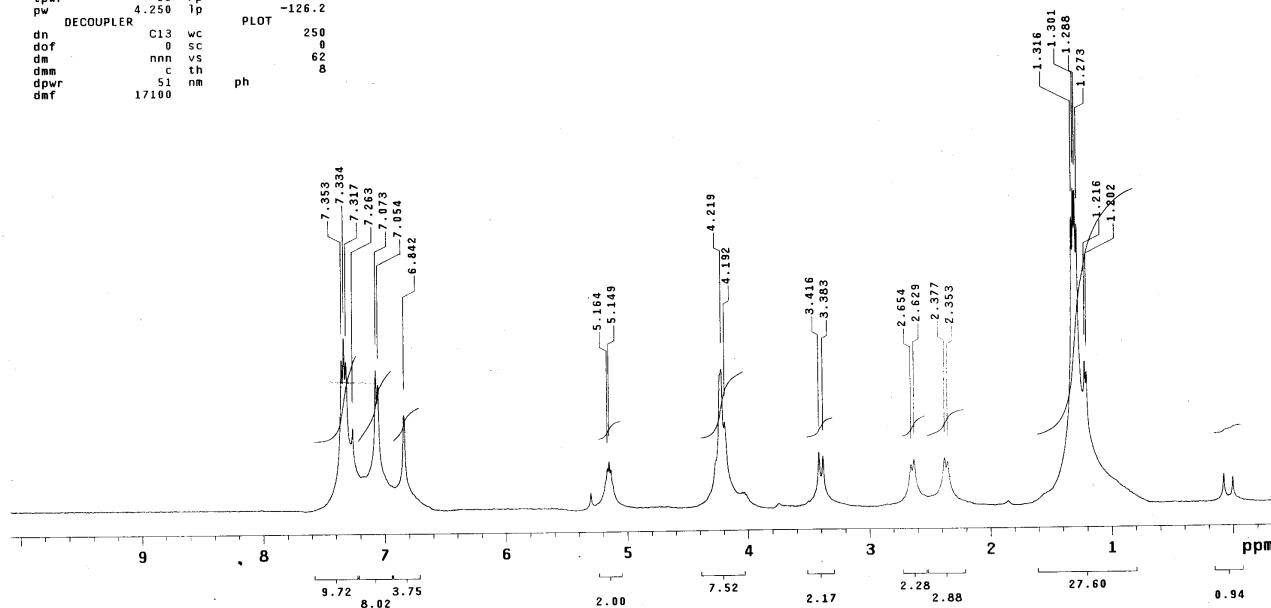
Figure S17. <sup>13</sup>C NMR spectrum of 6a in CDCl<sub>3</sub>.

```

ARR-2-172-1
exp4 PROTON
SAMPLE          SPECIAL
date Dec 5 2008 temp not used
solvent CDCl3 spin not used
file /export/home/~/spin not used
pg1/RAJSEKHAR/2008-
/Dec08/5-dec/PG-AR-
R-2-172-1.fid hst 0.008
pw90 8.500
alpha 20.000
ACQUISITION FLAGS
sw 1010.0 ll n
at 1.993 in
np 38902 dp y
fb not used hs nn
bs 4
di 1.000 lb 1.00
nt 400 fn not used
ct 8
PROCESSING
TRANSMITTER DISPLAY
sp -148.5
tn H1 wp 4182.2
sfreq 399.883 rf1 2753.1
tof 200.0 rfp 0
tpwr 55 rp -1.4
pw 4.250 ip -126.2
DECOUPLER PLOT
dn C13 wc 250
dof 0 sc 0
da mm s 62
dm c th 8
dpwr 51 nm ph
dmf 17100
    
```



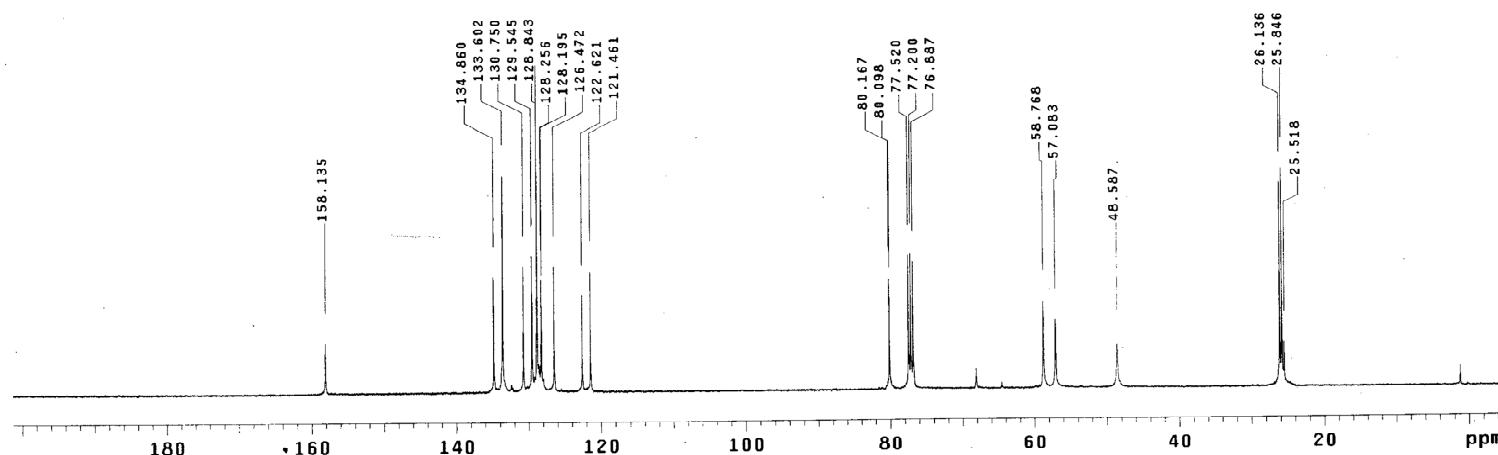
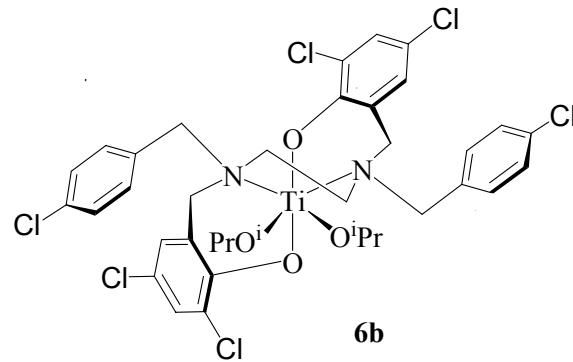
**6b**



**Figure S18.**  $^1\text{H}$  NMR spectrum of **6b** in  $\text{CDCl}_3$ .

```
ARR-2-172-13C
exp4 CARBON

SAMPLE          SPECIAL
date Dec 19 2008 temp not used
solvent CDCl3 gain not used
file /export/home/- spin not used
pg1/RAJSEKHKAR/2008- hst 0.008
/Dec08/20-dec/PG-A~ pw90 14.000
RR-2-172-13C.fid alfa 20.000
ACQUISITION FLAGS
sw 25125.6 ll n
at 1.199 in n
np 60270 dp y
tb 13800 hs nn
bs 4 PROCESSING
di 1.000 lb 1.00
nt 20000 fn not used
ct 14612 DISPLAY
TRANSMITTER sp -543.5
tn C13 wp 20784.0
sfrq 100.561 rfl 9252.9
t0f 1554.3 rfp 7762.5
tpwr 56 rp 119.6
pw 7.000 lp -331.2
DECOUPLER PLOT
dn H1 wc 250
dof 0 sc 0
dm vyy vs 127
dmm w th 5
dpwr 41 aj ph
dmf 11900
```



**Figure S19.**  $^{13}\text{C}$  NMR spectrum of **6b** in  $\text{CDCl}_3$ .