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New Aryloxy and Benzyloxy Derivatives of Titanium as Catalysts for Bulk Ring-Opening Polymerization of ε-Caprolactone and δ-Valerolactone

Ravikumar R. Gowda,[a] Debashis Chakraborty,*[a] and Venkatachalam Ramkumar[a]

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A variety of aryloxy compounds and benzyloxy derivatives of Ti^{IV} were synthesized from $Ti(iPrO)_4$ using the alcoholysis route. These compounds were characterized using various analytical methods and single-crystal X-ray diffraction. Multinuclear NMR studies prove high degree of fluxional behavior of these compounds in solution. They adopt a dimeric structure in the solid state as seen from X-ray diffraction studies on a few of them. These compounds are powerful catalysts for the ring-opening polymerization of ε-caprolactone (CL) and δ-valerolactone (VL) resulting in high polymers with good number average molecular weights (M_n). Significant control can be achieved by performing such polymerizations in the presence of benzyl alcohol (BnOH). This is reflected by higher M_n and much narrower molecular weight distributions (MWDs) of the resulting polymers. Kinetic studies reveal that the rates of such polymerizations are much higher in the presence of BnOH. ^1H NMR and MALDI-TOF studies of low molecular weight oligomers suggest that these polymerizations proceed by the activated monomer mechanism in the presence of BnOH.

Introduction

In the recent years, the increasing need to search alternative polymeric materials to those based on nonrenewable petroleum resources, along with the desire to produce environmentally benign biodegradable plastics has provided active impetus towards the polymerization of cyclic esters.[1–5] The applications of aliphatic polyesters have been popularly widespread in biomedical and pharmaceutical industries including drug delivery, production of implants and scaffolds for tissue engineering.[6] Their uses have been implicated in the film and fiber applications industry.[7] The potential for such utility stems as a result of their permeability, biocompatibility and biodegradability.[8–10]

One of the convenient strategies in synthesizing these polymers is the ring-opening polymerization of the corresponding cyclic lactone monomers or lactide.[6,11–12] The coordination-insertion ring-opening mode of polymerization is the most popular because of its capability in producing high polymers with narrow MWDs.[1,11,13–24] Group 4, the most versatile in homogeneous olefin polymerization catalysis[25–27], has been exploited in the ring-opening polymerization of cyclic esters.

The popular methodology of catalyst construction is to use a rigid ligating environment around the metal center with one or more alkoxide-based initiating groups. The establishment of such a principle has been documented recently by demonstrating the applications of alkoxides with a ligating backbone containing chiral phenoxyimine,[28] tris(phenoxy)amine,[29] bis(β-ketoamidate),[30] bis(iminophenoxy),[31–32] N-heterocyclic carbene,[33] bis(phenoxy)amine,[34–36] pyrrolylamine,[37] tris(alkoxy),[38–39] tris(alkoxy)amine,[40–42] bis(amido),[43] chalcogen-bridged bis(aryloxy)[44] and methylene-bridged bis(phenoxy)[45] derivatives. In addition, there are reports employing titanium *n*-butoxide, zirconium *n*-propoxide[46] and titanium phenoxide[47] as initiators. A Ti-alkoxide-based metal organic framework was recently reported to possess activity for such processes.[48] The use of metallocene ester enolates for the polymerization of lactide has been reported recently.[49] Only a few compounds derived from these ligands have been employed towards the polymerization of CL.[30,35–37,41,43–46,48] The polymerizations described from such initiators have exclusively relied upon the coordination-insertion mechanism.[1] Systematic correlation between the structural compositions of such ligands with polymer properties along with any practical advantage on polymer microstructure is not available.

Another approach to the polymerization of cyclic esters is the activated monomer mechanism[50–54] whose practical utility has not been substantially investigated as compared to the coordination-insertion mechanism. None of the initiators derived from the above ligand backbone have been investigated in this regard. A reason that may be attributed to this observation is the use of protic initiators along with these organometallic alkoxides as catalysts which may not

[a] Department of Chemistry, Indian Institute of Technology Madras,
Chennai-600 036, Tamil Nadu, India
Fax: +91-44-2257-4202
E-mail: dchakraborty@iitm.ac.in
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be tolerated by them. Hence, there are possibilities of loss of catalyst identity during the polymerization process.

Our recent results indicate that iron and ruthenium chloride catalysts in the presence of protic initiators like alcohols produce comparable or better results for CL and VL polymerization, using the activated monomer mechanism,[55] as compared to the ones reported for alkoxide initiators containing bulky ligands wherein the polymerization proceeds by the coordination-insertion mechanism.[20] Using such a methodology, much shorter polymerization time, far higher M_n and low MWDs were observed. This proved our initial contentions that elaborate ligands may not be an absolute necessary requirement in the development of such a technology.[55] The chain-end groups for the poly(caprolactone) and poly(valerolactone) obtained using either of the mechanisms are identical.[50–54] This has prompted us to investigate extensively the role of aryloxy and benzyloxy compounds of titanium in the polymerization of CL and VL using the coordination-insertion mechanism. The possibility to explore such compounds as catalysts in the presence of protic initiators was additionally an important milestone. This methodology is anticipated to illustrate possible advantages in terms of polymerization time, M_n and MWDs of the resulting polymers and may be thought to proceed via the activated monomer mechanism. It must be mentioned that VL polymerization using group 4 metals have not been reported.

Results and Discussion

Synthesis and Characterization of Compounds 1–20

The alcoholysis route[56–57] has been employed for the synthesis of a variety of titanium aryloxy compounds **1**–**18** starting from Ti(*i*PrO)$_4$ and several phenols, bearing different substituents on the phenyl ring (Scheme 1). Compounds **1**–**14** were prepared by heating Ti(*i*PrO)$_4$ with the appropriate phenol in 1:4 stoichiometric ratio in toluene at 80 °C with the exception of **5**, **9**, **12**, **13** and **14** where stirring the reaction mixture at room temperature in toluene followed by evaporation of solvent afforded the expected product. These products were purified by crystallization and obtained in high yields as orange-yellow to orange-red solids with high melting points (140–188 °C). Some of these compounds (**1**, **3**, **8**, **9**, **11**, and **13**) have been reported in the literature. Compound **1** and **8** are reported to be synthesized by reacting Ti(OBu)$_4$ with the corresponding phenol.[58] The reported procedure for **3**,[59] **9**[60] and **13**[61] is the direct reaction of titanium halide with the appropriate phenol. Compound **11**, was synthesized using the reported procedure.[62] These compounds were characterized by measuring ebullioscopic constants in benzene, measurement of melting point and elemental analyses. Our contribution has been in the synthesis of these compounds by the route shown in Scheme 1 and characterizing them completely by NMR, mass spectrometry and single-crystal X-ray diffraction studies on a few of them.

$$Ti(iPrO)_4 + HOAr \xrightarrow{\text{toluene}} [Ti(OAr)_a(iPrO)_b(iPrOH)_c]_2$$

Compound	Ar	*a*	*b*	*c*
1	2-MeC_6H_4	4	0	0
2	2-FC_6H_4	4	0	1
3	2-ClC_6H_4	4	0	0
4	2-BrC_6H_4	4	0	0
5	3-FC_6H_4	4	0	1
6	3-$CF_3C_6H_4$	4	0	1
7	3-$NO_2C_6H_4$	4	0	1
8	4-MeC_6H_4	4	0	0
9	4-*t*BuC_6H_4	4	0	0
10	4-$CF_3C_6H_4$	4	0	1
11	4-FC_6H_4	4	0	1
12	4-IC_6H_4	4	0	1
13	C_6F_5	4	0	1
14	C_6Cl_5	4	0	1
15	2,4,6-$F_3C_6H_2$	2	2	0
16	2,4,6-$Cl_3C_6H_2$	2	2	0
17	2,4,6-$Br_3C_6H_2$	2	2	0
18	2,4,6-$I_3C_6H_2$	2	2	0

Scheme 1. Synthesis of titanium aryloxy compounds.

For the synthesis of **15**–**18**, a 1:4 stoichiometry reaction between the reactants (Scheme 1) yielded the required product along with unreacted phenol. These were prepared by reacting Ti(*i*PrO)$_4$ with 2 equivalents of phenol in toluene at 80 °C.

The benzyloxy derivatives namely [Ti(OCH$_2$–4-MeC_6H_4)$_4$]$_2$ (**19**) and [Ti(OCH$_2$–4-OMeC_6H_4)$_4$(*i*PrOH)]$_2$ (**20**) were prepared by reacting Ti(*i*PrO)$_4$ with the appropriate substituted benzyl alcohol derivative, using a procedure identical to those of the aryloxy compounds. The yields of these viscous yellow oils were high.

The aforementioned compounds **1**–**20** have been characterized thoroughly by ^{1}H and ^{13}C NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and their purity has been assured by correct elemental analysis values.

The ^{1}H NMR of these compounds reveals the expected signals in the correct ratio of integration. Compounds **7**, **12**, **13** and **14** have residual lattice toluene which could not be removed by drying them under high vacuum (10^{-6} Torr) for several hours. These compounds (**1**–**18**) have a tendency for degradation when heated under such conditions. For the aryloxy compounds, which are *i*PrOH adducts (**2**, **5**–**7**, **10**–**14**), the signals appear broad, suggesting a high degree of fluxional behavior of such molecules (see Supporting Information). The CH signal of coordinated *i*PrOH is deshielded to a greater extent in **2**, **13** and **14** (δ = 4.69–4.83 ppm) as compared to the other derivatives (δ = 4.22–4.40 ppm) as a consequence of higher Lewis acidity of the titanium centers because of electron-withdrawing ligands. Such deshielding is also observed for the Me protons of coordinated *i*PrOH in **13** and **14** respectively. The OH proton of coordinated *i*PrOH remain NMR silent. For the others, broadening of signals is seen at lower temperatures (see Supporting Information). Such observations of fluxionality and oligomer formation have been well documented in the literature per-

taining to metal alkoxides.[63–64] For **15**–**18**, the extent of broadening of signals in ^{1}H NMR is moderate (see Supporting Information). The signals corresponding to the *i*PrO moiety are deshielded (δ = 4.77–4.92 ppm for CH and 1.24–1.36 for Me) significantly because of bond formation with titanium. The benzyloxy derivative **20** shows a higher degree of broadening of the signals in the ^{1}H NMR as compared to **19** as a result of *i*PrOH coordination. The presence of coordinatively unsaturated titanium atoms provides a relatively easy associative route for either internal ligand scrambling or external ligand exchange.

Variable-temperature ^{1}H NMR studies were conducted using **2** and **18**. For **2**, the spectrum becomes complicated as the temperature is lowered from 25 °C to –55 °C. New peaks appear in the aromatic region, whose intensities become prominent as the temperature is lowered gradually. The broad CH peak of coordinated *i*PrOH at δ = 4.69 ppm broadens gradually and eventually separates into two peaks at –55 °C (see Supporting Information). Such observations suggest fluxionality and are indicative of complicated solution dynamics.[63,65] We have done similar studies using **18** (Figure 1). Upon lowering the temperature gradually the peaks at δ = 7.97 ppm (phenyl), 4.92 ppm (CH of *i*PrO) and 1.36 (Me of *i*PrO) broaden and new peaks are eventually seen. In addition to the signal for the CH moiety constituting the *i*PrO group at δ = 4.92 ppm, there are two others at δ = 5.22 ppm and 5.95 ppm respectively. This may be rationalized by considering the equilibrium depicted in Scheme 2 where contributing structures have the *i*PrO moiety in different environments.

^{13}C NMR of these compounds at 25 °C shows broad signals with extremely poor intensities and resolution. However, the spectral characteristics at –55 °C were reasonable, in accord to the conclusions drawn from ^{1}H NMR studies (see Supporting Information). In all the aryloxy compounds **1**–**18**, the *ipso* carbon of the phenyl ring is deshielded with respect to the corresponding phenol and there is no appreciable change in the position of the signals

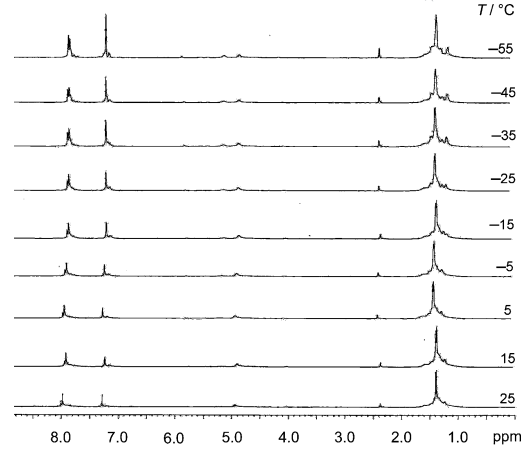
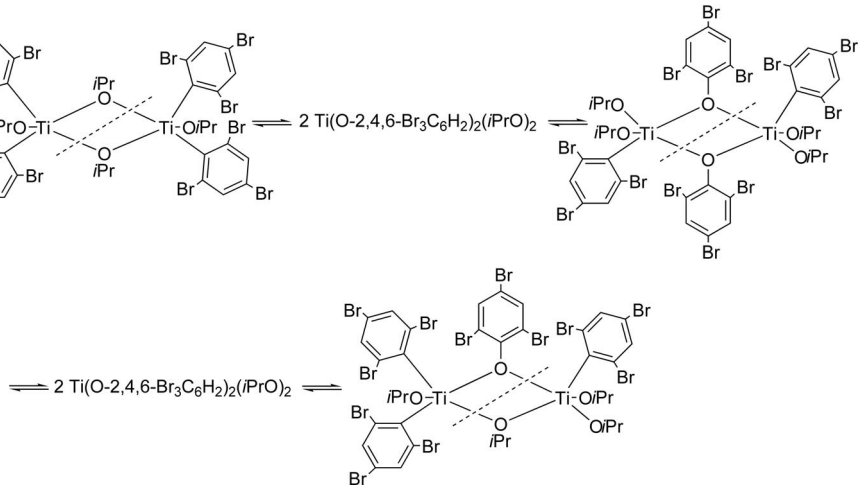


Figure 1. Variable-temperature ^{1}H NMR spectrum of **18** in $CDCl_3$.

contributed by the other carbon atoms of the phenyl ring. The CH peak of *i*PrO group in **15**–**18** (δ = 78.39–88.97 ppm) is deshielded considerably as compared to that seen for cases that have coordinated *i*PrOH (**2**, **5**–**7**, **10**–**14**) (δ = 70.94–76.94 ppm). Similar conclusions are seen for the benzyloxy derivatives **19** and **20** respectively.

The $^{47/49}$Ti NMR spectra for a few compounds (**6**, **10**, **12** and **17**) with different electronic environments on the titanium centers were studied. The results are concordant in correlation with the expectation that the position of the signal with be gradually deshielded with electronic withdrawing substituents on the phenyl ring.[66] The signals are broad (see Supporting Information), suggesting the fluxional behavior of such molecules.

ESI-MS studies reveal the presence of $\{M_2 - (OAr) + Na\}^+$ [M = $Ti(OAr)_4$ (**1**, **3**–**4**, **8**–**9**), $Ti(OAr)_4$(*i*PrOH) (**2**, **5**–**7**, **10**–**14**), $Ti(OAr)_2$(*i*PrO)$_2$ (**15**–**18**), $Ti(OCH_2Ar)_4$ (**19**–**20**)] peak as the sodium adduct in prominent intensity (see Supporting Information). These observations indicate that such molecules exist predominantly as dimers.



Scheme 2. Solution dynamics of **18**.

Single-Crystal X-ray Diffraction Studies

Among the several compounds synthesized in this study, suitable crystals for X-ray diffraction studies could be obtained from **2**, **5**, **6** and **11** respectively. Although the synthesis of **11** is reported, we considered it worthwhile undertaking crystallographic studies since it has substitution on the phenyl ring at the 4-position and crystals suitable for X-ray diffraction could be grown easily. Single crystals were grown in a glove box at –23 °C from dilute toluene solutions of the respective compounds over a period of two weeks. The molecular structures of **2** and **6** are depicted in Figures 2 and 3, respectively (for **5** and **11**, see Supporting Information).

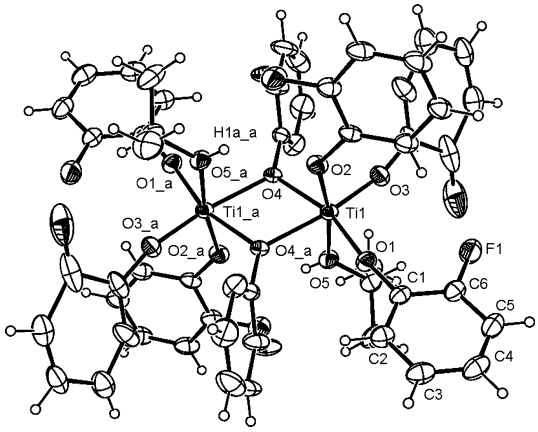


Figure 2. Molecular structure of **2**; thermal ellipsoids were drawn at 30% probability level.

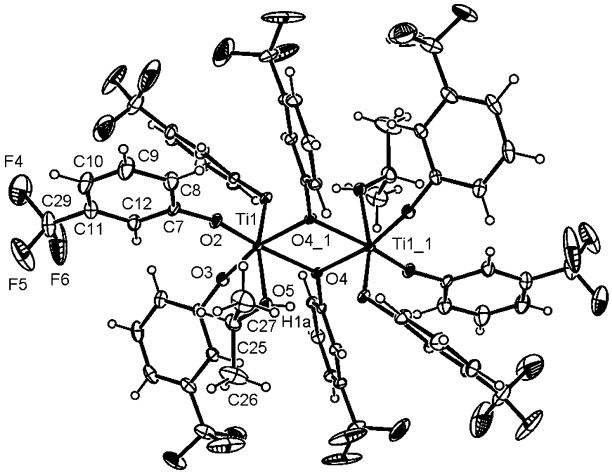


Figure 3. Molecular structure of **6**; thermal ellipsoids were drawn at 30% probability level.

The molecules discussed exhibit centrosymmetric dimeric structure in the solid state possessing edge shared distorted octahedral titanium centers coordinated to a molecule of *i*PrOH. The two titanium centers are separated by ca. 3.3 Å. The terminal Ti–O bonds of the phenoxy moieties are shorter than those contributing towards the formation of the bridged bonds. The four Ti–O bonds forming the core are almost indistinguishable suggesting nearly equal covalent and dative contributions, leading to a stable dimeric core. The coordinated *i*PrOH can be easily identified by the bond length Ti(1)–O(5), being much longer than the other Ti–O distances. The distorted octahedral environment around the titanium centers is apparent from the bond angles. There is hydrogen bonding [2.376(3) Å in **2**, 2.062(2) Å in **5**, 2.135(3) Å in **6** and 1.985(3) Å in **11**] between the OH group of *i*PrOH coordinated to a titanium and to one of the terminal OAr ligands of the neighboring titanium. All the structure parameters match well with the literature precedents.[62,66]

Examination of the structural differences between these compounds through space-filling models suggests steric congestion as a common feature. This is particularly enhanced in cases with a halogen substituent at the 2-position of the phenyl ring. This may be understood by considering the space-filling model of **2** (Figure 4). The titanium centers are embedded within the aryloxy periphery and coordination of *i*PrOH may not be as facile, although the enhancement of Lewis acidity of the Ti centers is expected. With larger electron-withdrawing substituents (Cl and Br in **3** and **4**) at the 2-position, the coordination of *i*PrOH may not be favored in spite of an increase in the Lewis acidity of the titanium center. Hence, *i*PrOH adducts are not seen. Such steric considerations do not play an important role with substituents at 3- and 4-positions of the phenyl ring. Hence compounds with electron-withdrawing substituents at these positions (**5**–**7** and **10**–**12**) appear as *i*PrOH adducts. In the case of **13** and **14**, the Lewis acidity of Ti is enhanced to a very large extent, forcing *i*PrOH coordination even under nonfavorable steric constraints.

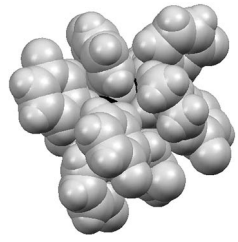


Figure 4. Space filling model of **2** (Ti in black).

Polymerization Activity and Characteristics

Recent results from our group indicate that metal initiators with elaborate ligands constituting the backbone are not an essential requirement towards the polymerization of lactones. Utilizing the activated monomer mechanism it is possible to produce high polymers with good MWDs by performing such polymerizations in the presence of alcoholic initiators.[55] Our impetus in this direction obtained a boost from the recent description of employing $Ti(OPh)_4$ as the initiator for the polymerization of CL.[47] The polymerizations were reported to proceed via the coordination-insertion mechanism. The conclusions were confirmed using rheological methods. The studies described did not

provide correlation between polymerization characteristics and ligand environment as they were confined to $Ti(OPh)_4$ alone. We surmised that a variation of electronic environments of the phenyl ring constituting the OAr moiety must have a consequence in such polymerizations.

Our studies were confined to using these compounds alone in the form of initiators for the polymerization of CL and VL and using them in the form of catalysts in the presence of BnOH as initiator. To the best of our belief, such polymerizations in the presence of an alcoholic initiator like BnOH has not been reported so far using titanium derivatives.[30,35–37,41,43–46,48] We also considered it appropriate to compare the results using different aryloxy compounds **1**–**18** to those using the benzyloxy derivatives **19** and **20**, respectively. These polymerizations were performed under bulk conditions at 80 °C using **1**–**20**. In addition, there is no report of bulk polymerization of lactones using organometallic titanium derivatives. Polymerization under ambient temperatures yielded low molecular weight oligomers. The results are summarized in Tables 1, 2, 3, and 4 respectively.

Table 1. Results of CL polymerization using various aryloxy compounds and benzyloxy derivatives in 200:1 ratio at 80 °C.

Entry	Initiator	Time[a] /s	% Yield[b]	10^3 M_n[c] / g/mol	PDI (M_w/M_n)
1	**1**	40	100	6.37	2.32
2	**2**	5	100	7.10	2.02
3	**3**	50	100	13.57	2.12
4	**4**	98	100	92.23	2.53
5	**5**	153	100	4.02	2.62
6	**6**	240	100	7.44	2.60
7	**7**	305	100	26.33	2.59
8	**8**	55	100	79.39	2.22
9	**9**	210	100	68.97	2.46
10	**10**	270	100	64.73	2.26
11	**11**	300	100	54.30	2.35
12	**12**	307	100	95.76	2.16
13	**13**	345	100	6.36	2.54
14	**14**	360	100	9.39	2.51
15	**15**	45	100	30.19	2.19
16	**16**	60	100	50.42	2.69
17	**17**	79	100	53.36	2.79
18	**18**	88	100	70.30	2.55
19	**19**	348	100	5.11	2.04
20	**20**	355	100	20.57	2.72

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b] Isolated yield. [c] Measured by GPC at 27 [°C] in THF relative to polystyrene standards with Mark–Houwink corrections for M_n.

Analysis of the results depicted in Table 1, Table 2, Table 3, and Table 4 reveal that for compounds containing strongly electron-withdrawing ligands **2**, **5**–**6**, **13**–**15**, comparatively faster transesterification reactions occur leading to the formation of poly(lactones) with low to modest M_n. The benzyloxy derivatives **19** and **20** are inferior to the aryloxy compounds **1**–**18**. In the presence of BnOH, reasonable degree of control in the polymerization process was reflected in terms of lower MWDs (Entry 1–20 of Table 1 vs. Entries 1–20 of Table 2 and Entry 1–20 of Table 3 vs. Entries 1–20 of Table 4) and enhanced molecular weights (M_n) of the resulting polymers. In such cases the polymerization

Table 2. Results of CL polymerization using various aryloxy compounds and benzyloxy derivatives in the presence of benzyl alcohol in 200:1:5 ratio at 80 °C.

Entry	Catalyst	Time[a] /s	% Yield[b]	10^3 M_n[c] / g/mol	PDI (M_w/M_n)
1	**1**	28	100	10.61	1.40
2	**2**	3	100	13.65	1.42
3	**3**	39	100	14.77	1.41
4	**4**	82	100	**136.45**	1.45
5	**5**	125	100	9.92	1.47
6	**6**	133	100	16.48	1.48
7	**7**	223	100	30.49	1.49
8	**8**	37	100	80.33	1.41
9	**9**	133	100	78.69	1.43
10	**10**	127	100	**136.75**	1.47
11	**11**	224	100	72.62	1.44
12	**12**	197	100	**114.38**	1.43
13	**13**	254	100	11.30	1.48
14	**14**	301	100	20.39	1.46
15	**15**	36	100	39.61	1.48
16	**16**	49	100	67.59	1.46
17	**17**	65	100	75.21	1.44
18	**18**	67	100	95.74	1.45
19	**19**	224	100	7.97	1.49
20	**20**	298	100	22.11	1.42

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b] Isolated yield. [c] Measured by GPC at 27 [°C] in THF relative to polystyrene standards with Mark–Houwink corrections for M_n.

Table 3. Results of VL polymerization using various aryloxy compounds and benzyloxy derivatives in 200:1 ratio at 80 °C.

Entry	Initiator	Time[a] /s	% Yield[b]	10^3 M_n[c] / g/mol	PDI (M_w/M_n)
1	**1**	420	100	23.13	2.34
2	**2**	510	100	24.20	2.80
3	**3**	600	100	60.10	2.40
4	**4**	720	100	70.37	2.49
5	**5**	98	100	19.17	2.20
6	**6**	720	100	11.45	2.25
7	**7**	790	100	19.29	2.17
8	**8**	310	100	32.86	2.03
9	**9**	800	100	138.12	2.79
10	**10**	820	100	18.88	2.16
11	**11**	1000	100	24.67	2.10
12	**12**	1200	100	22.58	2.73
13	**13**	960	100	10.41	2.65
14	**14**	1080	100	10.43	2.88
15	**15**	624	100	14.18	2.18
16	**16**	800	100	71.37	2.76
17	**17**	878	100	79.65	2.42
18	**18**	957	100	113.96	2.74
19	**19**	628	100	4.65	2.01
20	**20**	750	100	9.07	2.19

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b] Isolated yield. [c] Measured by GPC at 27 [°C] in THF relative to polystyrene standards.

was found to proceed to completion much faster as reflected by the polymerization time. In the presence of BnOH, the observed M_n of the polymers were found to be much higher in magnitude. Hence it may be concluded that the rates of initiation and propagation are much more rapid than that of chain transfer. As a consequence, a better con-

Table 4. Results of VL polymerization using various aryloxy compounds and benzyloxy derivatives in the presence of benzyl alcohol in 200:1:5 ratio at 80 °C.

Entry	Catalyst	Time[a] /s	% Yield[b]	10^3 M_n[c] / g/mol	PDI (M_w/M_n)
1	**1**	325	100	35.74	1.46
2	**2**	445	100	27.87	1.45
3	**3**	466	100	70.38	1.48
4	**4**	600	100	73.10	1.49
5	**5**	77	100	22.10	1.41
6	**6**	668	100	15.19	1.47
7	**7**	698	100	24.28	1.41
8	**8**	228	100	34.71	1.42
9	**9**	725	100	**272.86**	1.49
10	**10**	742	100	29.12	1.43
11	**11**	885	100	36.82	1.46
12	**12**	950	100	36.06	1.42
13	**13**	725	100	18.70	1.42
14	**14**	805	100	19.47	1.47
15	**15**	828	100	25.65	1.43
16	**16**	910	100	74.53	1.34
17	**17**	510	100	**111.57**	1.48
18	**18**	705	100	**255.68**	1.45
19	**19**	506	100	12.51	1.44
20	**20**	664	100	18.71	1.40

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b] Isolated yield. [c] Measured by GPC at 27 [°C] in THF relative to polystyrene standards.

trol over M_n is observed. For polymerizations where there is slow initiation or rapid transesterification, the observed M_n is lower in magnitude than those expected.[67–69]

Some of our results (Entries 4, 10 and 12 of Table 2 and Entries 9, 17 and 18 of Table 4) deserve special mention because of exceptionally high magnitudes of M_n of the respective polymers. We have obtained the highest molecular weight poly(caprolactone) in comparison to the results known for organometallic initiators of titanium.[30,35–37,41,43–46,48]

The variations of M_n with $[CL]_o/[Ti]_o$ ratio using **6**, **14**, **17** and **20** for CL polymerizations were studied. The plots are linear indicating that there is a continual rise in M_n with an increase in $[CL]_o/[Ti]_o$ ratio. Similar conclusions were drawn for VL polymerizations (see Supporting Information).

It may be intriguing to understand what happens to the identity of **1**–**20** in the presence of BnOH added during polymerization. To answer this, we have independently performed reactions by heating **9**, **13** and **20** in the presence of 5 equiv. BnOH at 80 °C in toluene for 4 hours. At the end, all volatiles were removed in vacuo and the residue was subjected to ^{1}H NMR studies. To our surprise in the case of **9** and **13**, peaks corresponding to BnOH alone were observed. This implies very clearly that the *i*PrOH coordination in **13** is loose and upon the addition of BnOH, it has a spontaneous tendency to escape the coordination sphere whereas BnOH being comparatively bulky finds it difficult to coordinate. These conclusions are in agreement to our expectations using space-filling model. Compound **20**, being a more open structure allows the replacement of *i*PrOH by BnOH since the latter is in excess and being a primary alcohol. This is concluded by analyzing the methylene peak in the ^{1}H NMR spectrum. The closed structure of **9** prevents the coordination of BnOH. In summary, the catalyst identity remains unaltered in the presence of BnOH during polymerization reactions (see Supporting Information).

The dependence of M_n upon varying the feed ratio of CL to BnOH as initiator was examined using **6**, **14**, **17** and **20**. The M_n increased almost linearly with increasing feed ratio of CL to BnOH. Similar inferences were drawn using VL (see Supporting Information).

Kinetics of Polymerization

The kinetic studies for the polymerization of CL and VL using **6**, **14**, **17** and **20** in the absence and presence of BnOH were studied. The kinetic studies for the polymerization of CL in ratio $[CL]_o/[Ti]_o$ = 1000 and $[CL]_o/[Ti]_o/[BnOH]_o$ = 1000:1:5 were performed at 80 °C (see Supporting Information). The results are depicted in Figure 5 and Figure 6 respectively. The plots suggest that there is a first-order dependence of the rate of polymerization on monomer concentration. There is no induction period.

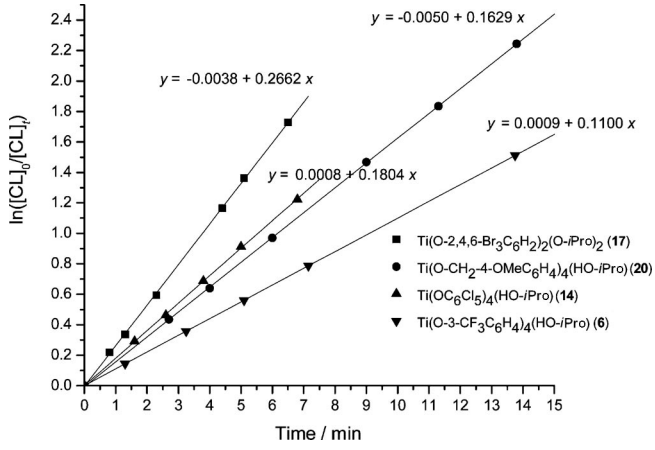


Figure 5. Semilogarithmic plots of CL conversion in time initiated by **6**, **14**, **17** and **20**: $[CL]_o/[Ti]_o$ = 1000 at 80 °C.

The $\ln[CL]_o/[CL]_t$ vs. time plots (Figures 5 and 6) exhibit linear variation. From the slope of the plots, the values of the apparent rate constant (k_{app}) for CL polymerizations initiated by **6**, **14**, **17** and **20** were found to be 11.00×10^{-2} min^{-1}, 18.04×10^{-2} min^{-1}, 26.62×10^{-2} min^{-1} and 16.29×10^{-2} min^{-1} in the absence of BnOH and 15.07×10^{-2} min^{-1}, 23.40×10^{-2} min^{-1}, 31.65×10^{-2} min^{-1} and 20.82×10^{-2} min^{-1} in the presence of BnOH. For VL, the conclusions are similar and the apparent rate constant (k_{app}) for polymerizations initiated by **6**, **14**, **17** and **20** were found to be 9.13×10^{-2} min^{-1}, 5.17×10^{-2} min^{-1}, 12.23×10^{-2} min^{-1} and 6.01×10^{-2} min^{-1} in the absence of BnOH and 12.42×10^{-2} min^{-1}, 14.15×10^{-2} min^{-1}, 19.14×10^{-2} min^{-1} and 11.36×10^{-2} min^{-1} in the presence of BnOH (see Supporting Information). These results indicate that the rates are faster in the presence of BnOH. To the

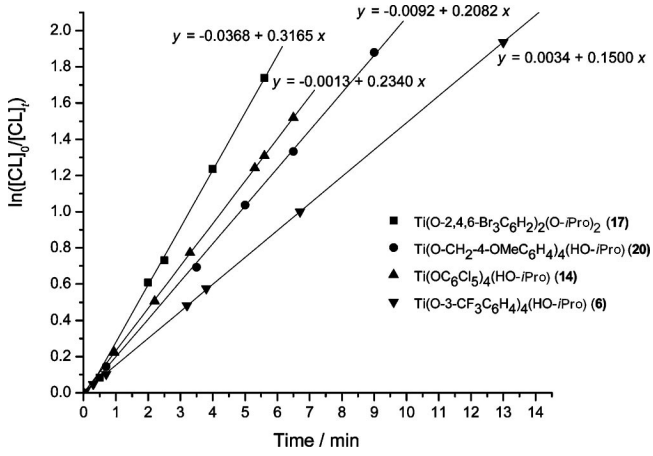


Figure 6. Semilogarithmic plots of CL conversion in time initiated by **6**, **14**, **17** and **20**: $[CL]_o/[Ti]_o/[BnOH]_o$ = 1000:1:5 at 80 °C.

best of our knowledge, there is no report stating k_{app} magnitudes using titanium derivatives for CL polymerization. Kinetic studies using a protic initiator like BnOH have not been attempted previously. Polymerization studies on VL using titanium compounds are not reported.

Insight into Polymerization Mechanism

A convenient tool to gain insight into the polymerization mechanism using **1**–**20** is a thorough understanding of the polymer composition upon using these compounds as initiators or catalyst through MALDI-TOF and ^{1}H NMR spectroscopy. We selected **2** and **9** as prototype representatives for compounds with *i*PrOH coordination and without. Low molecular weight oligomers of poly(caprolactone) were synthesized by stirring CL with **2** or **9** in 20:1 molar ratio under neat conditions at 80 °C. The product was extracted with heptane. In all the cases, the residue after removal of heptane were analyzed thoroughly using MALDI-TOF and ^{1}H NMR spectroscopy.

Using **2**, the major product of the composition *i*PrO-$[CO(CH_2)_5O]_nH$ is formed as understood through the analysis of MALDI-TOF and ^{1}H NMR spectra, depicted in Figures 7 and 8 respectively. This is an implication that coordinated *i*PrOH has an active role as an initiator and the polymerization proceeds through the activated monomer mechanism.[50–55]

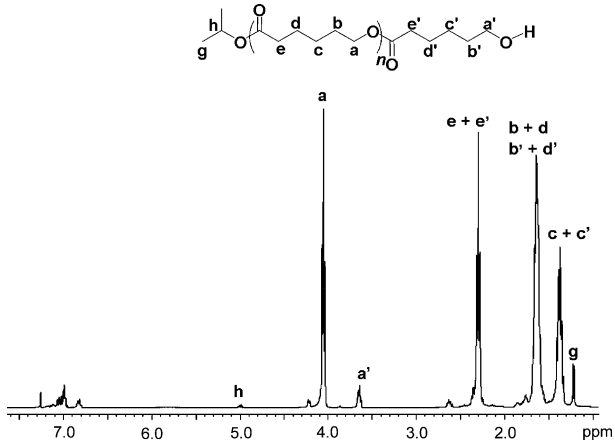


Figure 8. ^{1}H NMR spectrum of the crude product obtained from a reaction between CL and **2** in 20:1 ratio.

In case of **9**, the major product is 4-*t*BuC_6H_4O[CO-$(CH_2)_5O]_nH$ as seen from MALDI-TOF and ^{1}H NMR spectra (see Supporting Information). Here, the polymerization proceeds by the conventional coordination-insertion mechanism.[1]

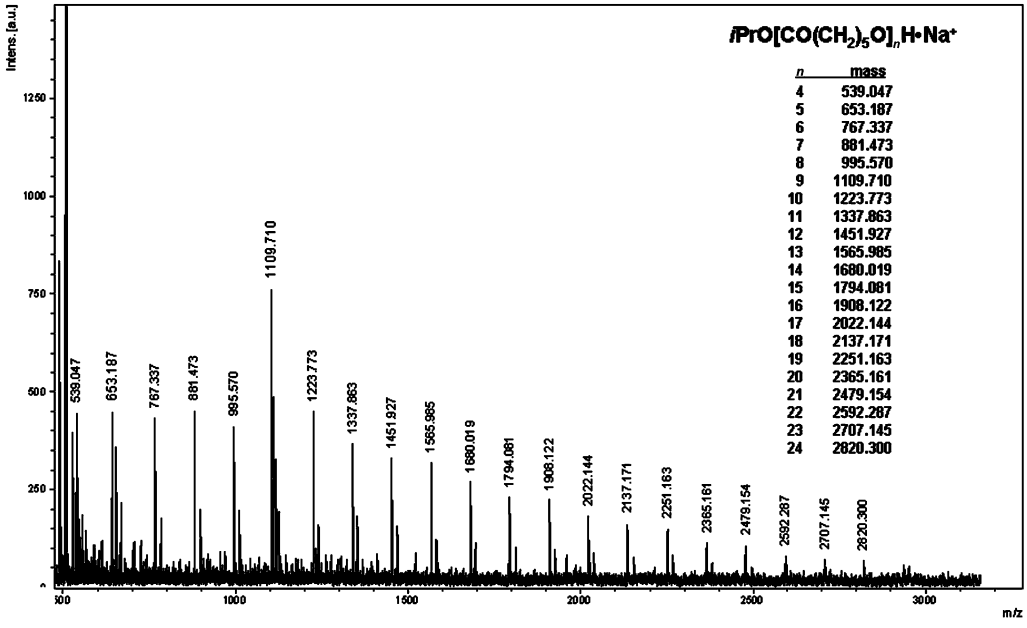


Figure 7. MALDI-TOF of the crude product obtained from a reaction between CL and **2** in 20:1 ratio.

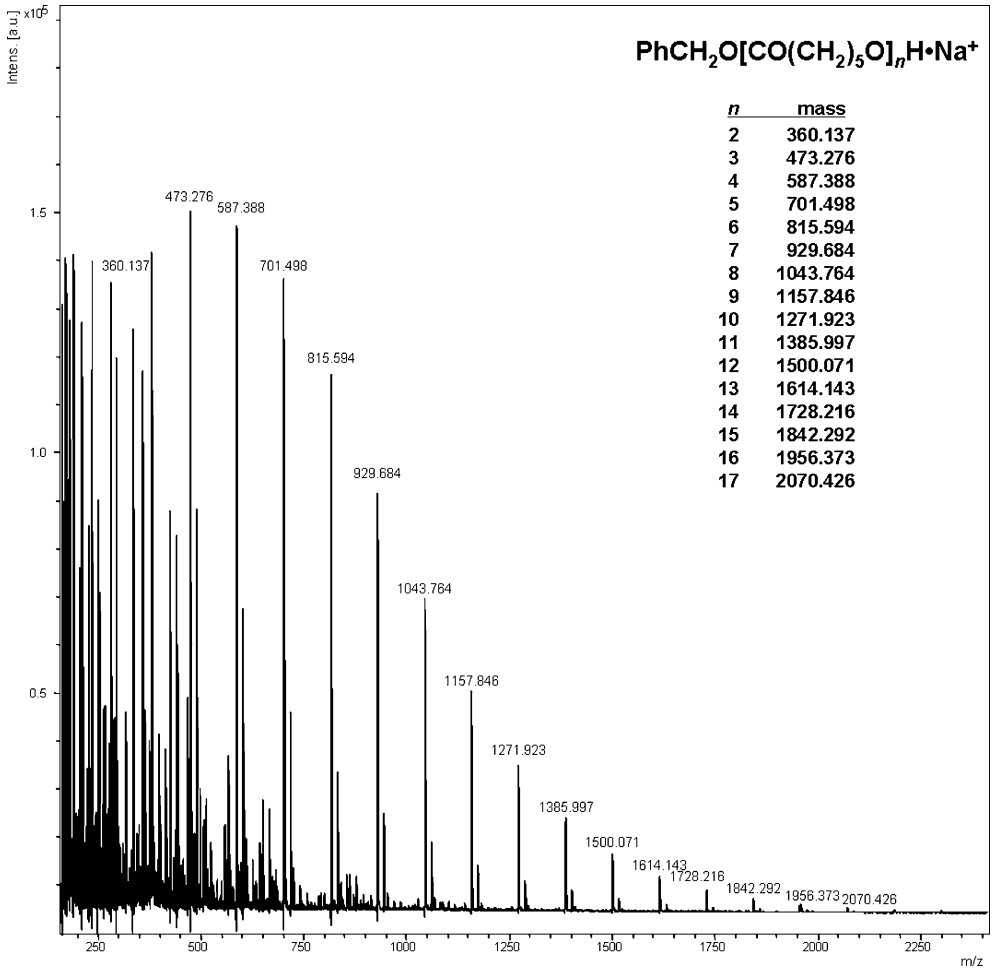


Figure 9. MALDI-TOF of the crude product obtained from a reaction between CL and **2** along with BnOH in 20:1:5 ratio.

To understand the effect of BnOH, CL along with **2** or **9** and BnOH in the ratio 20:1:5 were reacted neat at 80 °C. On a similar basis the reaction mixtures were analyzed using MALDI-TOF and ^{1}H NMR spectroscopy. In both cases an activated monomer mechanism[50–55] prevails and results in the formation of the product $PhCH_2O[CO(CH_2)_5O]_nH$. For **2**, BnOH dominates over *i*PrOH as the initiator since it is used in excess and being a primary alcohol. The role of *i*PrOH as a competing initiator is not seen from the results using MALDI-TOF and ^{1}H NMR spectroscopy. The results for **2** are shown in Figures 9 and 10, respectively (see Supporting Information for results using **9**).

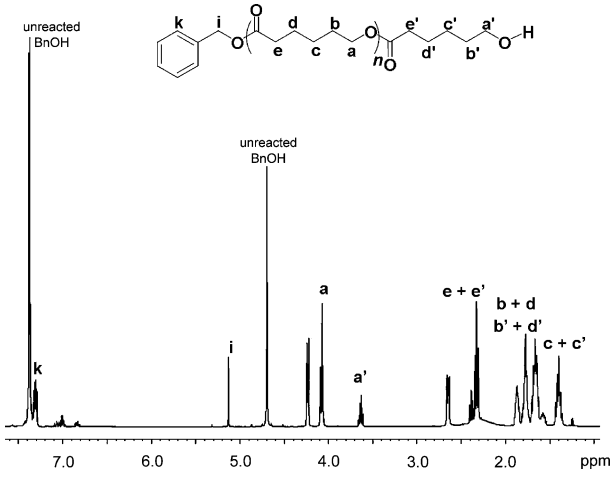


Figure 10. ^{1}H NMR spectrum of the crude product obtained from a reaction between CL and **2** along with BnOH in 20:1:5 ratio.

Comparison of Polymerization Results

In order to compare our results with those known for CL polymerization using titanium, we present here results for polymerizations conducted in the presence of toluene (Tables 5 and 6, respectively).

In the presence of toluene these polymerizations are more controlled and result in good MWDs. Our results are superior or at least comparable to literature reports.[30,35–37,41,43–46,48] Such observations are also seen for the bulk polymerizations conducted in the absence of solvents.

Table 5. Results of CL polymerization using **6**, **9**, **14**, **17** and **20** in 200:1 ratio at 80 °C in toluene.

Entry	Initiator	Time[a] /s	% Yield[b]	10^3 M_n[c] / g/mol	PDI (M_w/M_n)
1	**6**	560	100	5.15	1.30
2	**9**	480	100	50.86	1.31
3	**14**	740	100	9.12	1.35
4	**17**	280	100	45.36	1.37
5	**20**	820	100	11.57	1.34

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b] Isolated yield. [c] Measured by GPC at 27 [°C] in THF relative to polystyrene standards with Mark–Houwink corrections for M_n.

Table 6. Results of CL polymerization using **6**, **9**, **14**, **17** and **20** in the presence of BnOH in 200:1:5 ratio at 80 °C in toluene.

Entry	Initiator	Time[a] /s	% Yield[b]	10^3 M_n[c] / g/mol	PDI (M_w/M_n)
1	**6**	350	100	7.30	1.15
2	**9**	325	100	61.85	1.26
3	**14**	620	100	24.97	1.29
4	**17**	200	100	56.12	1.20
5	**20**	670	100	12.10	1.20

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b] Isolated yield. [c] Measured by GPC at 27 [°C] in THF relative to polystyrene standards with Mark–Houwink corrections for M_n.

Conclusions

In summary, we have used the alcoholysis route for synthesizing several new aryloxy compounds and benzyloxy derivatives of titanium. These compounds have high degree of fluxionality and possess an inherent tendency for oligomerization in solution. They are potent activators for the polymerization of CL and VL and some of them produce products with exceptionally high molecular weights. The tendency of such polymerizations can be enhanced considerably by using BnOH as an initiator, resulting in telechelic polymers. These results are based upon a simplified approach to the polymerization of cyclic esters using mild Lewis acids as catalysts and alcoholic initiators, using the activated monomer mechanism. The methodology employed and the concepts reported may be considered crucial for bulk scale procedures. The achievement of obtaining good molecular weights without having to resort to elaborate ligands is a noted feature for our system.

Experimental Section

General Procedure: All reactions were performed under dry argon atmosphere using standard Schlenk techniques or in a glove box with rigorous exclusion of moisture and air. Toluene was dried by heating under reflux over sodium and benzophenone and distilled fresh prior to use. $CDCl_3$ used for NMR spectral measurements was dried with calcium hydride, distilled and stored in a glove box. ^1H, ^{13}C and $^{47/49}Ti$ NMR spectra were recorded with a Bruker Avance 400 instrument. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to residual solvent resonances and are reported as parts per million relative to $SiMe_4$. $^{47/49}Ti$ NMR spectra were recorded relative to $TiCl_4$ as an external standard. ESI-MS spectra of the samples were obtained from Waters Q-Tof micro mass spectrometer. MALDI-TOF measurements were performed on a Bruker Daltonics instrument in dihydroxy benzoic acid matrix. Elemental analyses were done with a Perkin–Elmer Series 11 analyzer. All phenols and benzyl alcohol derivatives used in this study along with Ti(*i*PrO)$_4$ were purchased from Aldrich and used without subsequent purification. CL and VL were purchased from Aldrich, dried with CaH_2 overnight and distilled fresh prior to use. Compound **11** was prepared using the literature procedure.[62]

[Ti(O-2-MeC$_6$H$_4$)$_4$]$_2$ (1): Under an argon atmosphere, to a stirred solution of 2-MeC$_6$H$_4$OH (0.25 g, 2.32 mmol) in 5 mL of toluene at 27 °C, was added Ti(*i*PrO)$_4$ (0.16 g, 0.58 mmol). An orange solution resulted immediately. The reaction mixture was heated to 80 °C for a period of 3h. The contents were cooled to ambient temperature. The solvent was removed under reduced pressure to yield an orange-yellow solid which was purified by recrystallization from toluene at –20 °C. The crystallized solid was recovered by filtration and dried in vacuo; yield 0.49 g, 91%; m.p. 162 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.0–6.8 (16 H, *ortho*, *meta*, *para*), 2.11 (s, 12 H, Ar*Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 164.88 (Ar-O), 130.81 (Ar-C), 127.48 (Ar-C), 126.78 (Ar-CH$_3$), 122.74 (Ar-C), 115.23 (Ar-C), 16.85 (Ar-*C*H$_3$) ppm. ESI-MS: *m*/*z* = 868 {(Ti(O-2-MeC$_6$H$_4$)$_4$)$_2$ – (O-2-MeC$_6$H$_4$) + Na}$^+$. $C_{28}H_{28}O_4Ti$ (476.39): calcd. C 70.59, H 5.92; found C 70.78, H 5.69.

[Ti(O-2-FC$_6$H$_4$)$_4$(*i*PrOH)]$_2$ (2): 2-FC$_6$H$_4$OH (0.25 g, 2.24 mmol) and Ti(*i*PrO)$_4$ (0.16 g, 0.56 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed; yield 0.55 g, 89%; m.p. 168 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.9–6.7 (16 H, *ortho*, *meta*, *para*), 4.69 (br., 1 H, C*H*Me$_2$), 1.18 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 153.10 (Ar-F), 151.87 (Ar-O), 124.90 (Ar-C), 123.82 (Ar-C), 122.90 (Ar-C), 115.87 (Ar-C), 71.46 (*C*HMe$_2$), 24.1 (CH*Me*$_2$) ppm. ESI-MS: *m*/*z* = 1016 {(Ti(O-2-FC$_6$H$_4$)$_4$(*i*PrOH))$_2$ – (O-2-FC$_6$H$_4$) + Na}$^+$. $C_{27}H_{24}F_4O_5Ti$ (552.34): calcd. C 58.71, H 4.38; found C 59.01, H 4.52.

[Ti(O-2-ClC$_6$H$_4$)$_4$]$_2$ (3): 2-ClC$_6$H$_4$OH (0.25 g, 1.92 mmol) and Ti(*i*PrO)$_4$ (0.14 g, 0.48 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed; yield 0.46 g, 87%; m.p. 163 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.1–6.7 (16 H, *ortho*, *meta*, *para*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 161.50 (Ar-O), 129.43 (Ar-C), 128.80 (Ar-C), 123.83 (Ar-Cl), 123.12 (Ar-C), 121.14 (Ar-C) ppm. ESI-MS: *m*/*z* = 1012 {(Ti(O-2-ClC$_6$H$_4$)$_4$)$_2$ – (O-2-ClC$_6$H$_4$) + Na}$^+$. $C_{24}H_{16}Cl_4O_4Ti$ (558.06): calcd. C 51.65, H 2.89; found C 51.94, H 3.24.

[Ti(O-2-BrC$_6$H$_4$)$_4$]$_2$ (4): 2-BrC$_6$H$_4$OH (0.25 g, 1.44 mmol) and Ti(*i*PrO)$_4$ (0.10 g, 0.36 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed; yield 0.44 g, 85%; m.p. 158 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.2–6.6 (16 H, *ortho*, *meta*, *para*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 162.76 (Ar-O), 132.74 (Ar-C), 128.64 (Ar-C), 122.15 (Ar-C), 116.53 (Ar-C), 113.83 (Ar-Br) ppm. ESI-MS: *m*/*z* = 1323 {(Ti(O-2-BrC$_6$H$_4$)$_4$)$_2$ – (O-2-BrC$_6$H$_4$) + Na}$^+$. $C_{24}H_{16}Br_4O_4Ti$ (735.86): calcd. C 39.17, H 2.19; found C 39.38, H 1.87.

[Ti(O-3-FC$_6$H$_4$)$_4$(*i*PrOH)]$_2$ (5): Under an argon atmosphere, to a stirred solution of 3-FC$_6$H$_4$OH (0.25 g, 2.24 mmol) in 5 mL of toluene at 27 °C, was added Ti(*i*PrO)$_4$ (0.16 g, 0.56 mmol). An orange solution resulted immediately. The reaction mixture was stirred at this temperature for a period of 12h. The solvent was removed under reduced pressure to yield an orange yellow solid which was purified by recrystallization from toluene at –20 °C. The crystallized solid was recovered by filtration and dried in vacuo; yield

0.56 g, 90%; m.p. 173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.1–6.3 (16 H, *ortho*, *meta*, *para*), 4.24 (br., 1 H, C*H*Me$_2$), 1.16 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 164.74 (Ar-F), 162.29 (Ar-O), 130.29 (Ar-C), 114.87 (Ar-C), 109.20 (Ar-C), 106.60 (Ar-C), 72.13 (*C*HMe$_2$), 25.14 (CH*Me*$_2$) ppm. ESI-MS: *m*/*z* = 1016 {(Ti(O-3-FC_6H_4)$_4$(*i*PrOH))$_2$ – (O-3-FC_6H_4) + Na}$^+$. $C_{27}H_{24}F_4O_5Ti$ (552.34): calcd. C 58.71, H 4.38; found C 59.12, H 4.56.

[Ti(O-3-$CF_3C_6H_4$)$_4$(*i*PrOH)]$_2$ (6): 3-$CF_3C_6H_4OH$ (0.25 g, 1.56 mmol) and Ti(*i*PrO)$_4$ (0.11 g, 0.39 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed; yield 0.51 g, 89%; m.p. 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.2–6.6 (16 H, *ortho, meta, para*), 4.29 (br., 1 H, C*H*Me$_2$), 1.14 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 164.57 (Ar-O), 132.25 (Ar-CF_3), 130.14 (Ar-C), 123.73 (CF_3), 122.36 (Ar-C), 121.81 (Ar-C), 115.67 (Ar-C), 71.32 (*C*HMe$_2$), 24.85 (CH*Me*$_2$) ppm. $^{47/49}$Ti NMR (22.54 MHz, $CDCl_3$): δ = –28.07 ppm. ESI-MS: *m*/*z* = 1366 {(Ti(O-3-$CF_3C_6H_4$)$_4$(*i*PrOH))$_2$ – (O-3-$CF_3C_6H_4$) + Na}$^+$. $C_{31}H_{24}F_{12}O_5Ti$ (752.37): calcd. C 49.49, H 3.22; found C 49.65, H 2.96.

[Ti(O-3-$NO_2C_6H_4$)$_4$(*i*PrOH)]$_2$ (7): 3-$NO_2C_6H_4OH$ (0.25 g, 1.80 mmol) and Ti(*i*PrO)$_4$ (0.13 g, 0.45 mmol) were reacted. The reaction mixture was stirred at 80 °C for 12h and a procedure identical to that used for the synthesis of **1** was followed; yield 0.53 g, 90%; m.p. 184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.8–7.1 (16 H, *ortho, meta, para*), 7.25–7.18 (m, C_7H_8), 4.40 (br., 1 H, C*H*Me$_2$), 2.35 (m, C_7H_8), 1.19 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 156.17 (Ar-O), 148.39 (Ar-NO_2), 137.90 (C_7H_8), 130.45 (Ar-C), 129.07 (C_7H_8), 128.27 (C_7H_8), 125.26 (C_7H_8), 122.38 (Ar-C), 117.75 (Ar-C), 110.31 (Ar-C), 76.83 (*C*HMe$_2$), 24.87 (CH*Me*$_2$), 23.20 (C_7H_8) ppm. ESI-MS: *m*/*z* = 1205 {(Ti(O-3-$NO_2C_6H_4$)$_4$(*i*PrOH))$_2$ – (O-3-$NO_2C_6H_4$) + Na}$^+$. $C_{27}H_{24}N_4O_{13}Ti$ (660.37): calcd. C 49.11, H 3.66, N 8.48; found C 49.53, H 3.39, N 8.99.

[Ti(O-4-MeC_6H_4)$_4$]$_2$ (8): 4-MeC_6H_4OH (0.25 g, 2.32 mmol) and Ti(*i*PrO)$_4$ (0.16 g, 0.58 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed; yield 0.48 g, 89%; m.p. 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.02 (d, 8 H, *meta*), 6.71 (d, 8 H, *ortho*), 2.27 (s, 12 H, Ar*Me*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 173.62 (Ar-O), 153.81 (Ar-C), 130.40 (Ar-CH_3), 115.41 (Ar-C), 20.8 (Ar-*Me*) ppm. ESI-MS: *m*/*z* = 868 {(Ti(O-4-MeC_6H_4)$_4$)$_2$ – (O-4-MeC_6H_4) + Na}$^+$. $C_{28}H_{28}O_4Ti$ (476.39): calcd. C 70.59, H 5.92; found C 70.80, H 5.62.

[Ti(O-4-*t*BuC_6H_4)$_4$]$_2$ (9): 4-*t*BuC_6H_4OH (0.25 g, 1.68 mmol) and Ti(*i*PrO)$_4$ (0.12 g, 0.42 mmol) were reacted and an identical procedure used for the synthesis of **5** was employed; yield 0.47 g, 88%; m.p. 175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (d, 8 H, *meta*), 6.26 (d, 8 H, *ortho*), 1.15 (36 H, C*Me*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 163.93 (Ar-O), 143.77 (Ar-*t*-Bu), 125.56 (Ar-C), 118.18 (Ar-C), 34.35 (*C*Me$_3$), 31.69 (C*Me*$_3$) ppm. ESI-MS: *m*/*z* = 1163 {(Ti(O-4-*t*BuC_6H_4)$_4$)$_2$ – (O-4-*t*BuC_6H_4) + Na}$^+$. $C_{40}H_{52}O_4Ti$ (644.71): calcd. C 74.52, H 8.13; found C 74.76, H 7.89.

[Ti(O-4-$CF_3C_6H_4$)$_4$(*i*PrOH)]$_2$ (10): 4-$CF_3C_6H_4OH$ (0.25 g, 1.56 mmol) and Ti(*i*PrO)$_4$ (0.11 g, 0.39 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed; yield 0.50 g, 88%; m.p. 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.4–6.7 (16 H, *ortho, meta*), 4.27 (br., 1 H, C*H*Me$_2$), 1.11 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 166.90 (Ar-O), 126.50 (Ar-C), 122.38 (CF_3), 120.20 (Ar-C), 115.30 (Ar-C), 70.94 (*C*HMe$_2$), 24.82 (CH*Me*$_2$) ppm. $^{47/49}$Ti NMR (22.54 MHz, $CDCl_3$): δ = –19.14 ppm. ESI-MS: *m*/*z* = 1366 {(Ti(O-4-$CF_3C_6H_4$)$_4$-(*i*PrOH))$_2$ – (O-4-$CF_3C_6H_4$) + Na}$^+$. $C_{31}H_{24}F_{12}O_5Ti$ (752.37): calcd. C 49.49, H 3.22; found C 50.01, H 2.89.

[Ti(O-4-IC_6H_4)$_4$(*i*PrOH)]$_2$ (12): 4-IC_6H_4OH (0.25 g, 1.12 mmol) and Ti(*i*PrO)$_4$ (0.08 g, 0.28 mmol) were reacted and an identical procedure used for the synthesis of **5** was employed; yield 0.49 g, 89%; m.p. 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.4–6.4 (16 H, *ortho, meta*) 7.26–7.18 (m, C_7H_8), 4.22 (br., 1 H, C*H*Me$_2$), 2.38 (s, C_7H_8), 1.12 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 164.60 (Ar-O), 137.80 (C_7H_8), 137.76 (Ar-C), 129.18 (C_7H_8), 128.37 (C_7H_8), 125.44 (C_7H_8), 121.17 (Ar-C), 85.50 (Ar-I), 70.40 (*C*HMe$_2$), 24.76 (CH*Me*$_2$), 21.92 (C_7H_8) ppm. $^{47/49}$Ti NMR (22.54 MHz, $CDCl_3$): δ = –175.72 ppm. ESI-MS: *m*/*z* = 1772 {(Ti(O-4-IC_6H_4)$_4$(*i*PrOH))$_2$ – (O-4-IC_6H_4) + Na}$^+$. $C_{27}H_{24}I_4O_5Ti$ (983.96): calcd. C 32.96, H 2.46; found C 33.42, H 2.87.

[Ti(OC_6F_5)$_4$(*i*PrOH)]$_2$ (13): C_6F_5OH (0.25 g, 1.36 mmol) and Ti(*i*-PrO)$_4$ (0.1 g, 0.34 mmol) were reacted and an identical procedure used for the synthesis of **5** was employed; yield 0.50 g, 89%; m.p. 188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.18 (m, C_7H_8), 4.72 (br., 1 H, C*H*Me$_2$), 2.36 (s, C_7H_8), 1.34 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 141.29 (Ar-F), 139.41 (Ar-F), 137.00 (Ar-F), 136.99 (C_7H_8), 129.31 (C_7H_8), 129.29 (Ar-O), 128.48 (C_7H_8), 125.55 (C_7H_8), 76.94 (*C*HMe$_2$), 24.31 (CH*Me*$_2$), 21.20 (C_7H_8) ppm. ESI-MS: *m*/*z* = 1520 {[Ti(OC_6F_5)$_4$-(*i*PrOH)]$_2$ – (O-C_6F_5) + Na}$^+$. $C_{27}H_8F_{20}O_5Ti$ (840.18): calcd. C 38.60, H 0.96; found C 39.19, H 1.17.

[Ti(OC_6Cl_5)$_4$(*i*PrOH)]$_2$ (14): C_6Cl_5OH (0.25 g, 0.92 mmol) and Ti-(*i*PrO)$_4$ (0.07 g, 0.23 mmol) were reacted and an identical procedure used for the synthesis of **5** was employed; yield 0.47 g, 87%; m.p. 178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.18 (m, C_7H_8), 4.83 (br., 1 H, C*H*Me$_2$), 2.38 (s, C_7H_8), 1.33 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 147.76 (Ar-O), 138.42 (Ar-Cl), 138.09 (C_7H_8), 131.19 (Ar-Cl), 129.08 (C_7H_8), 128.28 (C_7H_8), 125.28 (C_7H_8), 122.79 (Ar-Cl), 119.39 (Ar-Cl), 76.84 (*C*HMe$_2$), 24.80 (CH*Me*$_2$) 21.72 (C_7H_8) ppm. ESI-MS: 2094 {[Ti(O-C_6Cl_5)$_4$(*i*PrOH)]$_2$–(O-C_6Cl_5) + Na}$^+$. $C_{27}H_8Cl_{20}O_5Ti$ (1169.28): calcd. C 27.73, H 0.69; found C 28.17, H 0.89.

[Ti(2,4,6-$F_3C_6H_2$)$_2$(*i*PrO)$_2$]$_2$ (15): 2,4,6-$F_3C_6H_2OH$ (0.20 g, 1.36 mmol) and Ti(*i*PrO)$_4$ (0.19 g, 0.68 mmol) were reacted. The reaction mixture was stirred at 80 °C for 12h and a procedure identical to that used for the synthesis of **1** was followed; yield 0.54 g, 86%; m.p. 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.48 (4 H, *meta*), 4.81 (br., 2 H, C*H*Me$_2$), 1.24 (br., 12 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 154.86 (Ar-F), 152.05 (Ar-F), 138.62 (Ar-O), 99.47 (Ar-C), 82.88 (*C*HMe$_2$), 24.88 (CH*Me*$_2$) ppm. ESI-MS: *m*/*z* = 795 {(Ti(2,4,6-$F_3C_6H_2$)$_2$(*i*PrO)$_2$)$_2$ – (O-2,4,6-$F_3C_6H_2$) + Na}$^+$. $C_{18}H_{18}F_6O_4Ti$ (460.19): calcd. C 46.98, H 3.94; found C 47.32, H 4.36.

[Ti(2,4,6-$Cl_3C_6H_2$)$_2$(*i*PrO)$_2$]$_2$ (16): 2,4,6-$Cl_3C_6H_2OH$ (0.50 g, 2.52 mmol) and Ti(*i*PrO)$_4$ (0.36 g,1.26 mmol) were reacted. The reaction mixture was stirred at 80 °C for 12h and a procedure identical to that used for the synthesis of **1** was followed; yield 1.20 g, 86%; m.p. 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (4 H, *meta*), 4.77 (br., 2 H, C*H*Me$_2$), 1.28 (br., 12 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 157.27 (Ar-O), 128.01 (Ar-C), 124.35 (Ar-Cl), 121.18 (Ar-Cl), 78.39 (*C*HMe$_2$), 24.71 (CH*Me*$_2$) ppm. ESI-MS: *m*/*z* = 944 {(Ti(2,4,6-$Cl_3C_6H_2$)$_2$(*i*PrO)$_2$)$_2$ – (O-2,4,6-$Cl_3C_6H_2$) + Na}$^+$. $C_{18}H_{18}Cl_6O_4Ti$ (558.92): calcd. C 38.68, H 3.25; found C 39.01, H 3.30.

[Ti(O–2,4,6-$Br_3C_6H_2$)$_2$(*i*PrO)$_2$]$_2$ (17): 2,4,6-$Br_3C_6H_2OH$ (0.25 g, 0.76 mmol) and Ti(*i*PrO)$_4$ (0.10 g, 0.38 mmol) were reacted. The reaction mixture was stirred at 80 °C for 12h and a procedure iden-

tical to that used for the synthesis of **1** was followed; yield 0.53 g, 84%; m.p. 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (4 H, *meta*), 4.82 (br., 2 H, C*H*Me$_2$), 1.32 (br., 12 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 158.29 (Ar-O), 133.70 (Ar-C), 114.43 (Ar-Br), 113.38 (Ar-Br), 89.03 (*C*HMe$_2$), 25.47 (CH*Me*$_2$) ppm. $^{47/49}$Ti NMR (22.54 MHz, $CDCl_3$): δ = –25.41 ppm. ESI-MS: *m*/*z* = 1343 {(Ti(2,4,6-$Br_3C_6H_2$)$_2$(*i*PrO)$_2$)$_2$ – (O-2,4,6-$Br_3C_6H_2$) + Na}$^+$. $C_{18}H_{18}Br_6O_4Ti$ (825.62): calcd. C 26.19, H 2.20; found C 26.28, H 2.32.

[Ti(O–2,4,6-$I_3C_6H_2$)$_2$(*i*PrO)$_2$]$_2$ (18): 2,4,6-$I_3C_6H_2OH$ (0.50 g, 1.06 mmol) and Ti(*i*PrO)$_4$ (0.15 g, 0.53 mmol) were reacted. The reaction mixture was stirred at 80 °C for 12h and a procedure identical to that used for the synthesis of **1** was followed; yield 1.0 g, 83%; m.p. 162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (4 H, *meta*), 4.92 (br., 2 H, C*H*Me$_2$), 1.36 (br., 12 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 162.91 (Ar-O), 146.32 (Ar-C), 88.97 (*C*HMe$_2$), 83.93 (Ar-I), 83.40 (Ar-I), 25.71 (CH*Me*$_2$) ppm. ESI-MS: *m*/*z* = 1767 {(Ti(2,4,6-$I_3C_6H_2$)$_2$(*i*PrO)$_2$)$_2$ – (O-2,4,6-$I_3C_6H_2$) + Na}$^+$. $C_{18}H_{18}I_6O_4Ti$ (1107.63): calcd. C 19.52, H 1.64; found C 19.93, H 1.31.

[Ti(O-CH_2–4-MeC_6H_4)$_4$]$_2$ (19): 4-Me$C_6H_4CH_2OH$ (0.25 g, 2.00 mmol) and Ti(*i*PrO)$_4$ (0.14 g, 0.50 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed. A yellow oil was obtained; yield 0.47 g, 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.1–7.0 (16 H, *ortho, meta*), 4.57 (s, 8 H, O*CH*$_2$Ar), 2.17 (s, 12 H, Ar*CH*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 138.32 (O*C*H$_2$Ar), 137.71 (Ar-*C*H$_3$), 129.40 (Ar-C), 127.49 (Ar-C), 64.96 (O*C*H$_2$Ar), 22.13 (Ar-*C*H$_3$) ppm. ESI-MS: *m*/*z* = 967 {(Ti(O-CH_2-4-MeC_6H_4)$_4$)$_2$ – (O-CH_2-4-MeC_6H_4) + Na}$^+$. $C_{32}H_{36}O_4Ti$ (532.49): calcd. C 72.18, H 6.81; found C 72.39, H 6.69.

[Ti(O-CH_2-4-OMeC_6H_4)$_4$(*i*PrOH)]$_2$ (20): 4-MeO$C_6H_4CH_2OH$ (0.25 g, 1.80 mmol) and Ti(*i*PrO)$_4$ (0.13 g, 0.45 mmol) were reacted and an identical procedure used for the synthesis of **1** was employed. A pale yellow oil was obtained; yield 0.53 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.1–6.7 (16 H, *ortho, meta*), 5.14 (br., 8 H, O*CH*$_2$Ar), 4.42 (br., 1 H, C*H*Me$_2$), 3.75 (br., 12 H, ArO*CH*$_3$), 1.12 (br., 6 H, CH*Me*$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, –55 °C): δ = 157.80 (Ar-O*C*H$_3$), 133.84 (O*C*H$_2$Ar), 128.13 (Ar-C), 112.97 (Ar-C), 76.35 (*C*HMe$_2$), 74 ppm. 59 (O*C*H$_2$Ar), 55.22 (Ar-O*C*H$_3$), 26.42 (CH*Me*$_2$) ppm. ESI-MS: *m*/*z* = 1199 {(Ti(O-CH_2-4-OMeC_6H_4)$_4$(*i*PrOH))$_2$ – (O-CH_2-4-OMeC_6H_4) + Na}$^+$. $C_{35}H_{44}O_9Ti$ (656.59): calcd. C 64.02, H 6.75; found C 64.29, H 6.71.

X-ray Structure Determination of Compounds 2, 5, 6 and 11: Single crystals suitable for structural studies were obtained by crystallization from toluene at –23 °C. X-ray data collection was performed with Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite-monochromated Mo (K_α) (λ = 0.7107 Å) radiation source. The data were collected with 100% completeness for θ up to 25°. ω and ϕ scans was employed to collect the data. The frame width for ω was set to 0.5° for data collection. The frames were integrated and data were reduced for Lorentz and polarization corrections using SAINT-NT. The multi-scan absorption correction was applied to the data set. All structures were solved using SIR-92 and refined using SHELXL-97.[70] The crystal data are summarized in Table 7. The non-hydrogen atoms were refined with anisotropic displacement parameter. All the hydrogen atoms could be located in the difference Fourier map. The hydrogen atoms bonded to carbon atoms were fixed at chemically meaningful positions and were allowed to ride with the parent atom during refinement. In **2**, the carbon atoms C(15), C(16) and C(17) in the phenyl ring are distorted over two orientations in the ratio of 0.3985(3): 0.6015(2). The fluorine atoms F(3) and F(4) are disordered over two orientations in the ratio of 0.8223(2): 0.1777(2) and 0.7103(3): 0.2897(3) respectively.

General Procedure for the Polymerization of CL and VL: For CL polymerization, 23.6 μmol of the aryloxy compound and benzyloxy derivative alone or along with requisite amount of benzyl alcohol were taken in a flask under an argon atmosphere. The contents were stirred at 80 °C and 0.50 mL of CL (0.54 g, 4.71 mmols) was added neat. The mixture was rapidly stirred at the given temperature. A rise in viscosity was observed and finally the stirring ceased. For VL polymerization, 26.9 μmol was used for 0.50 mL (0.54 g,

Table 7. Crystal data for the structures **2**, **5**, **6** and **11**.[a]

Compound	**2**	**5**	**6**	**11**
Empirical formula	$C_{54}H_{48}F_8O_{10}Ti_2$	$C_{27}H_{24}F_4O_5Ti$	$C_{31}H_{24}F_{12}O_5Ti$	$C_{27}H_{24}F_4O_5Ti$
Formula weight	1104.72	552.36	752.37	552.36
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Temp. [K]	173	173	173	173
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
a [Å]	10.6437(5)	11.1460(3)	11.2724(7)	19.1921(5)
b [Å]	17.6519(10)	13.5661(4)	12.0050(7)	15.2752(3)
c [Å]	13.9814(8)	18.7052(5)	13.1236(8)	17.7851(4)
α [°]	90	101.2210(10)	102.526(3)	90
β [°]	103.592(2)	96.7120(10)	103.107(3)	98.995(10)
γ [°]	90	110.5170(10)	105.029(3)	90
V [Å^3]	2553.3(2)	2545.04(12)	1598.01(17)	5149.8(2)
Z	2	4	2	8
D_{calc} [Mg/m^3]	1.432	1.442	1.562	1.425
Reflections collected	18679	34037	21633	65450
Independent reflections	5856	11677	6639	12563
GOF	1.030	1.028	1.023	1.225
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0462	R_1 = 0.0474	R_1 = 0.0633	R_1 = 0.0475
	wR_2 = 0.1150	wR_2 = 0.1379	wR_2 = 0.1613	wR_2 = 0.1485
R indices [all data]	R_1 = 0.0719	R_1 = 0.0623	R_1 = 0.0984	R_1 = 0.0763
	wR_2 = 0.1310	wR_2 = 0.1513	wR_2 = 0.1848	wR_2 = 0.1780

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma (F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

5.38 mmol) of monomer and a similar procedure was followed. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique.[55] The polymerizations were quenched by pouring the contents into cold heptane. The polymer was isolated by subsequent filtration and dried till a constant weight was attained.

Polymer Characterization: Molecular weights and the polydispersity indices of the polymers were determined by GPC instrument with Waters 510 pump and Waters 410 Differential Refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 × 300 mm) were connected in series. Measurements were done in THF at 27 °C. Number average molecular weights (M_n) and polydispersity (M_w/M_n) of polymers were measured relative to polystyrene standards. For CL, molecular weights (M_n) were corrected according to Mark–Houwink corrections.[71]

Supporting Information (see also the footnote on the first page of this article): Selected characterization data, polymerization data and X-ray data.

CCDC-724718 (for **2**), -724721 (for **5**), -724720 (for **6**) and -724719 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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