

Supporting Information

Synthesis of Aryloxo Cyclopentadienyl Group 4 Dendrimers

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Experimental Section

Synthesis of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\{\text{O}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{-CH=CH}_2)\}]]$ (**1**)

A solution of eugenol (0.40 g, 2.43 mmol), in CH_2Cl_2 (10 mL) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$ (0.65 g, 2.43 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred overnight at room temperature. The solvent was removed at reduced pressure affording a red solid. The product was extracted with hexane at 0 °C (5 mL). The resulting hexane solution was evaporated to dryness, giving **1** as a red solid (0.94 g, 93%). $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.90 (m, 1H, C_6H_3), 6.69-6.62 (m, 2H, C_6H_3), 5.87 (m, 1H, $\text{CH}_2\text{-CH=CH}_2$), 5.04 (m, 2H, $\text{CH}_2\text{-CH=CH}_2$), 3.80 (s, 3H, OMe), 3.33 (m, 2H, $\text{CH}_2\text{-CH=CH}_2$), 2.18 (s, 15H, C_5Me_5). $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 153.6 (C_{ipso} bonded to -OTi), 150.0 (C_{ipso} bonded to -OMe), 137.4 ($\text{CH}_2\text{-CH=CH}_2$), 135.7 (C_{ipso} bonded to - C_3H_5), 132.7 (C_5Me_5), 120.8, 120.3, 113.1 (C_6H_3), 115.8 ($\text{CH}_2\text{-CH=CH}_2$), 56.3 (OMe), 40.0 ($\text{CH}_2\text{-CH=CH}_2$), 12.7 (C_5Me_5). Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{O}_2\text{Ti}$: C, 57.57; H, 6.24. Found: C, 57.09; H, 6.02.

Synthesis of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\{\text{O}[\text{C}_6\text{H}_2(\text{OMe})_2(\text{CH}_2\text{-CH=CH}_2)\}]]$ (**2**)

A solution of 4-allyl-2,6-dimethoxyphenol (0.36 g, 1.85 mmol) in Et_2O (10 mL) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$ (0.50 g, 1.85 mmol) in Et_2O (5 mL). The mixture was stirred overnight at room temperature. A red solid precipitated. The solution was filtered off and the solid was dried under vacuum affording **2** as a red microcrystalline solid (0.66 g, 80%). Red crystals were obtained from a mixture Et_2O /hexane. $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.35 (s, 2H, C_6H_2), 5.95 (m, 1H, $\text{CH}_2\text{-CH=CH}_2$), 5.05 (m, 2H, $\text{CH}_2\text{-CH=CH}_2$), 3.78 (s, 6H, OMe), 3.32 (m, 2H, $\text{CH}_2\text{-CH=CH}_2$), 2.15 (s, 15H, C_5Me_5). $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 151.3 (C_{ipso} bonded to -OMe), 144.0 (C_{ipso} bonded to -OTi), 137.2 ($\text{CH}_2\text{-CH=CH}_2$), 134.8 (C_{ipso} bonded to - C_3H_5), 132.3 (C_5Me_5), 116.0 ($\text{CH}_2\text{-$

CH=CH₂), 106.1 (C₆H₂), 56.7 (OMe), 40.5 (CH₂-CH=CH₂), 12.6 (C₅Me₅). Anal. Calcd for C₂₁H₂₈Cl₂O₃Ti: C, 56.40; H, 6.31. Found: C, 56.79; H, 6.30.

Synthesis of [Ti(C₅Me₅)Cl₂{O[C₆H₃(OMe)(CH₂CH₂CH₂SiEt₃)]}] (3)

A solution of [HO{C₆H₃(OMe)(CH₂CH₂CH₂SiEt₃)] (0.40 g, 1.43 mmol) in CH₂Cl₂ (10 mL) was slowly added to a solution of [Ti(C₅Me₅)Cl₂Me] (0.38 g, 1.43 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred overnight at room temperature. The solvent was removed at reduced pressure affording a red oil. The product was extracted with hexane at 0 °C (5 mL). The resulting hexane solution was evaporated to dryness, affording **3** as an oily red compound (0.68 g, 90%). ¹H-NMR(CDCl₃): δ 6.89 (m, 1H, C₆H₃), 6.64 (m, 2H, C₆H₃), 3.81 (s, 3H, OMe). 2.56 (m, 2H, SiCH₂CH₂CH₂Ph), 2.19 (s, 15H, C₅Me₅), 1.58 (m, 2H, SiCH₂CH₂CH₂Ph), 0.90(t, 9H, SiCH₂CH₃), 0.51 (m, 8H, SiCH₂CH₃ and SiCH₂CH₂CH₂Ph overlapping). ¹³C-NMR(CDCl₃): δ 152.3 (C_{ipso} bonded to -OTi), 149.8 (C_{ipso} bonded to -OMe), 138.5 (C_{ipso} bonded to -CH₂), 132.5 (C₅Me₅), 120.7, 120.1, 113.0 (C₆H₃), 56.4 (OMe), 40.0 (SiCH₂CH₂CH₂Ph), 26.0 (SiCH₂CH₂CH₂Ph), 12.8 (C₅Me₅), 11.1 (SiCH₂CH₂CH₂Ph), 7.5(SiCH₂CH₃), 3.3 (SiCH₂CH₃). Anal. Calcd for C₂₆H₄₂Cl₂O₂SiTi: C, 58.54; H, 7.94. Found: C, 58.25; H, 7.81.

Synthesis of [Ti(C₅Me₅)Cl₂{O[C₆H₂(OMe)₂(CH₂CH₂CH₂SiEt₃)]}] (4)

A solution of {HO[C₆H₂(OMe)₂(CH₂CH₂CH₂SiEt₃)]} (0.40 g, 1.29 mmol) in CH₂Cl₂ (10 mL) was slowly added to a solution of [Ti(C₅Me₅)Cl₂Me] (0.35 g, 1.29 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred overnight at room temperature. The solvent was removed at reduced pressure, affording a red solid. The product was washed with hexane (2x3 mL), to give **4** as a red microcrystalline solid (0.65 g, 90%). ¹H-NMR(CDCl₃): δ 6.34 (s, 2H, C₆H₂), 3.79 (s, 6H, OMe). 2.54 (m, 2H, SiCH₂CH₂CH₂Ph), 2.15 (s, 15H, C₅Me₅), 1.56 (m, 2H, SiCH₂CH₂CH₂Ph), 0.90(t, 9H, SiCH₂CH₃), 0.49 (m, 8H, SiCH₂CH₃ and SiCH₂CH₂CH₂Ph overlapping). ¹³C-NMR(CDCl₃): δ 151.2

(C_{ipso} bonded to -OMe), 144.0 (C_{ipso} bonded to -OTi), 137.7 (C_{ipso} bonded to -CH₂), 132.2 (C₅Me₅), 106.2 (C₆H₃), 56.8 (OMe), 40.4 (SiCH₂CH₂CH₂Ph), 25.8 (SiCH₂CH₂CH₂Ph), 12.6 (C₅Me₅), 11.0 (SiCH₂CH₂CH₂Ph), 7.5 (SiCH₂CH₃), 3.3 (SiCH₂CH₃). Anal. Calcd for C₂₇H₄₄Cl₂O₃SiTi: C, 57.55; H, 7.87. Found: C, 57.39; H, 8.06.

Synthesis of 1G-[(CH₂)₃{[C₆H₃(OMe)]O}Ti(C₅Me₅)Cl₂]₄ (**5**)

A solution of 1G-[(CH₂)₃[C₆H₃(OMe)]OH]₄ (0.40 g, 0.37 mmol) in CH₂Cl₂ (10 mL) was slowly added to a solution of [Ti(C₅Me₅)Cl₂Me] (0.40 g, 1.48 mmol) in CH₂Cl₂ (5 mL). The mixture was allowed to stir overnight. The solvent was removed at reduced pressure, to obtain an oily red solid. The product was washed with a mixture of Et₂O/hexane (1:4) to give **5** as a red foamy solid (0.57g, 74 %). ¹H-NMR(CDCl₃): δ 6.89 (m, 1H, C₆H₃), 6.61 (m, 2H, C₆H₃), 3.79 (s, 3H, OMe), 2.54 (m, 2H, SiCH₂CH₂CH₂Ph), 2.17 (s, 15H, C₅Me₅), 1.54 (m, 2H, SiCH₂CH₂CH₂Ph), 1.29 (m, 2H, SiCH₂CH₂CH₂Si), 0.53 (m br, 6H, SiCH₂CH₂CH₂Si and SiCH₂CH₂CH₂Ph overlapping), -0.06 (s, 6H, SiMe₂). ¹³C-NMR(CDCl₃): δ 153.5 (C_{ipso} bonded to -OTi), 149.9 (C_{ipso} bonded to -OMe), 138.6 (C_{ipso} bonded to -CH₂), 132.6 (C₅Me₅), 120.6, 120.2 and 113.1 (C₆H₃), 56.3 (OMe), 39.9 (SiCH₂CH₂CH₂Ph), 26.1 (SiCH₂CH₂CH₂Ph), 15.3 (SiCH₂CH₂CH₂Ph), 20.3, 18.6, 17.6 (Si(CH₂)₃Si), 12.8 (C₅Me₅), -3.3 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃): δ 1.91 (G1-Si) and 0.86 (G0-Si). Anal. Calcd. for C₁₀₀H₁₅₆Cl₈O₈Si₅Ti₄: C, 57.14; H, 7.48. Found: C, 57.11; H, 7.51

Synthesis of 2G-[(CH₂)₃{[C₆H₃(OMe)]O}Ti(C₅Me₅)Cl₂]₈ (**6**)

This dendrimer was prepared by a similar method to that described for **5**, starting from 2G-[(CH₂)₃[C₆H₃(OMe)]OH]₈ (0.30 g, 0.12 mmol) and [Ti(C₅Me₅)Cl₂Me] (0.26 g, 0.96 mmol), affording **6** as a red foamy solid (0.38 g, 70%). ¹H-NMR(CDCl₃): δ 6.89 (m, 2H, C₆H₃), 6.62 (m, 4H, C₆H₃), 3.79 (s, 6H, OMe), 2.53 (m, 4H, SiCH₂CH₂CH₂Ph), 2.17 (s, 30H, C₅Me₅), 1.55 (m, 4H, SiCH₂CH₂CH₂Ph), 1.29 (m, 6H, SiCH₂CH₂CH₂Si) 0.53

(m br, 16H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ overlapping), -0.07 (s, 12H, SiMe_2), -0.09 (s, 3H, SiMe). ^{13}C -NMR(CDCl_3); δ 153.3 (C_{ipso} bonded to -OTi), 149.7 (C_{ipso} bonded to -OMe), 138.5 (C_{ipso} bonded to $-\text{CH}_2$), 132.6 (C_5Me_5), 120.6, 120.1 and 113.0 (C_6H_3), 56.3 (OMe), 39.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.2 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 15.4 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 20.2, 18.9, 18.5 and overlapped signals ($\text{Si}(\text{CH}_2)_3\text{Si}$), 12.8 (C_5Me_5), -3.1 (SiMe_2), -4.9 (SiMe). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.87 (G2-Si), 1.19 (G1-Si) and 0.80 (G0-Si). Anal. Calcd. for $\text{C}_{216}\text{H}_{348}\text{Cl}_{16}\text{O}_{16}\text{Si}_{13}\text{Ti}_8$: C, 57.44; H, 7.77. Found: C, 56.32; H, 8.02.

Synthesis of 4G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{OMe})\text{O}\}\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2]_{32}$ (7)

A solution of 4G- $\{(\text{CH}_2)_3[\text{C}_6\text{H}_3(\text{OMe})\text{OH}]\}_{32}$ (0.30 g, 2.75×10^{-2} mmol) in CH_2Cl_2 (10 mL) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_2\text{Me}]$ (0.24 g, 0.91 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred overnight. The solvent was removed at reduced pressure, to obtain a foamy red solid. The product was washed with Et_2O (2x2 mL) to give **7** as a red foamy solid (0.39 g, 75% rto). ^1H -NMR(CDCl_3): δ 6.84 (m, 8H, C_6H_3), 6.60 (m, 16H, C_6H_3), 3.77 (s, 24H, OMe), 2.52 (m, 16H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 2.16 (s, 120H, C_5Me_5), 1.54 (m, 16H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.24 (m, 30H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.52 (m br, 76H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ overlapping), -0.07 (m br, 69 H, SiMe_2 and SiMe overlapping). ^{13}C -NMR(CDCl_3); δ 153.4 (C_{ipso} bonded to -OTi), 149.9 (C_{ipso} bonded to -OMe), 138.6 (C_{ipso} bonded to $-\text{CH}_2$), 132.7 (C_5Me_5), 120.6, 120.1 and 113.0 (C_6H_3), 56.3 (OMe), 39.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.1 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 15.3 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 20.2, 18.9, 18.5 and overlapped signals ($\text{Si}(\text{CH}_2)_3\text{Si}$), 12.8 (C_5Me_5), -3.2 (SiMe_2), -4.9 (SiMe). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.91 (G4-Si), 1.28 (G3-Si) and the rest not observed. Anal. Calcd. for $\text{C}_{912}\text{H}_{1500}\text{Cl}_{64}\text{O}_{64}\text{Si}_{61}\text{Ti}_{32}$: C, 57.64; H, 7.95. Found: C, 56.82; H, 7.70.

Synthesis of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_2\{\text{O}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{-CH=CH}_2)]\}]$ (8)

A solution of eugenol (0.30 g, 1.83 mmol) in Et₂O (10 mL) was slowly added to a solution of [Ti(C₅Me₅)Cl₂Me] (0.42 g, 1.83 mmol) in Et₂O (5 mL). The mixture was stirred for 2h at room temperature. Then, the solvent was removed at reduced pressure to obtain **8** as a yellow oil in quantitative yield (0.68 g). ¹H-NMR(CDCl₃): δ 6.84 (m, 1H, C₆H₃), 6.69-6.61 (m, 2H, C₆H₃), 5.96 (m, 1H, CH₂-CH=CH₂), 5.06 (m, 2H, CH₂-CH=CH₂), 3.77 (s, 3H, OMe), 3.33 (m, 2H, CH₂-CH=CH₂), 1.91 (s, 15H, C₅Me₅), 0.41 (s, 6H, TiMe₂). ¹³C-NMR(CDCl₃): δ 151.5 (C_{ipso} bonded to -OTi), 150.5 (C_{ipso} bonded to -OMe), 137.9 (CH₂-CH=CH₂), 132.6 (C_{ipso} bonded to -C₃H₅), 122.3(C₅Me₅), 115.4 (CH₂-CH=CH₂), 120.5, 119.8, 112.6 (C₆H₃), 55.7 (OMe), 53.9 (TiMe₂), 40.0 (CH₂-CH=CH₂), 11.3 (C₅Me₅). Anal. Calcd. for C₂₂H₃₂O₂Ti: C, 70.21; H, 8.57. Found: C, 69.70; H, 8.40.

Synthesis of [Ti(C₅Me₅)Me₂{O[C₆H₂(OMe)₂(CH₂CH=CH₂)]} (9)

This product was prepared by a similar method to that described for **8**, starting from 4-allyl-2,6-dimethoxyphenol (0.34g, 1.75 mmol) and [Ti(C₅Me₅)Cl₂Me] (0.40 g, 1.75 mmol), affording **9** as an oily yellow solid in quantitative yield. ¹H-NMR(CDCl₃): δ 6.37 (s, 2H, C₆H₂), 5.96 (m, 1H, CH₂-CH=CH₂), 5.07 (m, 2H, CH₂-CH=CH₂), 3.77 (s, 6H, OMe), 3.31 (m, 2H, CH₂-CH=CH₂), 1.88(s, 15H, C₅Me₅), 0.42 (s, 6H, TiMe₂). ¹³C-NMR(CDCl₃): δ 151.0 (C_{ipso} bonded to -OMe), 142.8 (C_{ipso} bonded to -OTi), 137.8 (C_{ipso} bonded to -C₃H₅), 131.4 (CH₂-CH=CH₂), 122.1(C₅Me₅), 115.5 (CH₂-CH=CH₂), 106.0 (C₆H₂), 56.2 (OMe), 53.9 (TiMe₂), 40.4 (CH₂-CH=CH₂), 11.2 (C₅Me₅). Anal. Calcd. for C₂₃H₃₄O₃Ti: C, 67.97; H, 8.43. Found: C, 68.17; H, 8.58.

Synthesis of [Ti(C₅Me₅)Me₂{O[C₆H₃(OMe)(CH₂CH₂CH₂SiEt₃)]} (10)

A solution of [HO{C₆H₃(OMe)(CH₂CH₂CH₂SiEt₃)] (0.40 g, 1.43 mmol) in Et₂O (10 mL) was slowly added to a solution of [Ti(C₅Me₅)Me₃] (0.33 g, 1.43 mmol) in Et₂O (5 mL). The mixture was stirred for 2h at room temperature. Then, the solvent was removed at reduced pressure to obtain **10** as a yellow oil in quantitative yield (0.70 g).

$^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.82 (m, 1H, C_6H_3), 6.64 (m, 2H, C_6H_3), 3.78 (s, 3H, OMe). 2.56 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.90 (s, 15H, C_5Me_5), 1.58 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 0.90 (t, 9H, SiCH_2CH_3), 0.51 (m, 8H, SiCH_2CH_3 and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ overlapping), 0.40 (s, 6H, TiMe_2). $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 152.2 (C_{ipso} bonded to -OTi), 150.3 (C_{ipso} bonded to -OMe), 135.5 (C_{ipso} bonded to $-\text{CH}_2$), 122.2 (C_5Me_5), 120.4, 119.7, 112.6 (C_6H_3), 55.7 (OMe), 53.7 (TiMe_2), 40.4 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.1 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 11.3 (C_5Me_5), 11.1 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 7.5 (SiCH_2CH_3), 3.3 (SiCH_2CH_3). Anal. Calcd for $\text{C}_{28}\text{H}_{48}\text{O}_2\text{SiTi}$: C, 68.26; H, 9.82. Found: C, 67.91; H, 9.70.

Synthesis of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_2\{\text{O}[\text{C}_6\text{H}_2(\text{OMe})_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3)]\}]$ (**11**)

This product was prepared by a similar method to that described for **10**, starting from $[\text{HO}\{\text{C}_6\text{H}_2(\text{OMe})_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3)\}]$ (0.40 g, 1.29 mmol) and $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$ (0.29 g, 1.29 mmol), affording **11** as a yellow oil in quantitative yield (0.67 g). $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.36 (s, 2H, C_6H_2), 3.77 (s, 6H, OMe). 2.54 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.88 (s, 15H, C_5Me_5), 1.56 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 0.90 (t, 9H, SiCH_2CH_3), 0.48 (m, 8H, SiCH_2CH_3 and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ overlapping), 0.42 (s, 6H, TiMe_2). $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 150.9 (C_{ipso} bonded to -OMe), 142.6 (C_{ipso} bonded to -OTi), 134.3 (C_{ipso} bonded to $-\text{CH}_2$), 122.0 (C_5Me_5), 106.0 (C_6H_2), 56.3 (OMe), 53.6 (TiMe_2), 40.4 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.0 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 11.2 (C_5Me_5), 11.1 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 7.5 (SiCH_2CH_3), 3.3 (SiCH_2CH_3). Anal. Calcd for $\text{C}_{29}\text{H}_{50}\text{O}_3\text{SiTi}$: C, 66.64; H, 9.64. Found: C, 66.30; H, 9.48.

Synthesis of $1\text{G}-(\text{CH}_2)_3\{[\text{C}_6\text{H}_3(\text{OMe})\text{O}]\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_2\}_4$ (**12**)

A solution of $1\text{G}-(\text{CH}_2)_3[\text{C}_6\text{H}_3(\text{OMe})\text{OH}]_4$ (0.47 g, 0.43 mmol) in Et_2O (10 mL) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$ (0.40 g, 1.74 mmol) in Et_2O (5 mL). The reaction mixture was stirred for 2h at room temperature. Then, the solvent was removed at reduced pressure to obtain **12** as a brown-yellow oil in quantitative yield (0.84 g). $^1\text{H-}$

NMR(CDCl₃): δ 6.83 (m, 1H, C₆H₃), 6.63 (m, 2H, C₆H₃), 3.77 (s, 3H, OMe), 2.55 (m, 2H, SiCH₂CH₂CH₂Ph), 1.91 (s, 15H, C₅Me₅), 1.58 (m, 2H, SiCH₂CH₂CH₂Ph), 1.32 (m, 2H, SiCH₂CH₂CH₂Si), 0.55 (m br, 6H, SiCH₂CH₂CH₂Si and SiCH₂CH₂CH₂Ph overlapping), 0.40 (s, 6H, TiMe₂) -0.04 (s, 6H, SiMe₂). ¹³C-NMR(CDCl₃): δ 152.2(C_{ipso} bonded to -OTi), 150.2 (C_{ipso} bonded to -OMe), 135.5 (C_{ipso} bonded to CH₂), 122.1 (C₅Me₅) 120.3, 119.7, and 112.5 (C₆H₃), 55.7 (OMe), 53.8 (TiMe₂), 39.9 (SiCH₂CH₂CH₂Ph), 26.4 (SiCH₂CH₂CH₂Ph), 15.5 (SiCH₂CH₂CH₂Ph), 20.4, 18.7, 17.7 (Si(CH₂)₃Si), 11.4 (C₅Me₅), -3.1 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃): δ 1.89 (G1-Si) and 0.86 (G0-Si). Anal. Calcd. for C₁₀₈H₁₈₀O₈Si₅Ti₄: C, 66.92; H, 9.36. Found: C, 66.90; H, 9.20.

Synthesis of 2G-[(CH₂)₃{[C₆H₃(OMe)]O}Ti(C₅Me₅)Me₂]₈ (13)

This dendrimer was obtained by a similar procedure to that described for **12**, starting from 2G-[(CH₂)₃[C₆H₃(OMe)]OH]₈ (0.54 g, 0.22 mmol) and [Ti(C₅Me₅)Me₃] (0.40 g, 1.74 mmol), to obtain **13** as a brown-yellow oil in quantitative yield (0.92 g). ¹H-NMR(CDCl₃): δ 6.84 (m, 2H, C₆H₃), 6.62 (m, 4H, C₆H₃), 3.76 (s, 6H, OMe), 2.54 (m, 4H, SiCH₂CH₂CH₂Ph), 1.90 (s, 30H, C₅Me₅), 1.57 (m, 4H, SiCH₂CH₂CH₂Ph), 1.30 (m, 6H, SiCH₂CH₂CH₂Si) 0.54 (m br, 16H, SiCH₂CH₂CH₂Si and SiCH₂CH₂CH₂Ph overlapping), 0.40 (s, 12H, TiMe₂), -0.05 (s, 12H, SiMe₂), -0.07 (s, 3H, SiMe). ¹³C-NMR(CDCl₃): δ 152.2 (C_{ipso} bonded to -OTi), 150.3 (C_{ipso} bonded to -OMe), 135.5 (C_{ipso} bonded to -CH₂), 122.2 (C₅Me₅), 120.3, 119.7 and 112.5 (C₆H₃), 55.7 (OMe), 53.7(TiMe₂) 39.9 (SiCH₂CH₂CH₂Ph), 26.3 (SiCH₂CH₂CH₂Ph), 15.4 (SiCH₂CH₂CH₂Ph), 20.2, 18.8, 18.5 and overlapped signals (Si(CH₂)₃Si), 11.4 (C₅Me₅), -3.2 (SiMe₂), -4.9 (SiMe). ²⁹Si{¹H} NMR (CDCl₃): δ 1.90 (G2-Si), 1.18 (G1-Si) and 0.79 (G0-Si). Anal. Calcd. for C₂₃₂H₃₉₆O₁₆Si₁₃Ti₈: C, 66.51; H, 9.53. Found: C, 65.10; H, 9.38.

Synthesis of 4G-[(CH₂)₃{[C₆H₃(OMe)]O}Ti(C₅Me₅)Me₂]₃₂ (14)

This dendrimer was prepared following a similar procedure to that described in the preparation of **12**, starting from 4G- $\{(\text{CH}_2)_3[\text{C}_6\text{H}_3(\text{OMe})]\text{OH}\}_{32}$ (0.30 g, 2.75×10^{-2} mmol) and $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Me}_3]$ (0.20 g, 0.88 mmol), affording **14** as a brown-yellow oil in quantitative yield (0.48g). $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.80 (m, 8H, C_6H_3), 6.60 (m, 16H, C_6H_3), 3.73 (s, 24H, OMe), 2.53 (m, 16H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.88 (s, 120H, C_5Me_5), 1.56 (m, 16H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.30 (m, 30H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.54 (m br, 76H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ overlapping), 0.38 (s, 48H, TiMe_2), -0.06 (m br, 69 H, SiMe_2 and SiMe overlapping). $^{13}\text{C-NMR}(\text{CDCl}_3)$; δ 152.3 (C_{ipso} bonded to -OTi), 150.3 (C_{ipso} bonded to -OMe), 135.5 (C_{ipso} bonded to - CH_2), 122.2 (C_5Me_5), 120.3, 119.7 and 112.5 (C_6H_3), 55.7 (OMe), 53.8 (TiMe_2), 39.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.3 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 15.4 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 20.2, 18.8, 18.5 and overlapped signals ($\text{Si}(\text{CH}_2)_3\text{Si}$), 11.4 (C_5Me_5), -3.2 (SiMe_2), -4.9 (SiMe). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.94 (G4-Si), 1.31 (G3-Si) and the rest not observed. Anal. Calcd. for $\text{C}_{976}\text{H}_{1692}\text{O}_{64}\text{Si}_{61}\text{Ti}_{32}$: C, 66.24; H, 9.64. Found: C, 65.02; H, 9.40.

Synthesis of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}\{\text{O}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH}=\text{CH}_2)]\}]$ (**15**)

A solution of eugenol (0.33 g, 2.0 mmol), in toluene (10 mL) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (0.50 g, 2.0 mmol) in toluene (50 mL), to this mixture a slight excess of NEt_3 (0.30 mL, 2.9 mmol) was added. The reaction mixture was stirred for 12h and then filtered through celite to remove $\text{NEt}_3\cdot\text{HCl}$. The resulting red solution was evaporate under reduced pressure to obtain a red oil that was washed with hexane (2x5 mL) to give **15** as red microcrystalline solid (0.45 g, 60 %). $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.69 – 6.62 (m, 3H, C_6H_3), 6.33 (s, 10H C_5H_5), 5.93 (m, 1H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 5.01 (m, 2H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 3.77 (s, 3H, OMe), 3.30 (d, 2H, $\text{CH}_2\text{-CH}=\text{CH}_2$). $^{13}\text{C-NMR}$ (CDCl_3): δ 159.5 (C_{ipso} bonded to -OTi), 146.3 (C_{ipso} bonded to -OMe), 138.0 ($\text{CH}_2\text{-CH}=\text{CH}_2$), 132.1 (C_{ipso} bonded to - C_3H_5), 120.9, 117.4, and 111.9 (C_6H_3), 117.6 (C_5H_5),

115.3 ($\text{CH}_2\text{-CH=CH}_2$), 55.8 (OMe), 39.9 ($\text{CH}_2\text{-CH=CH}_2$). Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{ClO}_2\text{Ti}$: C, 63.77; H, 5.62. Found: C, 64.02; H, 6.12.

Synthesis of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}\{\text{O}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3)]\}]$ (**16**)

A solution of $[\text{OH}\{\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3)\}]$ (0.12 g, 0.44 mmol) in toluene (10 mL) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (0.11 g, 0.44 mmol) in toluene (50 mL). To this mixture a slight excess of NEt_3 (90 μL , 0.64 mmol) was added. The reaction mixture was stirred for 12h and then filtered through celite to remove $\text{NEt}_3\cdot\text{HCl}$. The resulting red solution was evaporated under reduced pressure, affording **16** as an oily red compound (0.12 g, 55%). ^1H - NMR (CDCl_3): δ 6.67 – 6.60 (m, 3H, C_6H_3), 6.34 (s, 10H, C_5H_5), 3.78 (s, 3H, OMe), 2.53 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.56 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 0.89 (t, 9H, SiCH_2CH_3), 0.49 (m, 8H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ and SiCH_2CH_3 overlapping). ^{13}C - NMR (CDCl_3): δ 159.4 (C_{ipso} bonded to $-\text{OTi}$), 146.1 (C_{ipso} bonded to $-\text{OMe}$), 135 (C_{ipso} bonded to $-\text{CH}_2$), 120.8, 120.1 and 111.9 (C_6H_3), δ 117.5 (C_5H_5), 55.8 (OCH_3), 39.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.2. ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 11.1($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 7.5 (SiCH_2CH_3), 3.3(SiCH_2CH_3). Anal. Calcd. for $\text{C}_{26}\text{H}_{37}\text{ClO}_2\text{SiTi}$: C, 63.38; H, 7.52. Found: C, 63.08; H, 7.37.

Synthesis of $1\text{G}-[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{OMe})\text{O}\}\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}]_4$ (**17**)

A solution of $1\text{G}-\{(\text{CH}_2)_3[\text{C}_6\text{H}_3(\text{OMe})]\text{OH}\}_4$ (0.14 g, 0.12 mmol) in toluene (10 mL) was slowly added to a solution of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (0.12 g, 0.50 mmol) in toluene (50 mL), over this mixture a slight excess of NEt_3 (80 μL , 0.57 mmol) was added. The reaction mixture was stirred for 12h and then filtered through celite to remove $\text{NEt}_3\cdot\text{HCl}$. The resulting red solution was evaporated under reduced pressure to give **17** as red microcrystalline solid (0.18 g, 68%). ^1H - NMR (CDCl_3): δ 6.67 – 6.60 (m, 3H, C_6H_3), 6.33 (s, 10H, C_5H_5), 3.77 (s, 3H, OMe), 2.34 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.56 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.29 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{-Si}$), 0.50 (m, 6H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$

and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ overlapping), -0.06 (s, 6H, SiMe_2). ^{13}C - NMR (CDCl_3): δ 159.3 (C_{ipso} bonded to $-\text{OTi}$), 146.1 (C_{ipso} bonded to $-\text{OMe}$), 135.2 (C_{ipso} bonded to $-\text{CH}_2$), 120.7, 120.1 and 111.9 (C_6H_3), 117.2 (C_5H_5), 55.8 (OMe), 39.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.4. ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 15.4 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 20.3, 18.6 and 17.6 ($\text{Si}(\text{CH}_2)_3\text{Si}$), -3.3 (SiMe_2). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.91 (G2-Si), 0.86 (G0-Si). Anal. Calcd for $\text{C}_{100}\text{H}_{136}\text{Cl}_4\text{O}_8\text{Si}_5\text{Ti}_4$: C, 61.91; H, 7.07. Found: C. 62.41; H, 7.26.

Synthesis of 2 G-[(CH_2)₃{[$\text{C}_6\text{H}_3(\text{OMe})\text{O}$]}Ti(C_5H_5)₂Cl]₈ (**18**)

This dendrimer was prepared by a similar method to that described for **17**, starting from 2G-[(CH_2)₃[$\text{C}_6\text{H}_3(\text{OMe})\text{OH}$]]₈ (0.10 g, 0.04 mmol), $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (0.08 g, 0.30 mmol), and NEt_3 (50 μL , 0.36 mmol), affording **18** as red microcrystalline solid (0.127 g, 79%). ^1H - NMR (CDCl_3): δ 6.67 – 6.60 (m, 6H, C_6H_3), 6.32 (s, 20H, C_5H_5), 3.76 (s, 6H, OMe), 2.51 (m, 4H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.54 (m, 4H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 1.29 (m, 6H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.50 (m, 16H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$ and $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ overlapping), -0.07 (s, 12H, SiMe_2), -0.09 (s, 3H, SiMe). ^{13}C - NMR (CDCl_3): δ 159.1 (C_{ipso} bonded to $-\text{OTi}$), 145.8 (C_{ipso} bonded to $-\text{OMe}$), 134.9 (C_{ipso} bonded to $-\text{C}_6\text{H}_3$), 125.1, 120.5 and 111.8 (C_6H_3), 117.4 (C_5H_5), 55.9 (OCH_3), 39.9 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 26.4. ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 15.6 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$), 22.7, 19.1, 18.7 and overlapped signals ($\text{Si}(\text{CH}_2)_3\text{Si}$), -2.9 (SiMe_2), -4.6 (SiMe). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.87 (G2-Si), 1.19 (G1-Si) and 0.77 (G0-Si). Anal. Calcd for $\text{C}_{216}\text{H}_{308}\text{Cl}_8\text{O}_{16}\text{Si}_{13}\text{Ti}_8$: C, 61.88; H, 7.40. Found: C, 61.52; H, 7.46.

Synthesis of $[\text{Zr}(\text{C}_5\text{H}_5)_2\{\text{O}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH}=\text{CH}_2)]_2\}]$ (**19**)

A solution of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (0.99 g, 3.4 mmol) in THF (10 mL) was added to a solution of eugenol (1.1 g, 6.7 mmol) in THF (10 mL). To this mixture a slight excess of NEt_3 (1.05 mL, 7.5 mmol) was added. The reaction mixture was stirred for 12h and then filtered through celite to remove $\text{NEt}_3\cdot\text{HCl}$. The resulting yellow solution was

evaporate under reduced pressure to obtain a yellow oil that was extracted with hexane. The resulting hexane solution was evaporated under reduced pressure affording **19** as a yellow solid (0.78 g, 42%). $^1\text{H-NMR}$ (CDCl_3): δ 6.67 - 6.63 (m, 6H, C_6H_3), 6.28 (s, 10H, C_5H_5), 5.97 (m, 2H, $\text{CH}_2\text{-CH=CH}_2$), 5.06 (m, 4H, $\text{CH}_2\text{-CH=CH}_2$), 3.84 (s, 6H, OMe), 3.32 (d, 4H, $\text{CH}_2\text{-CH=CH}_2$). $^{13}\text{C-NMR}$ (CDCl_3): δ 153.6 (C_{ipso} bonded to $-\text{OZr}$), 149.1 (C_{ipso} bonded to $-\text{OMe}$), 138.2 ($\text{CH}_2\text{-CH=CH}_2$), 130.4 (C_{ipso} bonded to $-\text{C}_3\text{H}_5$), 120.8, 118.4, and 112.4 (C_6H_3), 113.3 (C_5H_5), 115.2 ($\text{CH}_2\text{-CH=CH}_2$), 55.7 (OCH_3), 39.9 ($\text{CH}_2\text{-CH=CH}_2$). Anal. Calcd. for $\text{C}_{30}\text{H}_{32}\text{O}_4\text{Zr}$: C, 65.79; H, 5.85. Found: C, 65.22; H, 5.53.

Synthesis of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}\{\text{O}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH=CH}_2)]\}]$ (**20**)

A solution of eugenol, $\{\text{OH}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH=CH}_2)]\}$, (0.14 g, 0.50 mmol) in THF (10 mL) was slowly added to a suspension of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{HCl}]$ (0.13 g, 0.50 mmol) in THF (10 mL). After hydrogen evolution ceased, the resulting yellow solution was evaporated under reduced pressure, affording **20** as a yellow oil. $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.62 – 6.56 (m, 3H, C_6H_3), 6.34 (s, 10H, C_5H_5), 5.93 (m, 1H, $\text{CH}_2\text{-CH=CH}_2$), 5.02 (m, 2H, $\text{CH}_2\text{-CH=CH}_2$), 3.83 (s, 3H, OMe), 3.29 (d, 2H, $\text{CH}_2\text{-CH=CH}_2$). $^{13}\text{C-NMR}(\text{CDCl}_3)$: δ 153.3 (C_{ipso} bonded to $-\text{OZr}$), 148.5 (C_{ipso} bonded to $-\text{OMe}$), 138.2 ($\text{CH}_2\text{-CH=CH}_2$), 121.4, 118.1, and 112.3 (C_6H_3), 114.3 (C_5H_5), 116.2 ($\text{CH}_2\text{-CH=CH}_2$), 55.8 (OCH_3), 40.2 ($\text{CH}_2\text{-CH=CH}_2$). Anal. Calcd. for $\text{C}_{20}\text{H}_{21}\text{ClO}_2\text{Zr}$: C, 57.19; H, 5.00. Found: C, 56.99; H, 4.88.

Synthesis of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}\{\text{O}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3)]\}]$ (**21**)

A solution of $\{\text{OH}[\text{C}_6\text{H}_3(\text{OMe})(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3)]\}$ (0.14 g, 0.50 mmol) in THF (10 mL) was slowly added to a suspension of $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{HCl}]$ (0.13g, 0.50 mmol) in THF (10 mL). After hydrogen evolution ceased, the resulting yellow solution was evaporated under reduced pressure, affording **21** as a yellow oil. $^1\text{H-NMR}(\text{CDCl}_3)$: δ 6.66 – 6.59

(m, 3H, C₆H₃), 6.34 (s, 10H, C₅H₅), 3.83 (s, 3H, OMe), 2.53 (m, 2H, SiCH₂CH₂CH₂Ph), 1.56 (m, 2H, SiCH₂CH₂CH₂Ph), 0.89 (t, 9H, SiCH₂CH₃), 0.49 (m, 8H, SiCH₂CH₂CH₂Ph and SiCH₂CH₃ overlapping). ¹³C-NMR (CDCl₃): δ 153.4 (C_{ipso} bonded to –OZr), 149.1 (C_{ipso} bonded to –OCH₃), 130.8 (C_{ipso} bonded to –CH₂), 120.8, 119.1 and 111.9 (C₆H₃), 114.5 (C₅H₅), 55.8 (OMe), 39.9 (SiCH₂CH₂CH₂Ph), 26.2. (SiCH₂CH₂CH₂Ph), 11.1 (SiCH₂CH₂CH₂Ph), 7.5 (SiCH₂CH₃), 3.3(SiCH₂CH₃). Anal. Calcd. for C₂₆H₃₇ClO₂SiZr: C, 58.25; H, 6.91. Found: C, 58.02; H, 6.93.

Synthesis of 1G-[(CH₂)₃{[C₆H₃(OMe)]O}Zr(C₅H₅)₂Cl]₄ (**22**)

A solution of 1G-[(CH₂)₃[C₆H₃(OMe)]OH]₄ (0.081 g, 0.07 mmol) in THF (5 mL) was slowly added to a suspension containing [Zr(C₅H₅)₂HCl] (0.077 g, 0.29 mmol) in THF (5 mL). The reaction mixture was stirred for 15 min. After hydrogen evolution ceased, the resulting yellow solution was evaporated under reduced pressure, affording quantitatively **22** as a yellow oil (0.148 g). ¹H-NMR(CDCl₃): δ 6.62 - 6.55 (m, 3H, C₆H₃), 6.34 (s, 10H, C₅H₅), 3.82 (s, 3H, OMe), 2.52 (m, 2H, SiCH₂CH₂CH₂Ph), 1.55 (m, 2H, SiCH₂CH₂CH₂Ph), 1.29 (m, 2H, SiCH₂CH₂CH₂Si), 0.51 (m, 6H, SiCH₂CH₂CH₂Ph and SiCH₂CH₂CH₂Si overlapping), -0.05 (s, 6H, SiMe₂). ¹³C-NMR(CDCl₃): δ 152.6 (C_{ipso} bonded to –OZr), 147.9 (C_{ipso} bonded to –OMe), 134.6 (C_{ipso} bonded to –CH₂), 120.5, 117.6 and 115.9 (C₆H₃), 114.4 (C₅H₅), 55.6 (OMe), 39.8 (SiCH₂CH₂CH₂Ph), 26.4. (SiCH₂CH₂CH₂Ph), 15.4 (SiCH₂CH₂CH₂Ph), 20.3, 18.6 and 17.6 (Si(CH₂)₃Si), -3.2 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃): δ 1.85 (G1-Si) and 0.82 (G0-Si). Anal. Calcd for C₁₀₀H₁₃₆Cl₄O₈Si₅Zr₄: C, 56.86; H, 6.44. Found: C, 56.41; H, 6.26.

Synthesis of 2G-[(CH₂)₃{[C₆H₃(OMe)]O}Zr(C₅H₅)₂Cl]₈ (**23**)

This dendrimer was prepared by a similar method to that described for **22**, starting from 2G-[(CH₂)₃[C₆H₃(OMe)]OH]₈ (0.05 g, 0.02 mmol) and [Zr(C₅H₅)₂HCl] (0.04 g, 0.17 mmol), affording quantitatively **23** as yellow oil (0.088 g). ¹H-NMR(CDCl₃):

δ 6.67–6.60 (m, 6H, C₆H₃), 6.33 (s, 20H, C₅H₅), 3.82 (s, 6H, OMe), 2.51 (m, 4H, SiCH₂CH₂CH₂Ph), 1.54 (m, 4H, SiCH₂CH₂CH₂Ph), 1.29 (m, 6H, SiCH₂CH₂CH₂Si), 0.52 (m, 16H, SiCH₂CH₂CH₂Ph and SiCH₂CH₂CH₂Si overlapping), -0.07 (s, 12H, SiMe₂), -0.12 (s, 3H, SiMe). ¹³C-NMR(CDCl₃): δ 152.6 (C_{ipso} bonded to -OZr), 147.9 (C_{ipso} bonded to -OMe), 134.6 (C_{ipso} bonded to -CH₂), 120.5, 117.6 and 115.9 (C₆H₃), 114.4 (C₅H₅), 55.6 (OMe), 39.8 (SiCH₂CH₂CH₂Ph), 26.4. (SiCH₂CH₂CH₂Ph), 15.4 (SiCH₂CH₂CH₂Ph), 20.7, 19.1, 17.7 and overlapped signals (Si(CH₂)₃Si), -2.9 (SiMe₂), -4.6 (SiMe). ²⁹Si{¹H} NMR (CDCl₃): δ 1.86 (G2-Si), 1.19 (G1-Si) and 0.77 (G0-Si).
 Anal. Calcd for C₂₁₆H₃₀₈Cl₈O₁₆Si₁₃Zr₈: C, 57.18; H, 6.79. Found: C, 56.92; H, 6.56.

NMR data of -SiMe₃ protected phenols and phenol ended dendrimers.

See for example NMR data of: IIIa. ¹H-NMR(CDCl₃): δ 6.75 (m, 1H, C₆H₃), 6.65 (m, 2H, C₆H₃), 3.79 (s, 3H, OMe), 2.54 (t, 2H, SiCH₂CH₂CH₂Ph), 1.58 (m, 2H, SiCH₂CH₂CH₂Ph), 0.90 (t, 9H, SiCH₂CH₃), 0.50 (m, 8H, SiCH₂CH₃ y SiCH₂CH₂CH₂Ph overlapped), 0.22 (s, 9H, OSiMe₃). *IIIb.* ¹H-NMR(CDCl₃): δ 6.34 (s, 2H, C₆H₂), 3.78 (s, 6H, OMe), 2.53 (t, 2H, SiCH₂CH₂CH₂Ph), 1.57 (m, 2H, SiCH₂CH₂CH₂Ph), 0.89 (t, 9H, SiCH₂CH₃), 0.50 (m, 8H, SiCH₂CH₃ y SiCH₂CH₂CH₂Ph overlapped), 0.20 (s, 9H, OSiMe₃). *Va.* ¹H-NMR(CDCl₃): δ 6.72 (m, 1H, C₆H₃), 6.62 (m, 2H, C₆H₃), 3.77 (s, 3H, OMe), 2.52 (t, 2H, SiCH₂CH₂CH₂Ph), 1.55 (m, 2H, SiCH₂CH₂CH₂Ph), 1.29 (m, 2H, SiCH₂CH₂CH₂Si), 0.52 (m broad, 6H, SiCH₂CH₂CH₂Si y SiCH₂CH₂CH₂Ph overlapped), 0.21 (s, 9H, OSiMe₃) -0.07 (s, 6H, SiMe₂). ¹³C-NMR{¹H} (CDCl₃): δ 150.4 (C_{ipso} bonded to -OSiMe₃), 142.3 (C_{ipso} bonded to -OMe), 136.4 (C_{ipso} bonded to -CH₂), 120.4, 120.3, 112.4, (C₆H₃), 55.5 (OMe), 39.8 (SiCH₂CH₂CH₂Ph), 26.3 (SiCH₂CH₂CH₂Ph), 15.5 (SiCH₂CH₂CH₂Ph), 20.4, 18.6, 17.6 (Si(CH₂)₃Si), 0.40 (OSiMe₃), -3.2 (SiMe₂). *VIa:* ¹H-NMR (CDCl₃): δ 6.72 (m, 2H, C₆H₃), 6.62 (m, 4H, C₆H₃), 3.77 (s, 6H, OMe), 2.52 (t, 4H, SiCH₂CH₂CH₂Ph), 1.55 (m, 4H, SiCH₂CH₂CH₂Ph), 1.29 (m, 6H,

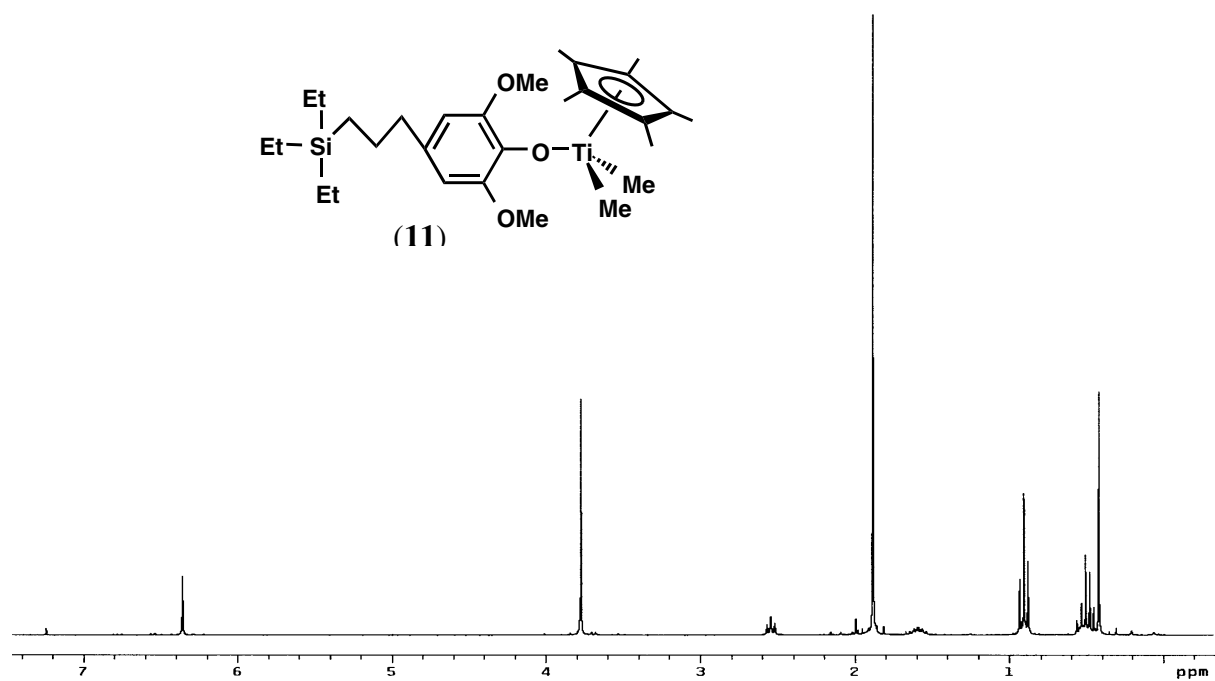
SiCH₂CH₂CH₂Si), 0.52 (m broad, 16H, SiCH₂CH₂CH₂Si y SiCH₂CH₂CH₂Ph overlapped), 0.21 (s, 18H, OSiMe₃), -0.07 (s, 12H, SiMe₂), -0.10 (s, 3H, SiMe). ¹³C-NMR{¹H} (CDCl₃): δ 150.5 (C_{ipso} bonded to -OSiMe₃), 142.4 (C_{ipso} bonded to -OMe), 136.4 (C_{ipso} bonded to -CH₂), 120.5, 120.4, 112.4 (C₆H₃), 55.5 (OMe), 39.8 (SiCH₂CH₂CH₂Ph), 26.2 (SiCH₂CH₂CH₂Ph), 15.4 (SiCH₂CH₂CH₂Ph), 20.2, 18.8, 18.5 and overlapped signals (Si(CH₂)₃Si), 0.30 (OSiMe₃), -3.2 (SiMe₂), -4.9 (SiMe).

Crystal structure determinations of 2

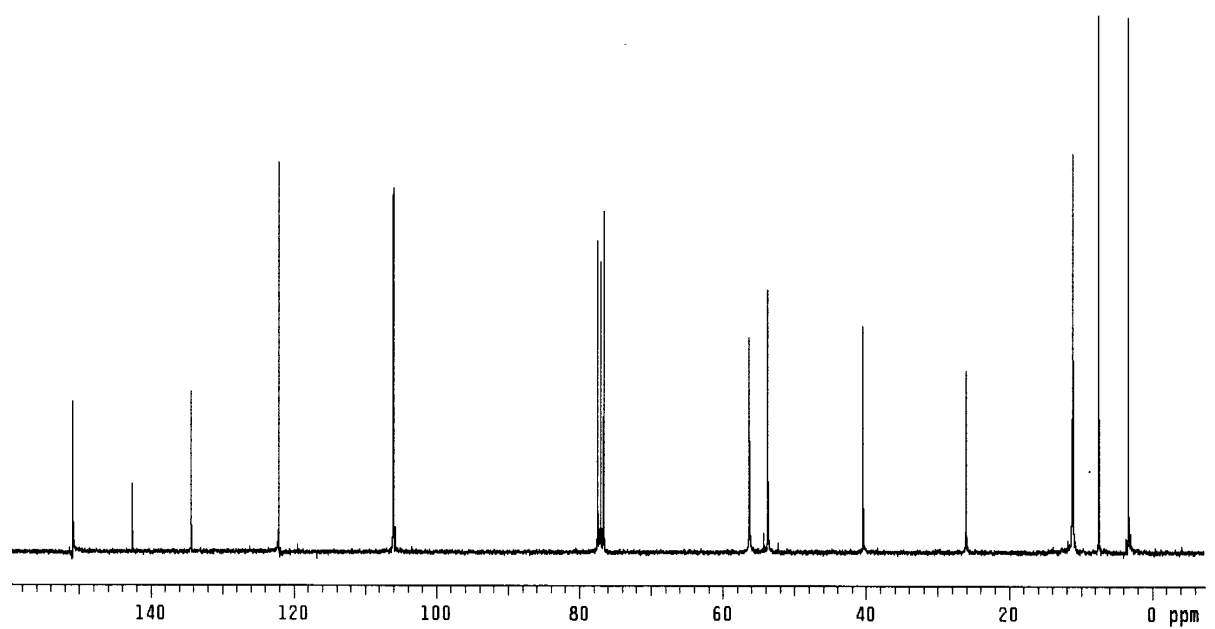
Red crystals of compound 2 were obtained from a mixture of Et₂O/hexane cooled at -20°C and a suitable sized crystal was mounted in a Lindemann tube and mounted in an Enraf-Nonius CAD 4 automatic four-circle diffractometer with graphite monochromated MoKα radiation (λ=0.71073 Å). Crystallographic and experimental details are summarized in Table 2. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved using the WINGX package^{#1} by direct methods (SHELXS 97) and refined by least squares against F² (SHELXL 97)^{#2}. All non hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with thermal parameters equivalent to those of the carbon atom to which they were attached.

(#1): Farrugia, L.J., *J. Appl. Crystallgr.* **1999**, 32, 837. (#2) Sheldrick, G.M. SHELX-97; Program for Crystal Structure Analyses (Release 97-2); Universität Göttingen, Göttingen, Germany, **1998**.

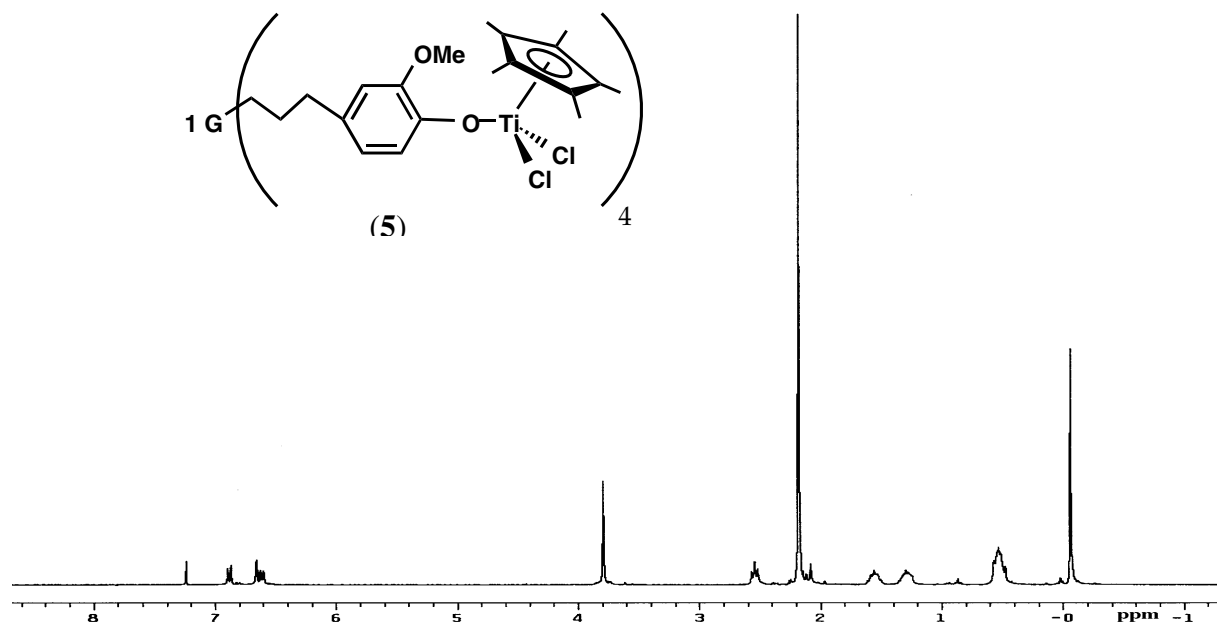
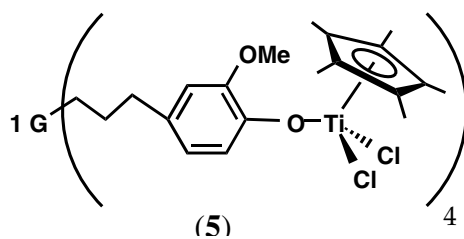
^1H -NMR



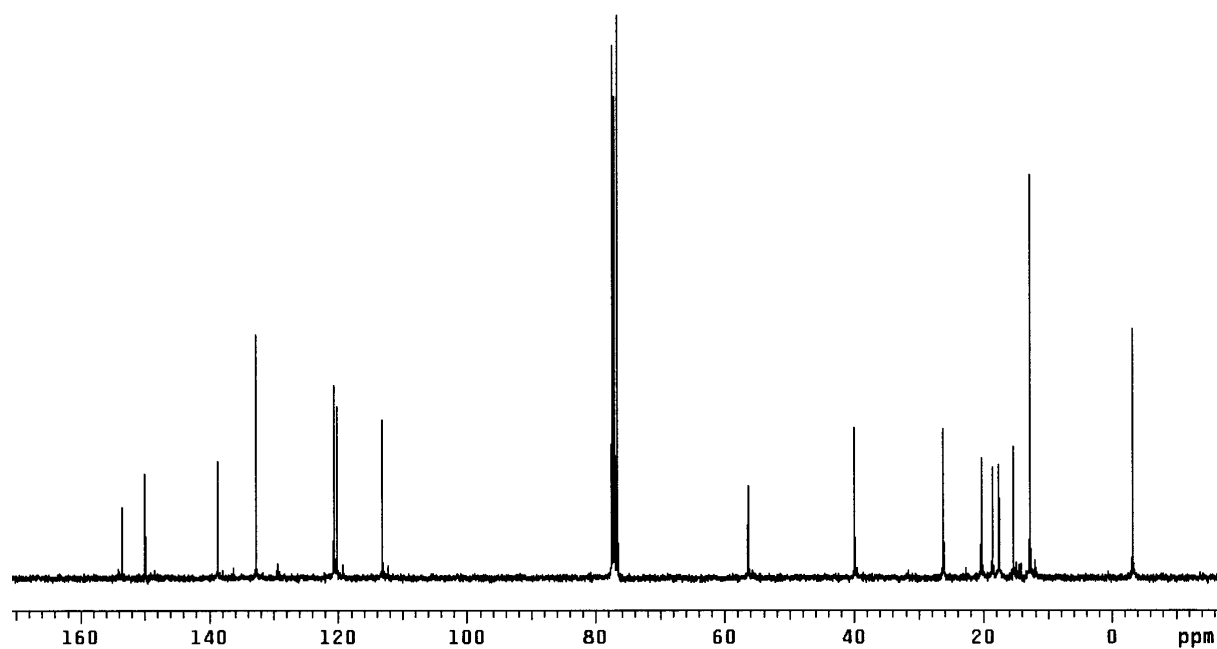
$^{13}\text{C}\{^1\text{H}\}$ -NMR



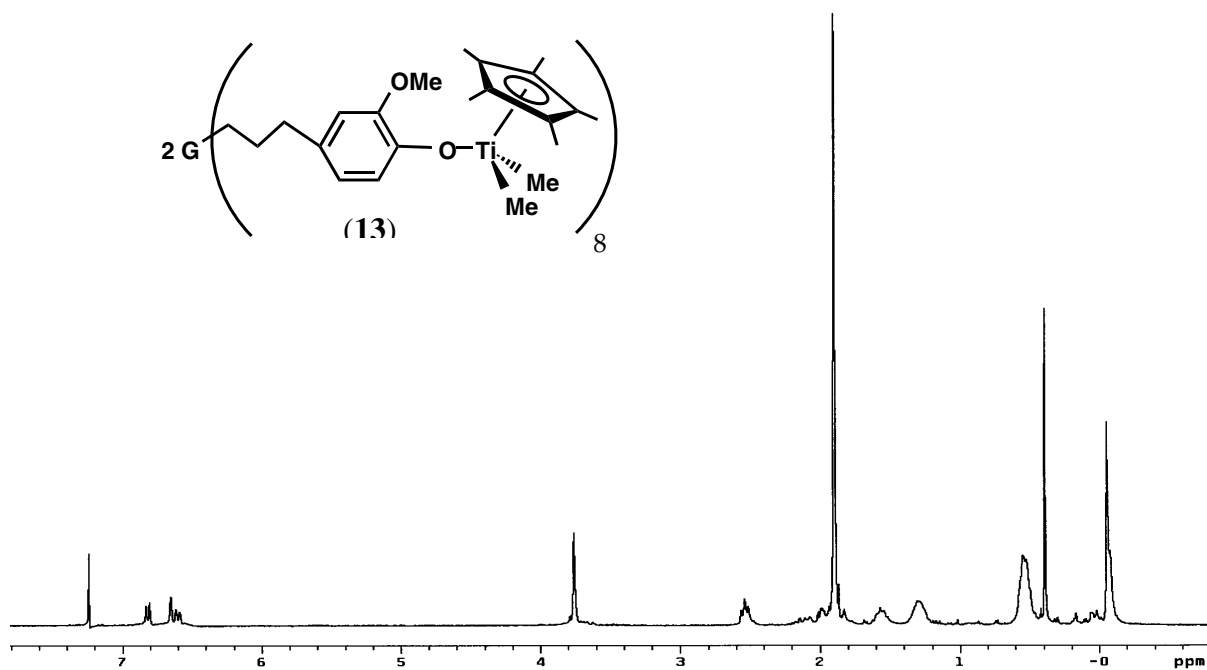
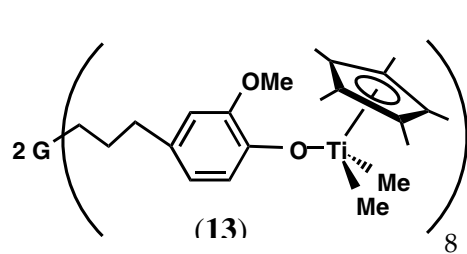
^1H -NMR



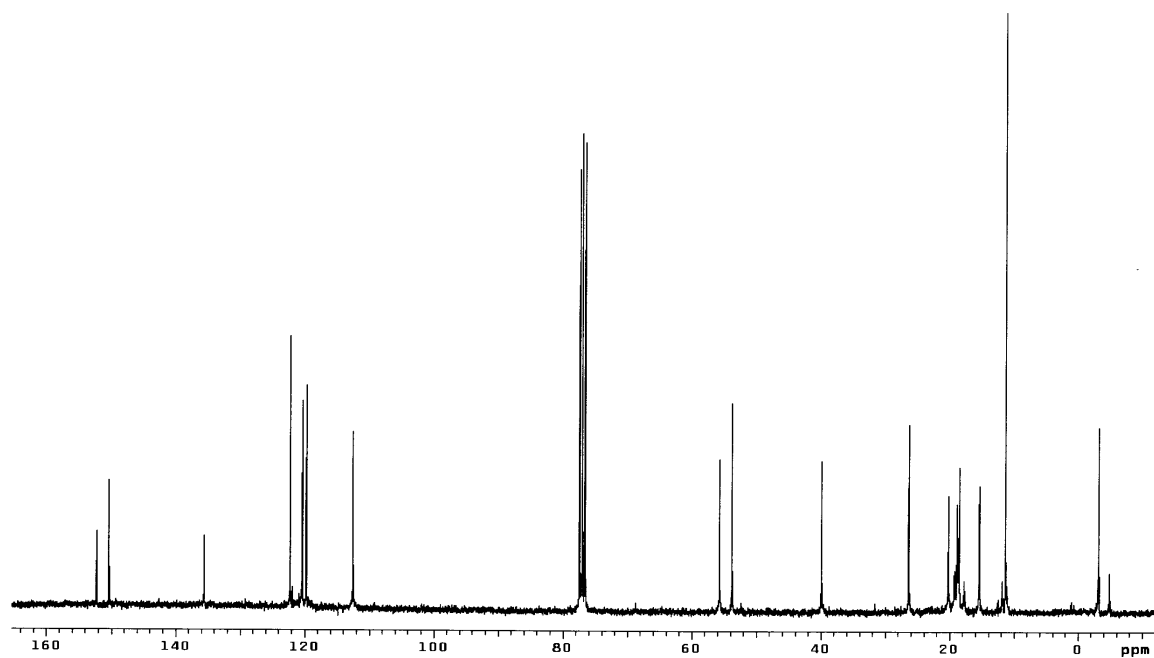
$^{13}\text{C}\{^1\text{H}\}$ -NMR



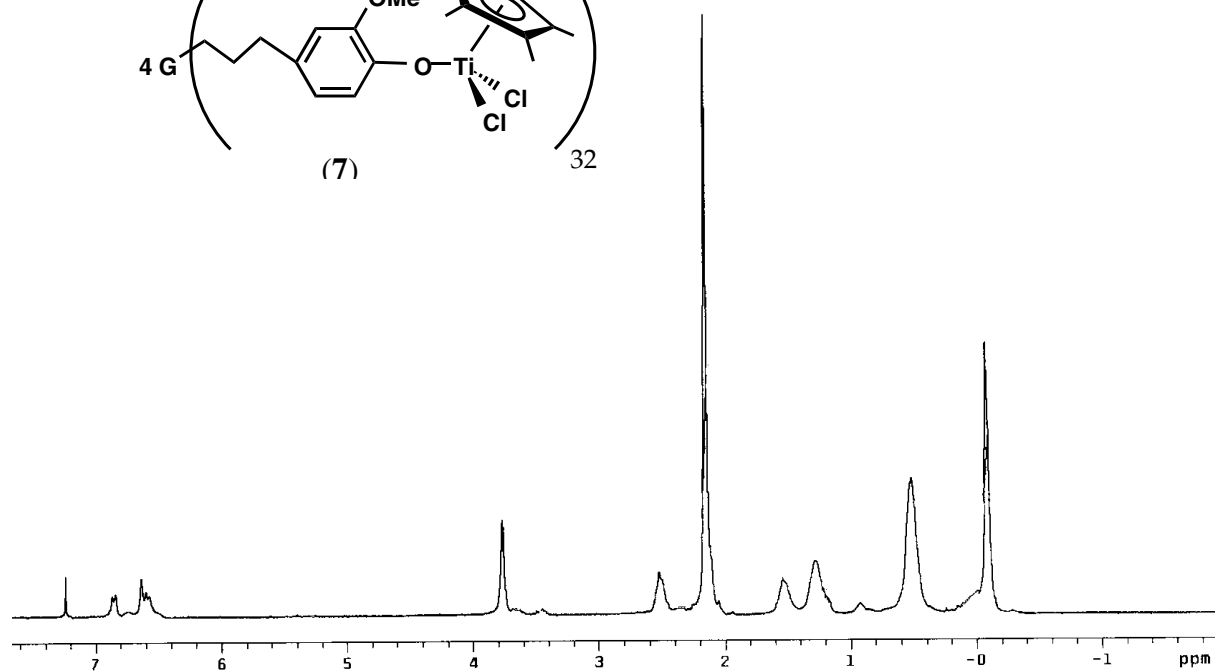
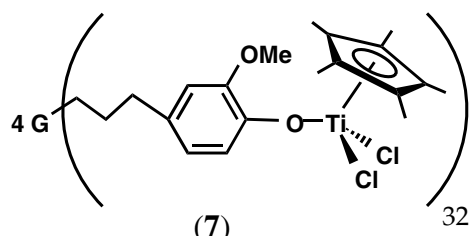
^1H -NMR



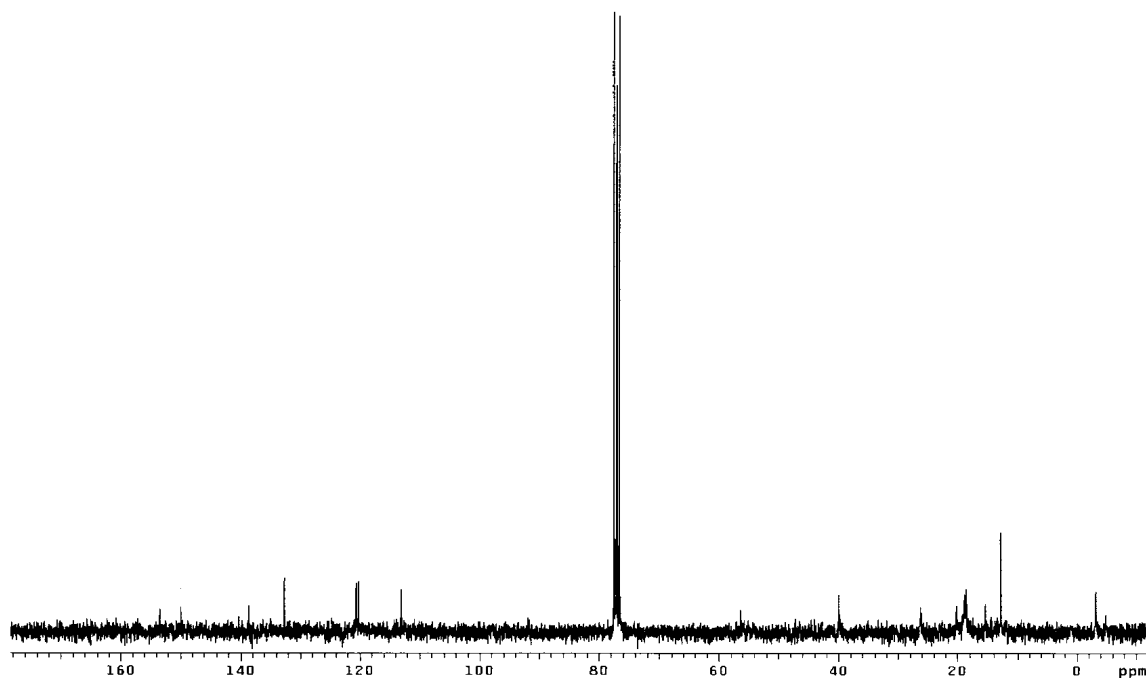
$^{13}\text{C}\{^1\text{H}\}$ -NMR



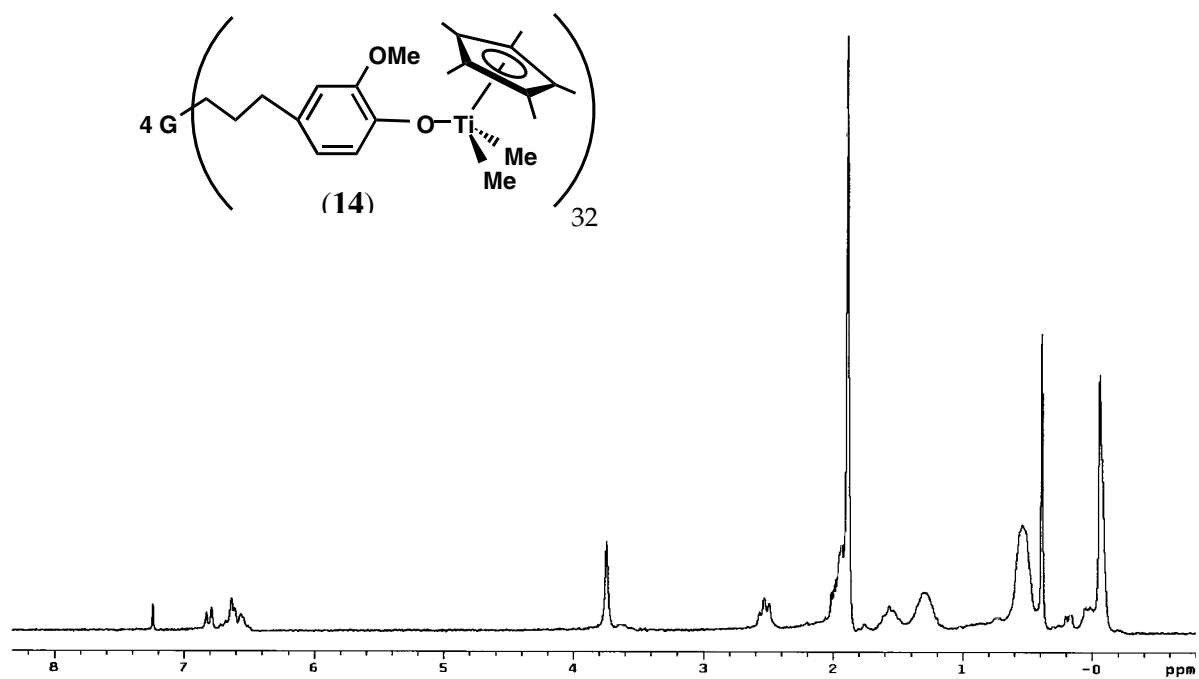
^1H -NMR



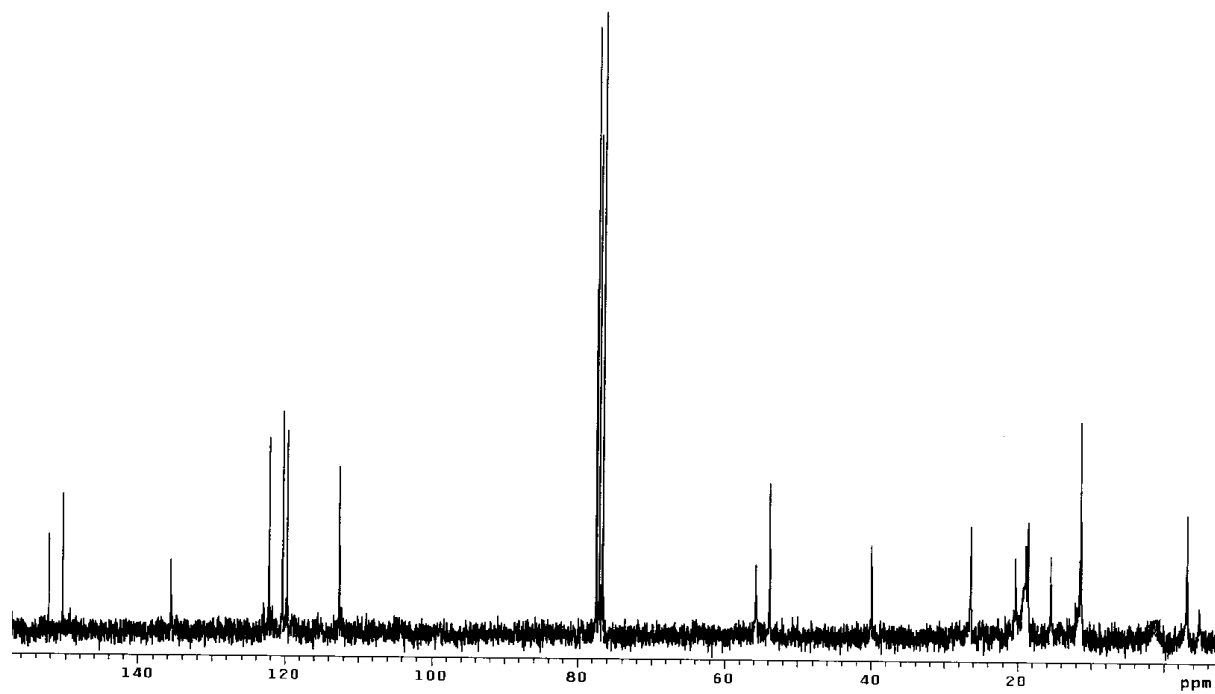
$^{13}\text{C}\{^1\text{H}\}$ -NMR



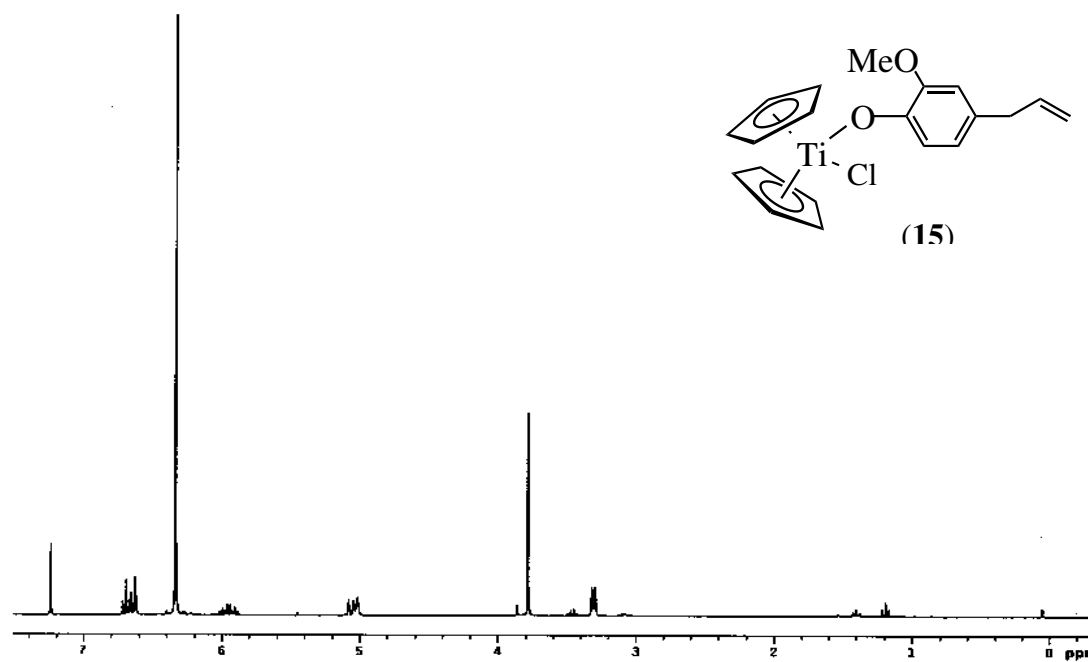
^1H -NMR



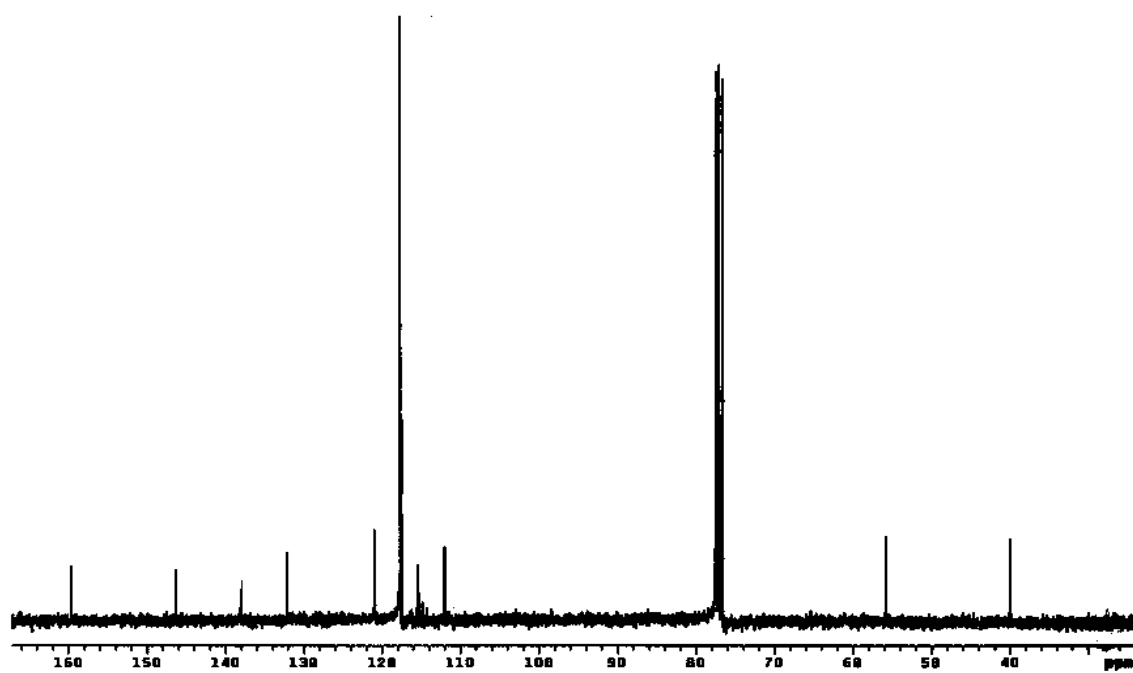
$^{13}\text{C}\{^1\text{H}\}$ -NMR



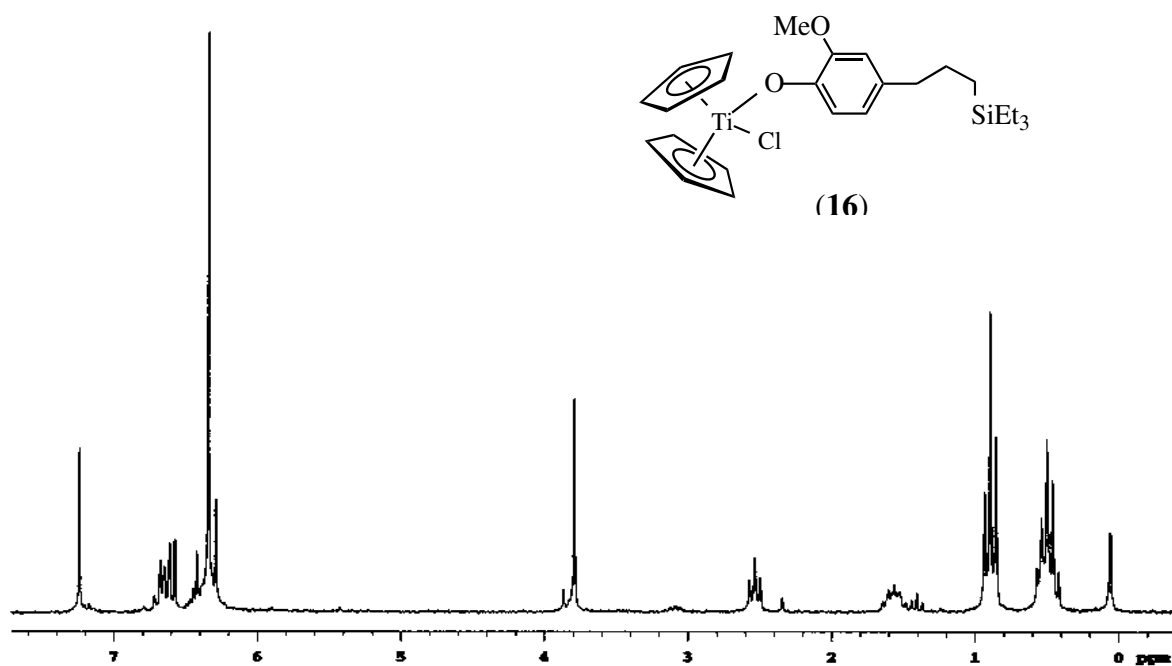
^1H -NMR



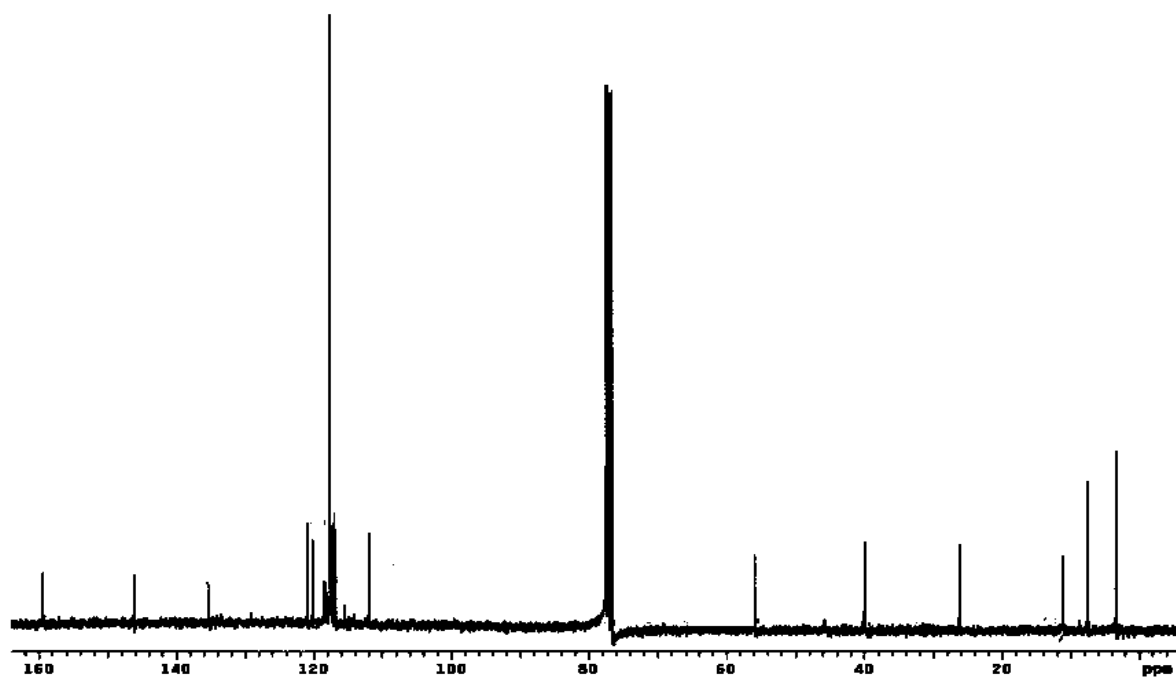
$^{13}\text{C}\{^1\text{H}\}$ -NMR



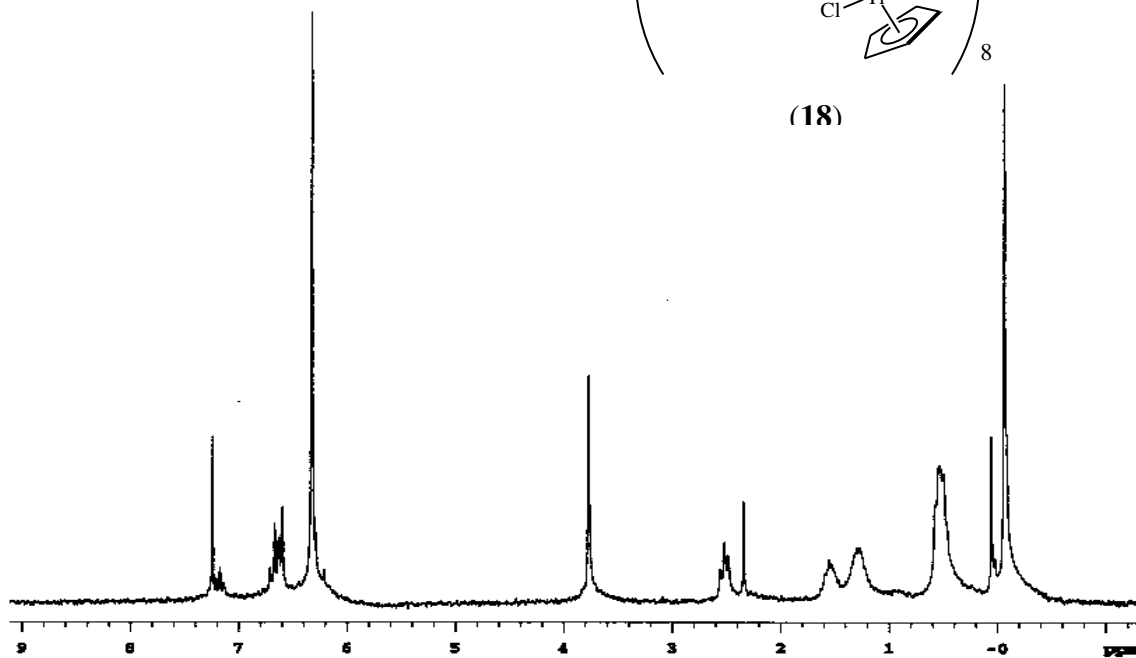
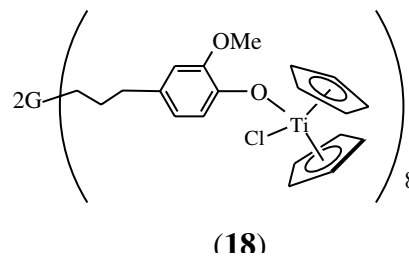
^1H -NMR



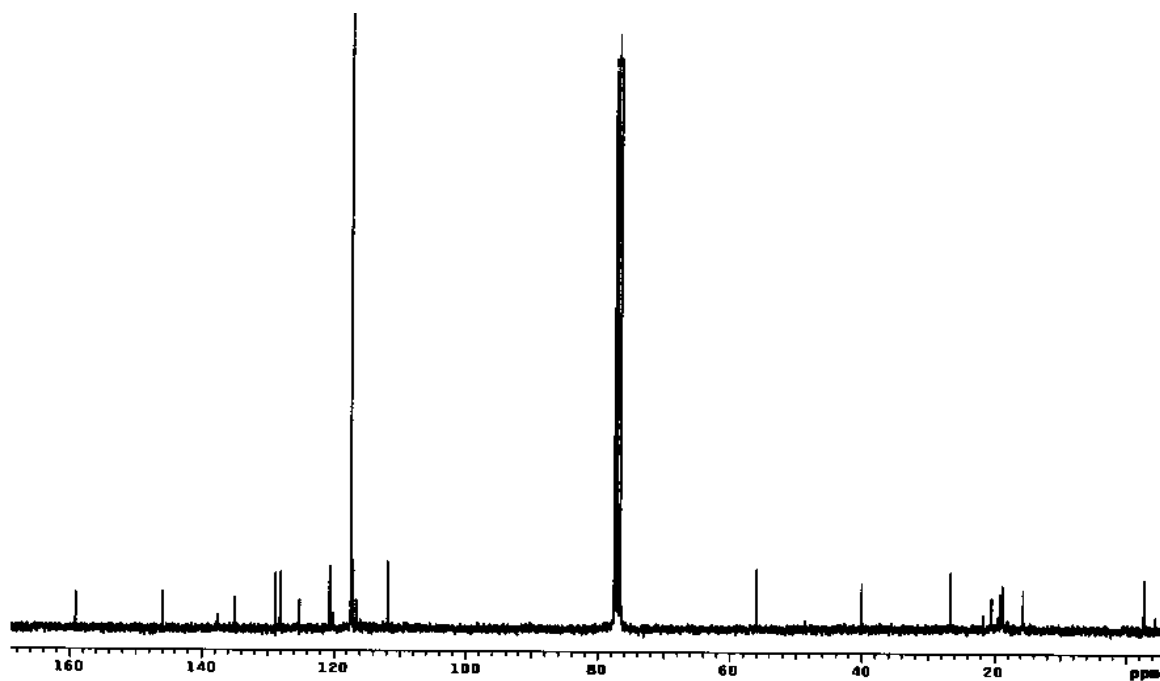
$^{13}\text{C}\{^1\text{H}\}$ -NMR



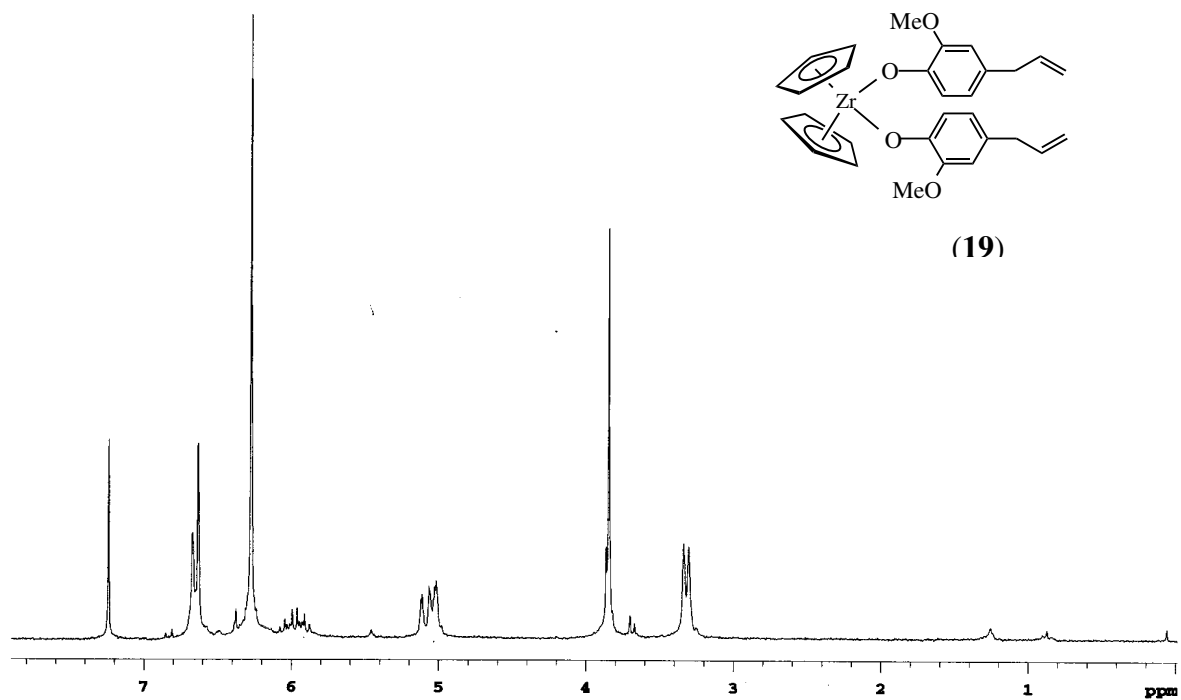
^1H -NMR



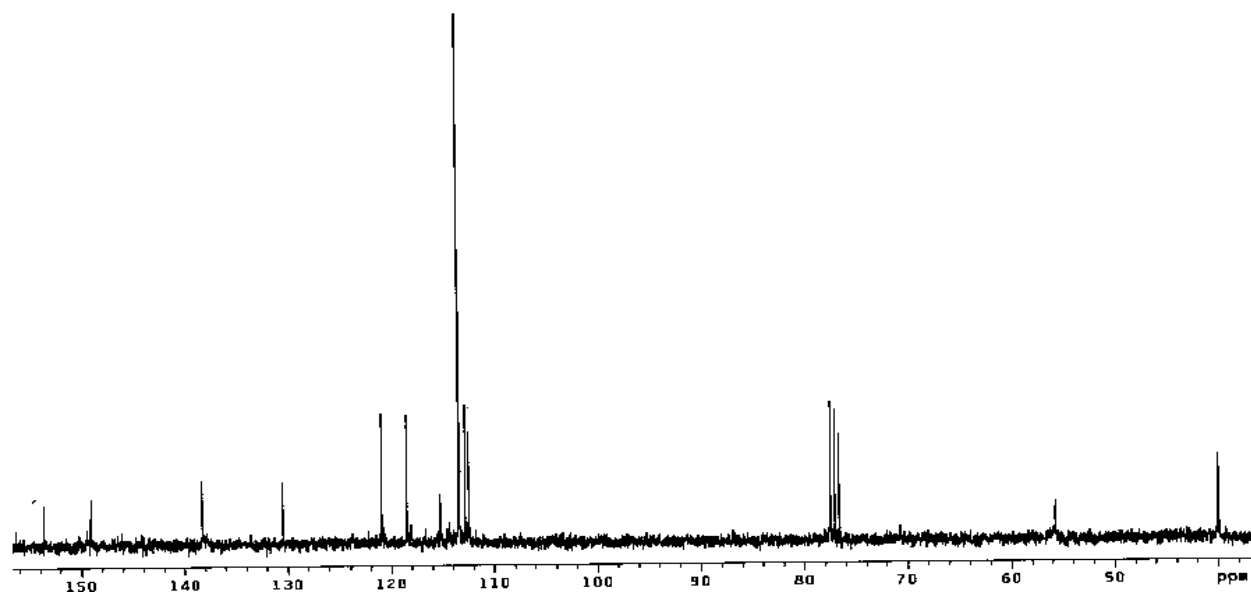
$^{13}\text{C}\{^1\text{H}\}$ -NMR



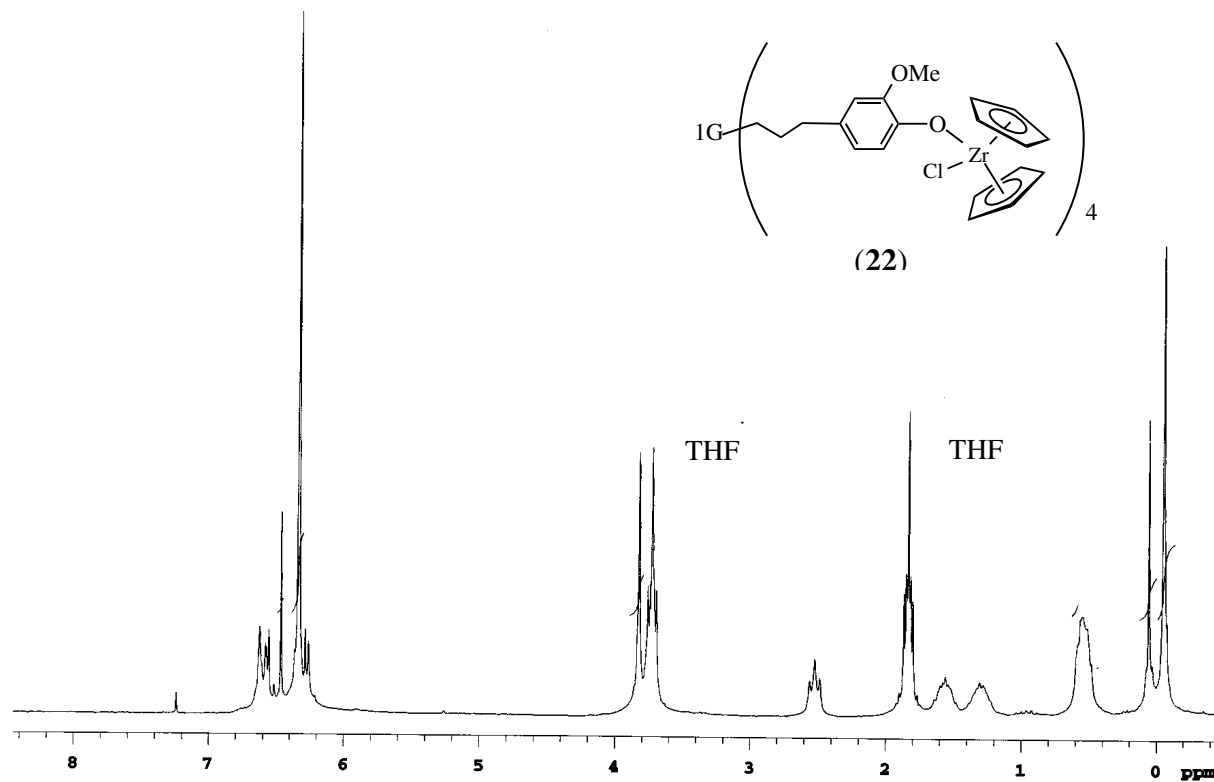
^1H -NMR



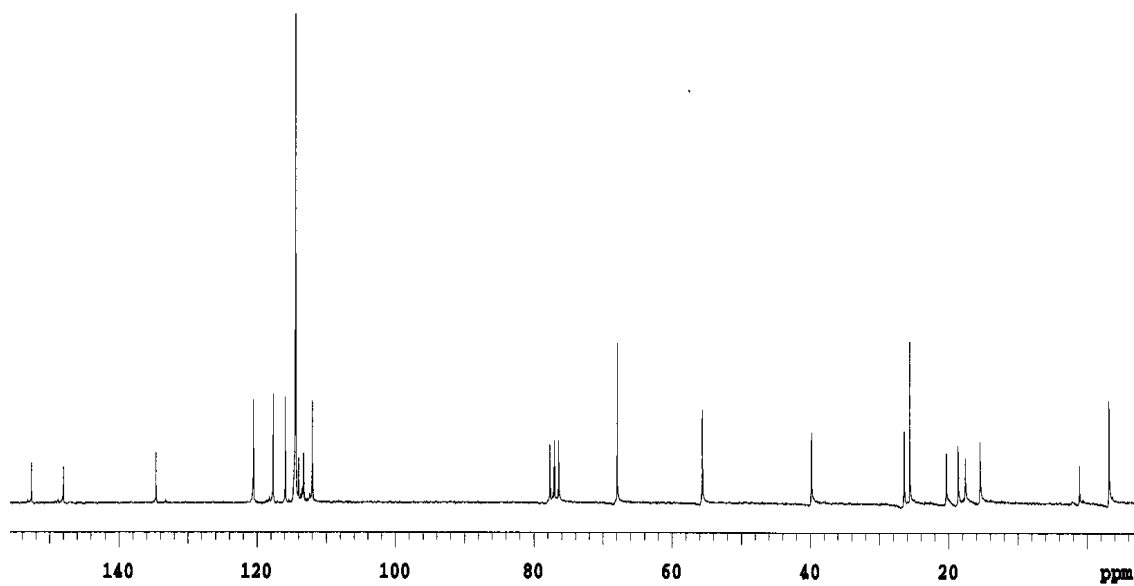
$^{13}\text{C}\{\text{H}\}$ -NMR



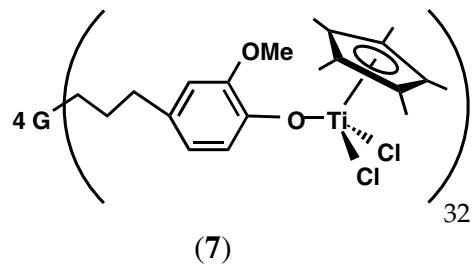
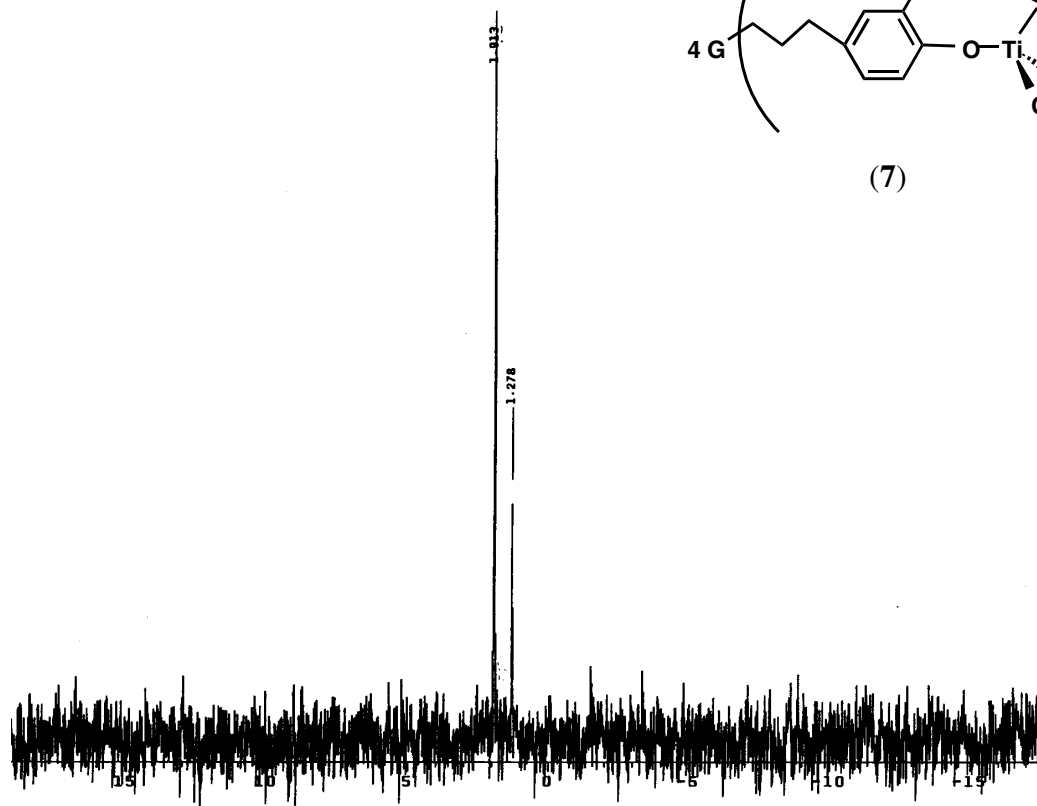
^1H -NMR



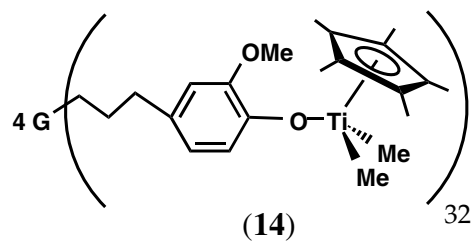
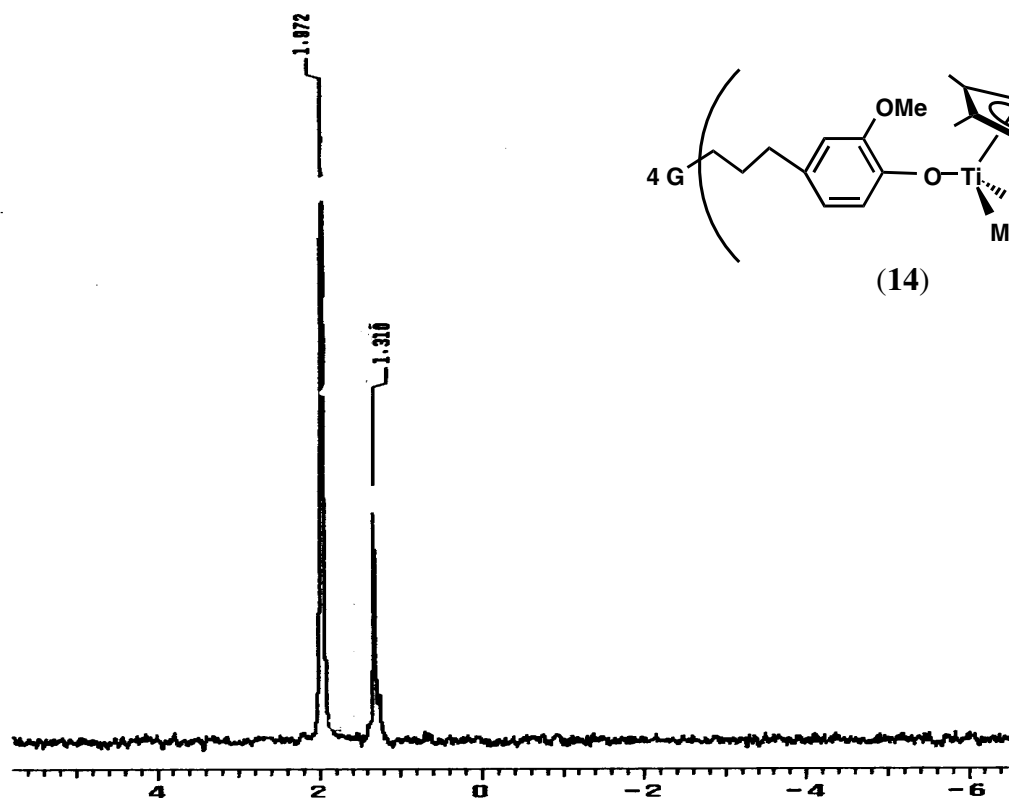
$^{13}\text{C}\{\text{H}\}$ -NMR



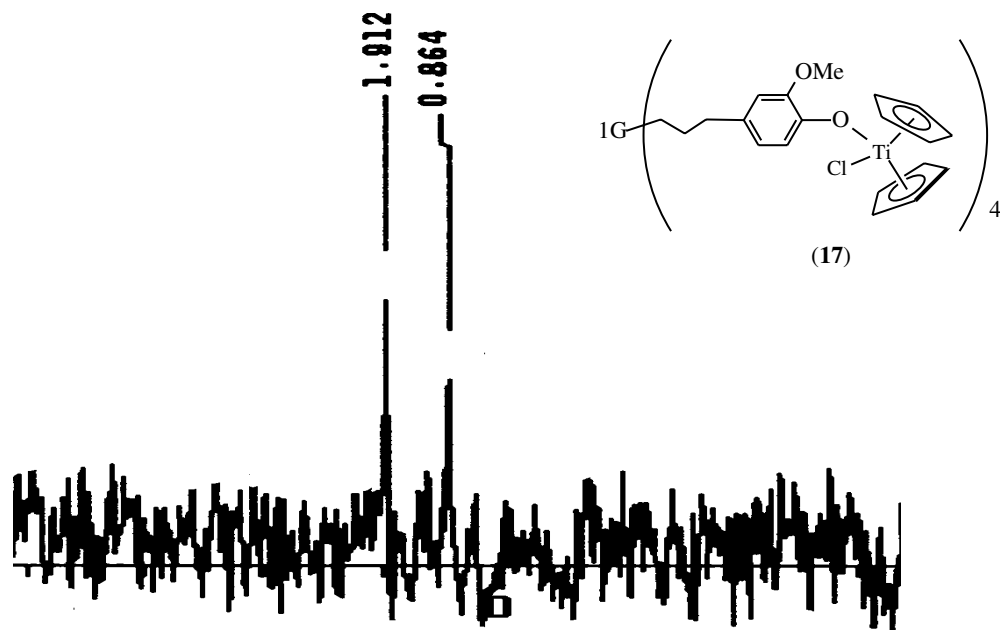
^{29}Si -RMN



^{29}Si -RMN



²⁹Si-RMN



²⁹Si-RMN

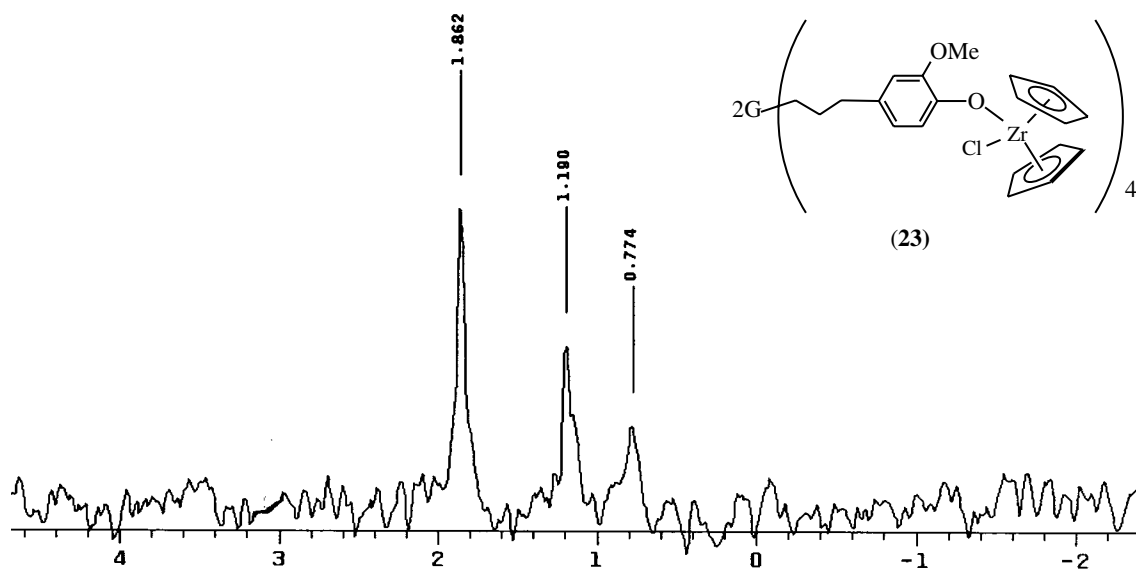


Table 1. Bond lengths [Å] and angles [°] for compound 2.

Ti(1)-O(1)	1.770(3)	C(22)-O(2)	1.348(7)
Ti(1)-Cl(2)	2.2638(18)	O(2)-C(43)	1.438(7)
Ti(1)-Cl(1)	2.2661(18)	O(3)-C(44)	1.417(8)
O(1)-C(21)	1.363(6)	C(31)-C(32)	1.433(10)
C(26)-O(3)	1.375(6)	C(32)-C(33)	1.277(10)
C(24)-C(31)	1.543(8)	Cp(1)-Ti(1)	2.026
O(1)-Ti(1)-Cl(2)	104.35(14)	O(2)-C(22)-C(23)	125.8(6)
O(1)-Ti(1)-Cl(1)	102.50(13)	O(2)-C(22)-C(21)	115.4(5)
Cl(2)-Ti(1)-Cl(1)	100.31(8)	C(22)-O(2)-C(43)	116.6(5)
C(21)-O(1)-Ti(1)	163.1(3)	C(26)-O(3)-C(44)	117.8(5)
O(1)-C(21)-C(26)	120.7(5)	C(32)-C(31)-C(24)	116.9(7)
O(1)-C(21)-C(22)	119.6(5)	C(33)-C(32)-C(31)	130.4(9)
C(25)-C(26)-O(3)	125.8(6)	Cp(1)-Ti(1)-O(1)	118.9
O(3)-C(26)-C(21)	114.2(5)	Cp(1)-Ti(1)-Cl(1)	114.5
C(25)-C(24)-C(31)	120.7(6)	Cp(1)-Ti(1)-Cl(2)	113.8
C(23)-C(24)-C(31)	119.3(6)	Ti(1)-O(1)-C(21)	163.1(3)

Cp(1) is the centroid of C(1), C(2),C(3),C(4),C(5).

Table 2. Crystal data and structure refinement for compound 2.

Empirical formula	C ₂₁ H ₂₈ Cl ₂ O ₃ Ti
Formula weight	447.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 30.543(2)$ Å $b = 9.5370(10)$ Å $c = 16.588(2)$ Å
	$\beta = 112.41(2)^\circ$
Volume	$4467.0(8)$ Å ³
Z	8
Density (calculated)	1.330 Mg/m ³
Absorption coefficient	0.640 mm ⁻¹
$F(000)$	1872
Crystal size	$0.35 \times 0.30 \times 0.15$ mm ³
θ range for data collection	2.25 to 25.00°
Index ranges	$-36 \leq h \leq 33$, $0 \leq k \leq 11$, $0 \leq l \leq 19$
Reflections collected	4065
Independent reflections	3912 [$R(\text{int}) = 0.0312$]
Completeness to $\theta = 25.00^\circ$	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3912 / 0 / 239
Goodness-of-fit on F^2	0.998
Final R indices [$I > \sigma(I)$] ^a	$R1 = 0.0606$, $wR2 = 0.1308$
R indices (all data)	$R1 = 0.1587$, $wR2 = 0.1619$
Largest diff. peak and hole	0.517 and -0.342 e Å ⁻³

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; \quad wR2 = \{ [\Sigma w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2] \}^{1/2}.$$