Supporting Information for:

Titanium (IV) Catalysts with Ancillary Imino-spiroketonato Ligands: Synthesis, Structure and Olefin Polymerization

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Contents:

Experimental Section

General Methods

All manipulations of air- and/or moisture-sensitive materials were performed under a dry nitrogen atmosphere by means of standard Schlenk techniques or using a Braun Labmaster drybox. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica gel coated glass plate (Merck) with F254 indicator. Flash chromatography was performed on ICN Silitech 32-63 D 60 Å silica gel.

Routine ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 (300 MHz), Varian Mercury-300 (300 MHz), Varian Inova-400 (400 MHz) and Varian Inova-500 (500 MHz) instruments in chloroform-*d* ($CDCl_3$) unless otherwise noted. Chemical shifts are reported in parts per million (ppm) with referencing to the residual non-deuterated solvent. Coupling constants are reported in Hertz (Hz). ^{19}F NMR spectra were recorded on a Varian Mercury-300 (282 MHz), Varian Inova-400 (376 MHz) and Varian Inova-500 (470 MHz) instruments and were referenced versus internal C_6F_6. ^{13}C NMR spectra of the polymers were recorded on a Varian Inova-500 (125 MHz) spectrometer at 130 ºC in 1,1,2,2-tetrachloroethane-d_2. For quantitative analysis, an inverse gated decoupling sequence was employed with a 30° pulse width over a 220 ppm spectral width at a 2.0 s acquisition.

Molecular weight data (M_n and M_w) were determined by high temperature gel-permeation chromatography (GPC). All analyses were performed with a Waters Alliance GPCV 2000 liquid chromatograph equipped with a Waters DRI detector and four Waters HT 6E styrene-divinylbenzene linear mixed-bed columns and one waters HT 2 column. The GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) at 140 ºC at 1.0 mL/min and were calibrated using monodisperse polyethylene standards. Polymer samples were typically placed in the oven at 140 ºC for 24 h to eliminate aggregates prior to molecular weight measurement.

Differential Scanning Calorimetry (DSC) analyses were performed on a TA DSC Q1000 instrument using Universal Analysis 2000 processing software. The measurements were made in aluminum pans under nitrogen with a heating rate of 10

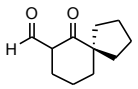
ºC/min from –70 to 200 ºC. The reported T_m values originate from the second heating scan. X-ray crystallographic data was collected using a SMART CCD Area Detector System (Mo Kα, λ = 0.71073 Å), and frames were integrated with the Siemens SAINT program.

Elemental analyses were performed by the Robertson Microlit Lab at Madison, NJ. Mass spectra (MS) were obtained on a Micromass 70-VSE (EI/FAB) mass spectrometer and a Micromass Quattro Tandem Quadrupole/Hexapole/Quadrupole Instrument (ESI) at the University of Illinois School of Chemical Sciences.

The following solvents were freshly distilled under N_2 prior to use: tetrahydrofuran (THF) and diethyl ether (Et_2O) from sodium and benzophenone ketyl, triethylamine (Et_3N) from calcium hydride. The following solvents were purified over columns of alumina and copper (Q5) prior to use: methylene chloride (CH_2Cl_2), toluene, hexane, and pentane. Ethylene and propylene (Matheson, polymer grade) were purified through a mixed-bed column (R&D Separations, BOT-4). Methylaluminoxane (PMAO-IP, 13% Al in toluene, Akzo Nobel) was concentrated in *vacuo* to dryness at 40 ºC overnight to remove residual trimethylaluminum, yielding a white powder. All other solvents and reagents were of reagent grade quality and used without further purification. All reactions were run under a nitrogen atmosphere.

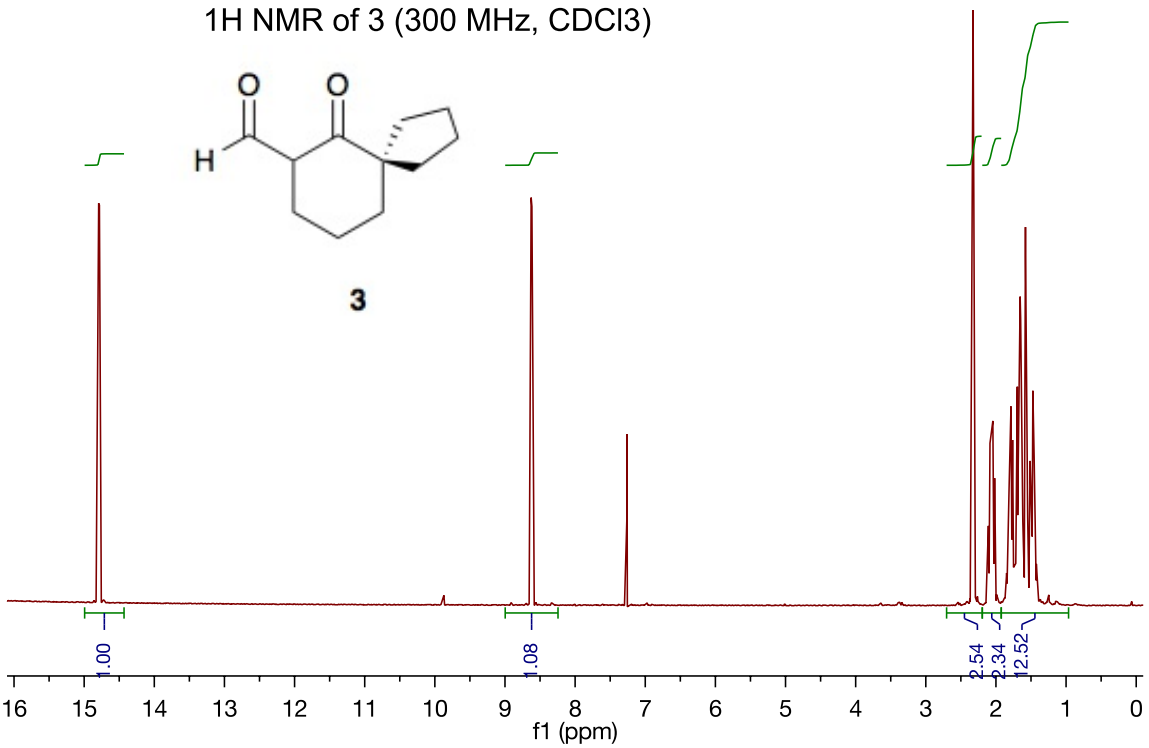
Experimental Procedures

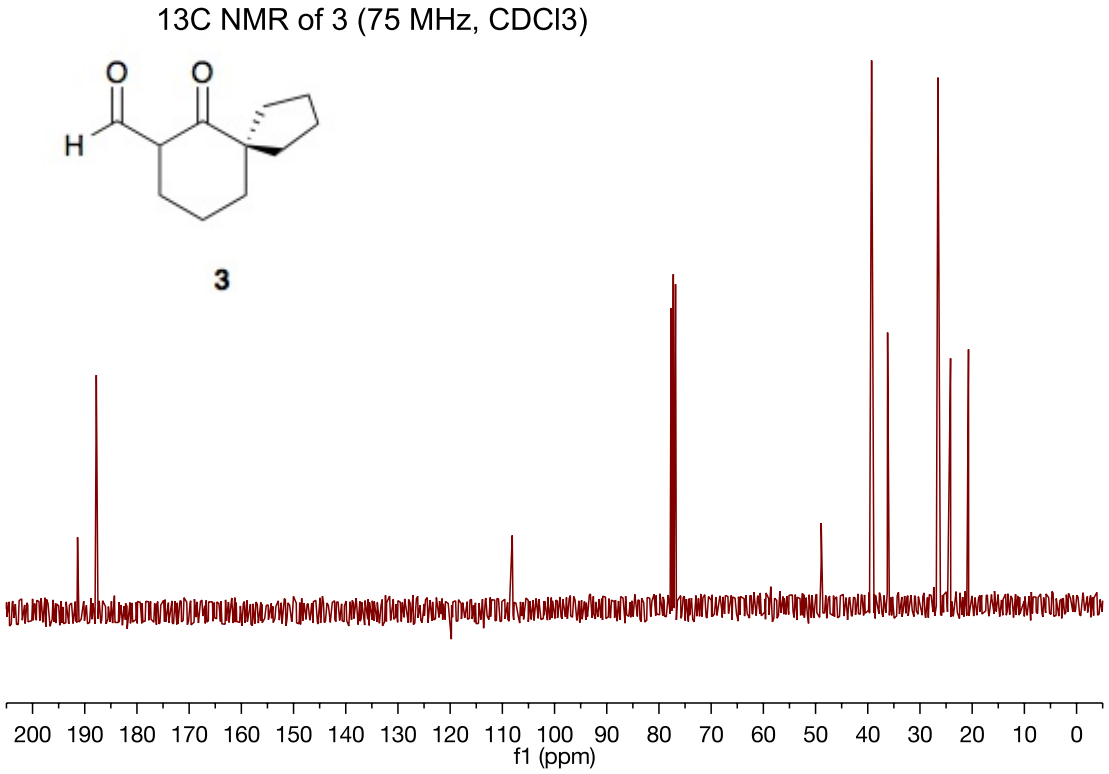
Spiro[4,5]decan-6-one[1] and ***N*-phenyl-2,2,2-trifluoroacetimidoyl chloride**[2] were synthesized following the literature procedure with minor modifications.

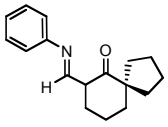


6-Oxo-spiro[4.5]decane-7-carbaldehyde (3) A procedure similar to that reported in literature[3] for formylation under basic conditions was followed. A solution of spiro[4,5]decan-6-one (2.70 g, 17.7 mmol) in dry toluene (40 mL) was added dropwise by a gas tight syringe at room temperature to a suspension of sodium methoxide (4.29 g, 75.4 mmol) in dry toluene (75 mL). The reaction mixture turned from white to pale yellow and was cooled to 0 ºC. After 20 min, ethyl formate (5.61 g, 75.7 mmol) was added dropwise by a gas tight syringe, and the reaction mixture was stirred at room

temperature (RT) overnight. Diethyl ether (80 mL) was then added, and the suspension was washed with water (40 mL x 2) and was titrated to pH = 6 by 2 N HCl (aq.). The ethereal solution was dried over Na_2SO_4, filtrated, and concentrated under reduced pressure to yield 3.04 g (95%) of the product as light yellow oil. ^{1}H NMR (300 MHz): δ 14.79 (d, J = 3.3, 1H, O*H*/CH), 8.62 (d, J = 3.3, 1H, C*H*O), 2.33 (t, J = 6.2, 2H, CH_2), 2.12-2.01 (m, 2H, CH_2), 1.82-1.42 (m, 10H, CH_2). ^{13}C NMR (75 MHz): δ 191.4, 187.8, 108.1, 48.9, 39.3, 36.2, 26.5, 24.1, 20.7. MS (ESI): 181.1 $(M + H)^+$; HRMS (ESI) Calcd for $C_{11}H_{17}O_2$: 181.1229, found 181.1235.

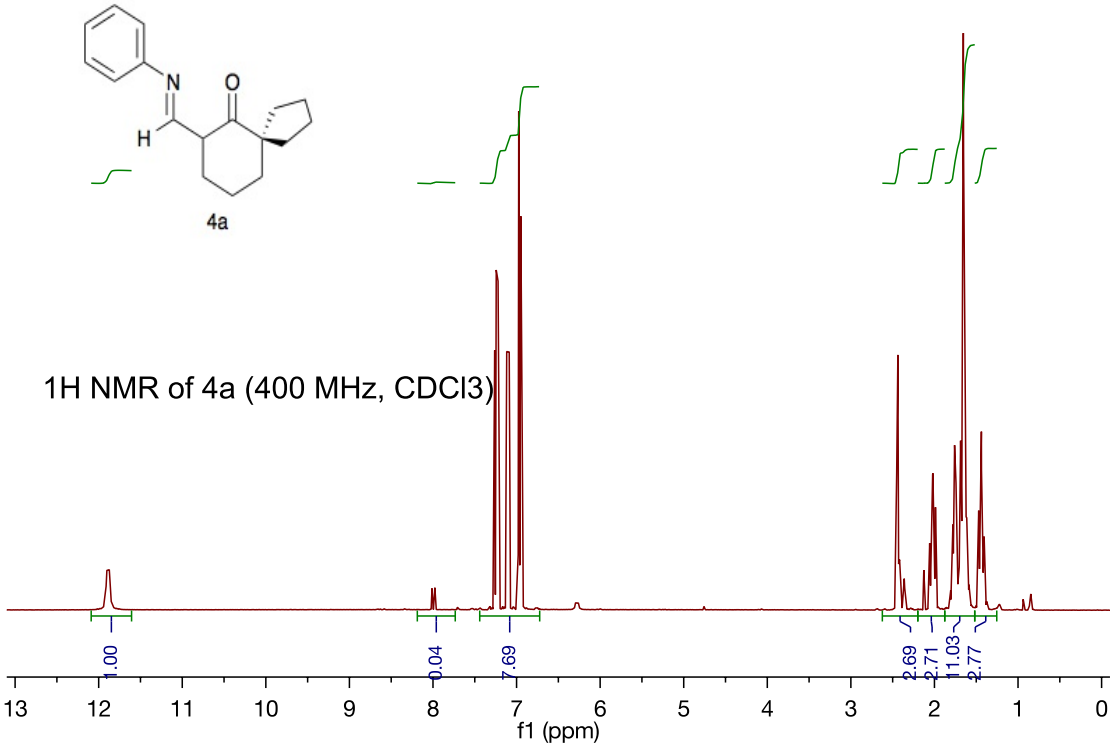


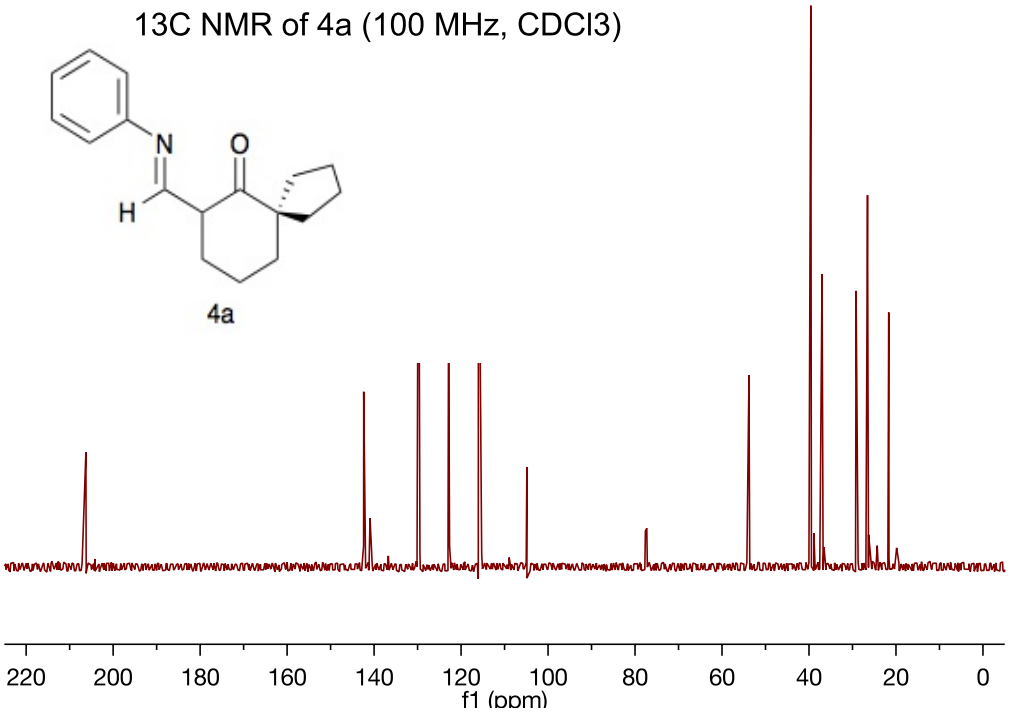


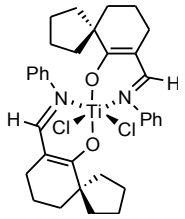


7-Phenyliminomethyl-spiro[4.5]decan-6-one (4a) A 150 mL round bottom flask was charged with spiroaldehyde **3** (1.00 g, 5.55 mmol), aniline (0.65 g, 6.9 mmol) and the mixture was stirred for ca. 10 min to achieve total dissolution of **3**. *p*-Toluenesulfonic acid (*p*-TSA, 50 mg) and phosphorous pentoxide (P_2O_5, 50 mg) were added, and then the stirred mixture was heated to 110 ºC (oil bath) for 2 h under nitrogen. After cooling down to room temperature, CH_2Cl_2 (180 mL) was added to dissolve the brown slurry and the solution was washed by water (60 mL × 2), brine and then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel (10% (v/v) EtOAc/hexanes) to give 1.24 g (88%) of the product as a red oil. ^{1}H NMR (400 MHz): δ 11.89 (d, J = 11.6, 1H, O*H*/C*H*), 7.23 (m, 2H, Ar*H-ortho*), 7.10 (dt, J = 12.0. 1.0, 1H, C*H*N), 6.98-6.93 (m, 3H, Ar*H-para* + Ar*H-meta*), 2.45-2.42 (m, 2H, CH_2), 2.04-2.00 (m,

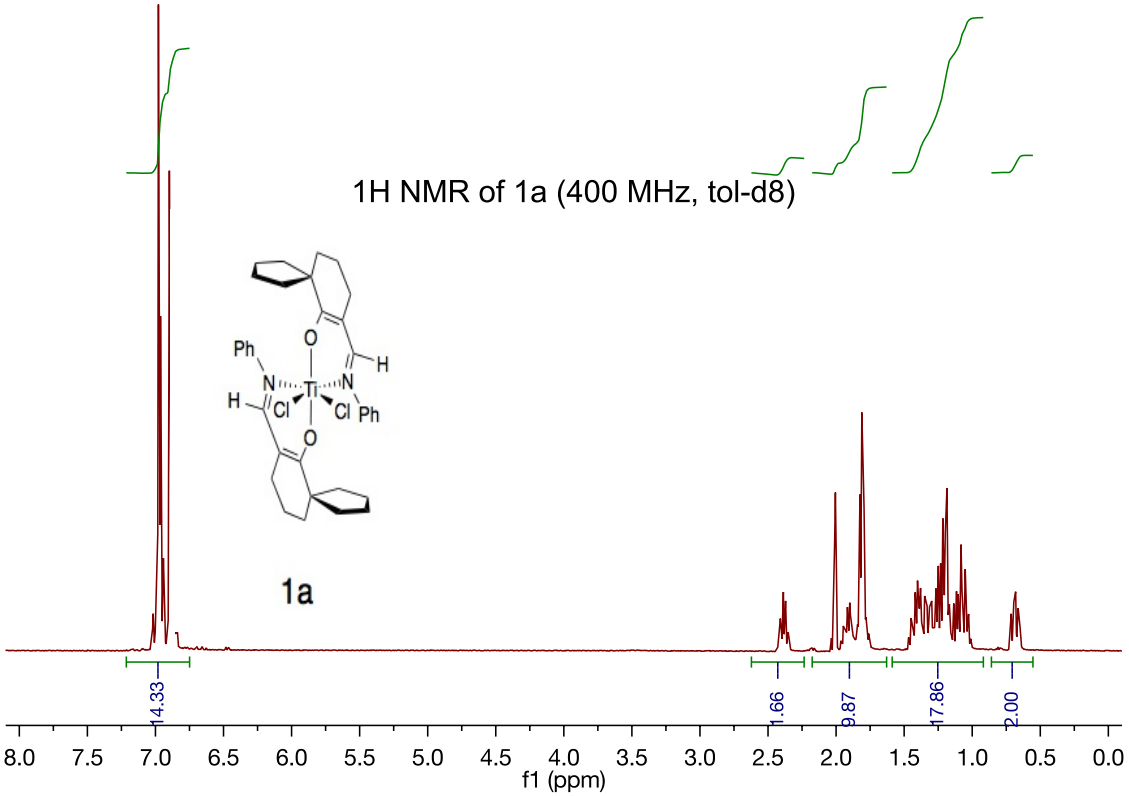
2H, CH_2), 1.78-1.61 (m, 8H, CH_2), 1.47-1.41 (m, 2H, CH_2). ^{13}C NMR (100 MHz): δ 206.0, 142.1, 140.6, 129.5, 122.6, 115.7, 104.6, 53.5, 39.3, 36.7, 28.9, 26.2, 21.4.

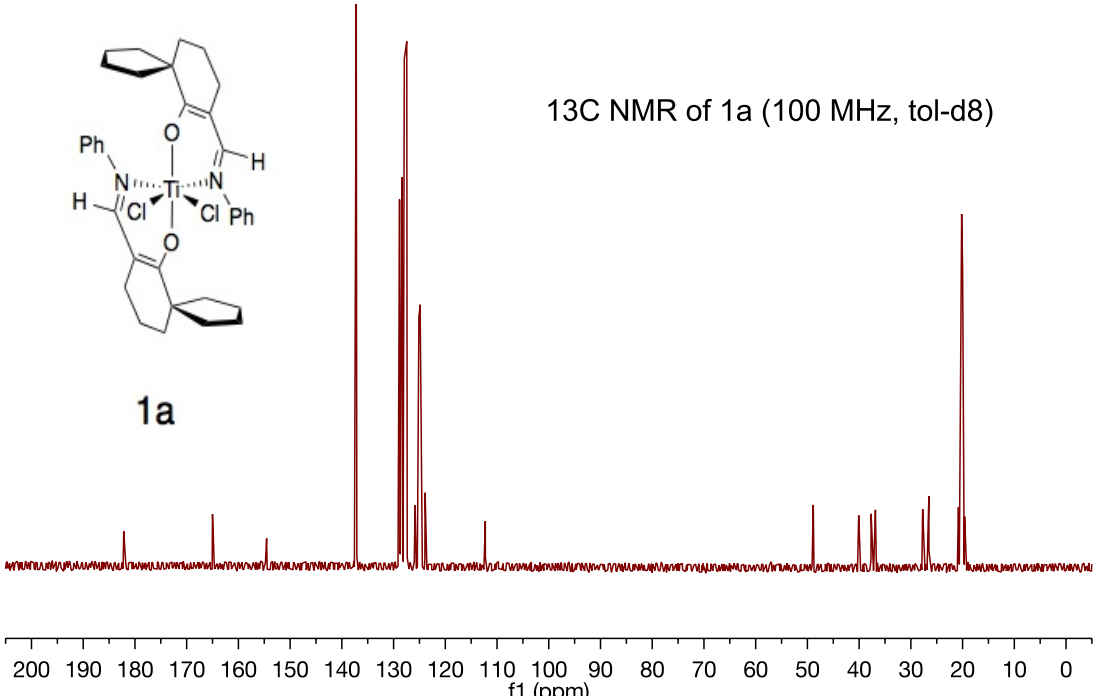


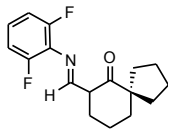




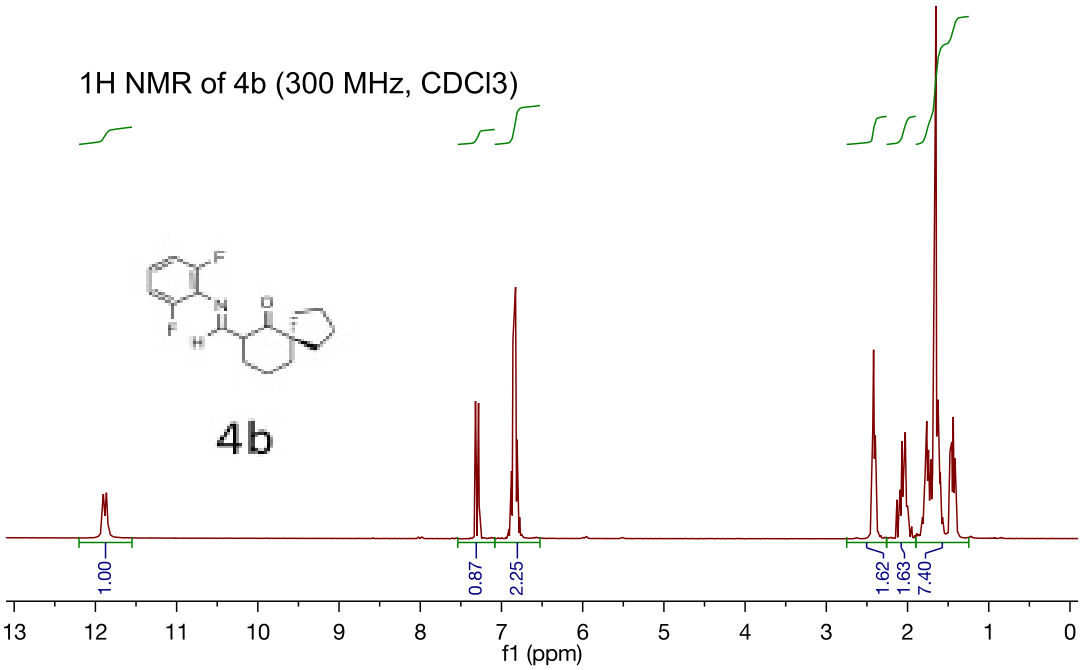
Ti complex 1a The Ti complex **1e** was synthesized following the procedure similar to that reported in the literature to make phenoxyimine Ti complexes.[4] To a stirred solution of ligand 7-phenyliminomethyl-spiro[4.5]decan-6-one (4a, 1.24 g, 4.86 mmol) in 20 mL of diethyl ether (Et_2O) at –78 ºC was added *n*-BuLi (1.6 M in hexanes, 3.03 mL, 4.86 mmol) dropwise using a gas tight syringe. This solution was allowed to slowly warm to room temperature and stirred for an additional half hour. The solution was then added dropwise via cannula to a solution of $TiCl_4$ (1.0 M in toluene, 2.43 mL, 2.43 mmol) in Et_2O (15 mL) at –78 ºC. The resulting deep red solution was allowed to warm to room temperature and stirred for additional 16 h. After removal of the solvent under vacuum, the residue was taken up in toluene and the precipitated LiCl was removed by filtration over a Celite plug. Removal of solvent in *vacuo* gave a deep red powder that was crystallized from a mixture of toluene/pentane to give the desired complex as a deep red powder (81 mg, 6%). ^{1}H NMR (toluene-d_8, 400 MHz): δ 7.02-6.84 (m, 12H, Ar*H*+C*H*N), 2.39 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 1.80 (m, 4H, CH_2), 1.46-1.02 (m, 18H, CH_2), 0.70 (m, 2H, CH_2). ^{13}C NMR (toluene-d_8, 100 MHz): δ 182.2, 165.0, 154.6, 128.3, 125.8, 123.9, 112.3, 48.9, 40.1, 37.7, 36.9, 27.7, 26.6.


1H NMR of 1a (400 MHz, tol-d8)
1a
14.33
1.66
9.87
17.86
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

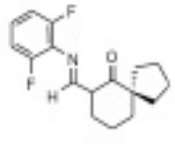

13C NMR of 1a (100 MHz, tol-d8)
1a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



7-[(2,6-Difluoro-phenylimino)-methyl]-spiro[4.5]decan-6-one (4b) The procedure to make *N*-phenyl analogue **4a** was followed. Thus, spiroaldehyde **3** (0.72 g, 4.0 mmol) was reacted with 2,6-difluoroaniline (0.62 g, 4.8 mmol) in the presence of *p*-TSA (40 mg) and P_2O_5 (50 mg) to afford 1.04 g (89%) of pure product as a yellow oil after column chromatography over silica gel (10% (v/v) EtOAc/hexanes). ^{1}H NMR (300 MHz): δ 11.88 (d, J = 11.3, 1H, O*H*/C*H*), 7.30 (d, J = 11.5, 1H, C*H*N), 6.87-6.79 (m, 3H, Ar*H*), 2.42 (t, J = 5.4, 2H, CH_2), 2.09-2.00 (m, 2H, CH_2), 1.79-1.60 (m, 8H, CH_2), 1.48-1.40 (m, 2H, CH_2). ^{13}C NMR (75 MHz): δ 207.0, 153.8 (dd, J_{CF} = 246.2, 5.8), 144.3 (t, J_{CF} = 6.4), 121.6 (t, J_{CF} = 9.7), 119.3 (t, J_{CF} = 12.6), 112.3 (dd, J_{CF} = 16.0, 7.7), 106.6, 54.1, 39.4, 36.8, 29.2, 26.4, 21.5. ^{19}F NMR (282 MHz): δ -126.2. MS (ESI): 292.1 (M + H)$^+$; HRMS (ESI) Calcd for $C_{17}H_{20}F_2NO$: 292.1513, found 292.1518.

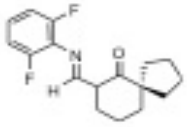


13C NMR of 4b (75 MHz, CDCl3)

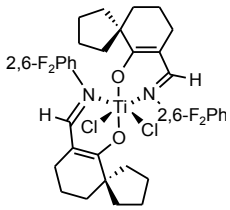


4b

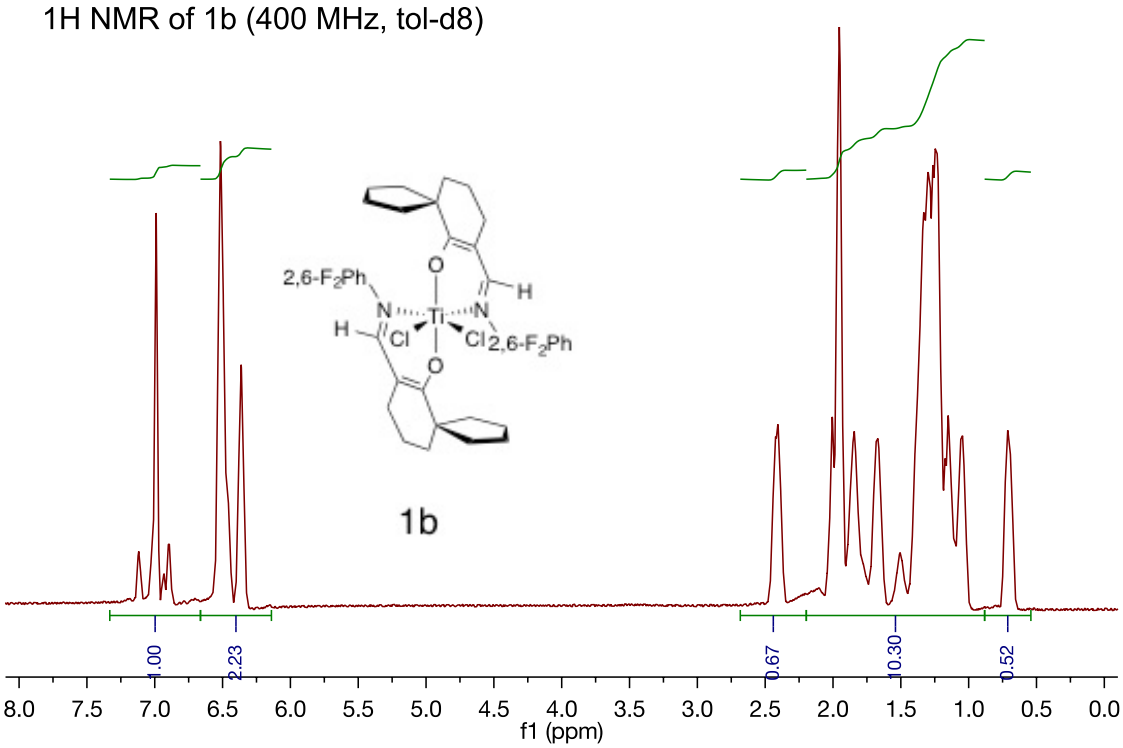
19F NMR of 4b (282 MHz, CDCl3)

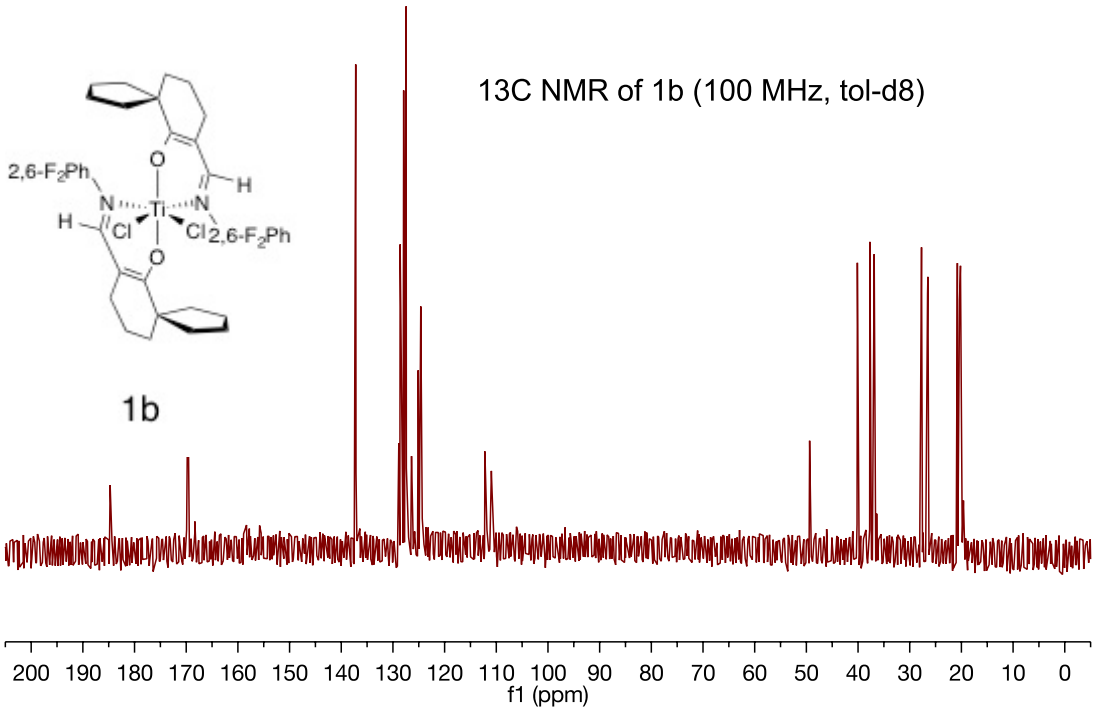


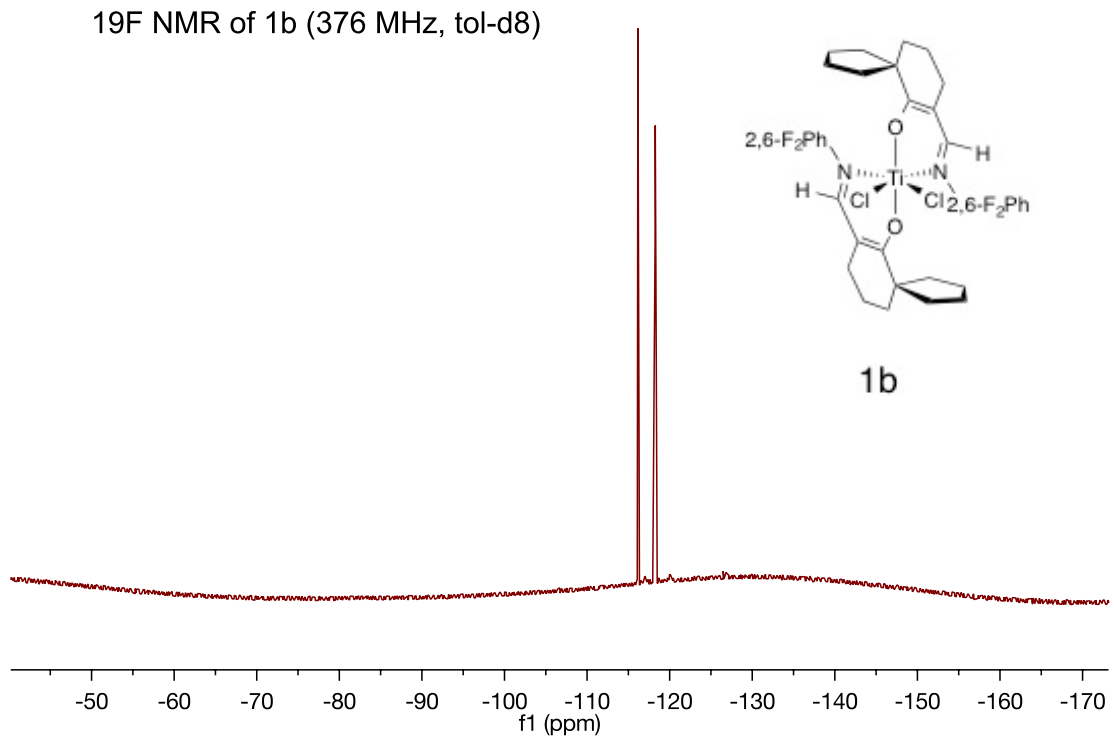
4b

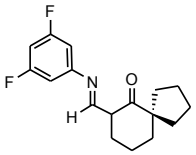


Ti complex 1b The Ti complex **1b** was synthesized following the procedure to make **1a**. Thus, ligand 7-[(2,6-difluoro-phenylimino)-methyl]-spiro[4.5]decan-6-one (**4b**, 1.03 g, 3.54 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 2.21 mL, 3.54 mmol) and then $TiCl_4$ (1.0 M in toluene, 1.77 mL, 1.77 mmol) to give a deep red powder that was crystallized from toluene to give the desired complex as a deep red crystalline solid (0.83 g, 67%). ^{1}H NMR (toluene-d_8, 400 MHz): δ 7.07 (s, 2H, C*H*N), 6.55 (m, 4H, Ar*H*), 6.38 (m, 2H, Ar*H*), 2.20-0.80 (m, 28H, CH_2). ^{13}C NMR (toluene-d_8, 100 MHz): δ 185.4, 170.4, 127.1, 112.8, 112.7, 112.6, 111.6, 50.1, 40.8, 38.4, 37.6, 28.4, 27.2. ^{19}F NMR (toluene-d_8, 376 MHz): δ -116.1, -118.2. MS (EI): 696.3 $(M)^+$. Anal Calcd for $C_{34}H_{36}Cl_2F_4N_2O_2Ti$: C, 58.39; H, 5.19; N, 4.01. Found: C, 58.45; H, 4.98; N, 3.79.

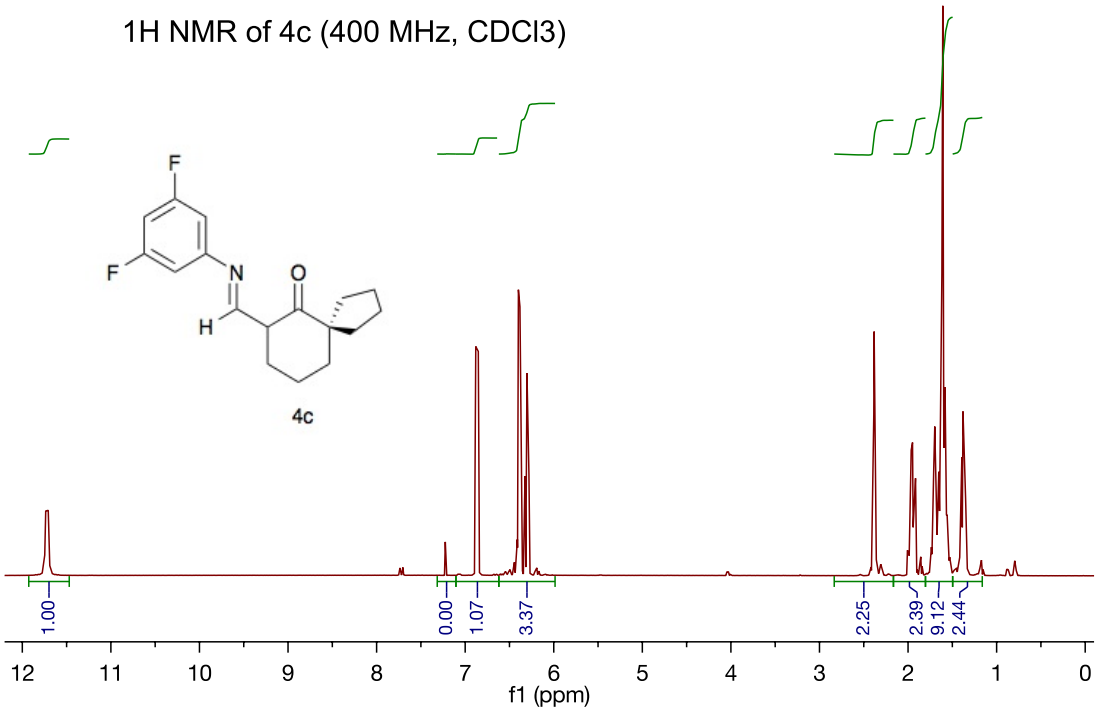



13C NMR of 1b (100 MHz, tol-d8)
2,6-F2Ph
O
H
N
Ti
N
H
Cl
Cl
2,6-F2Ph
O
1b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

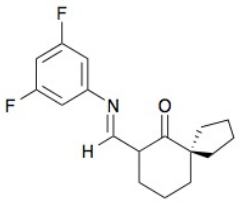

19F NMR of 1b (376 MHz, tol-d8)
2,6-F2Ph
O
H
N
Ti
N
H
Cl
Cl
2,6-F2Ph
O
1b
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)



7-[(3,5-Difluoro-phenylimino)-methyl]-spiro[4.5]decan-6-one (4c) The procedure to make *N*-phenyl analogue **4a** was followed. Thus, spiroaldehyde **3** (1.04 g, 5.77 mmol) was reacted with 3,5-difluoroaniline (0.91 g, 6.92 mmol) in the presence of *p*-TSA (50 mg) and P_2O_5 (50 mg) to afford 1.35 g (81%) of pure product as a light yellow oil after column chromatography over silica gel (10% (v/v) EtOAc/hexanes). ^{1}H NMR (400 MHz): δ 11.72 (d, J = 11.6, 1H, O*H*/C*H*), 6.87 (dt, J = 11.6, 1.1, 1H, C*H*N), 6.39 (dd, J = 9.0, 2.2, 2H, Ar*H-ortho*), 6.30 (tt, J = 8.9, 2.2, 1H, Ar*H-para*), 2.82 (t, J = 5.6, 2H, CH_2), 1.97-1.92 (m, 2H, CH_2), 1.72-1.56 (m, 8H, CH_2), 1.41-1.36 (m, 2H, CH_2). ^{13}C NMR (100 MHz): δ 207.4, 164.1 (dd, J_{CF} = 246.6, 15.0), 143.5 (t, J_{CF} = 12.8), 140.1, 106.7, 98.7 (dd, J_{CF} = 20.4, 8.4), 97.5 (t, J_{CF} = 26.1), 54.1, 39.4, 36.8, 29.2, 26.4, 21.5. ^{19}F NMR (376 MHz): δ -108.9.

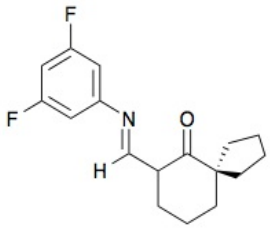


13 NMR of 4c (100 MHz, CDCl3)

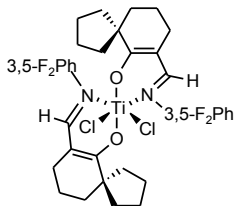


4c

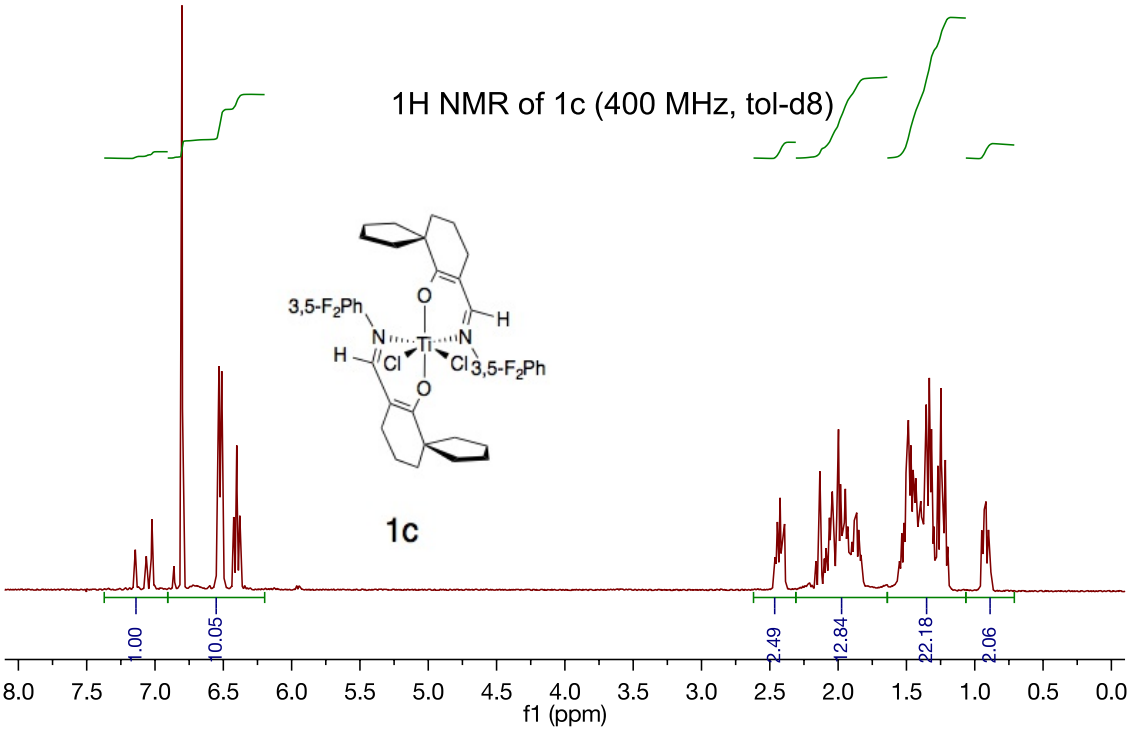
19F NMR of 4c (376 MHz, CDCl3)

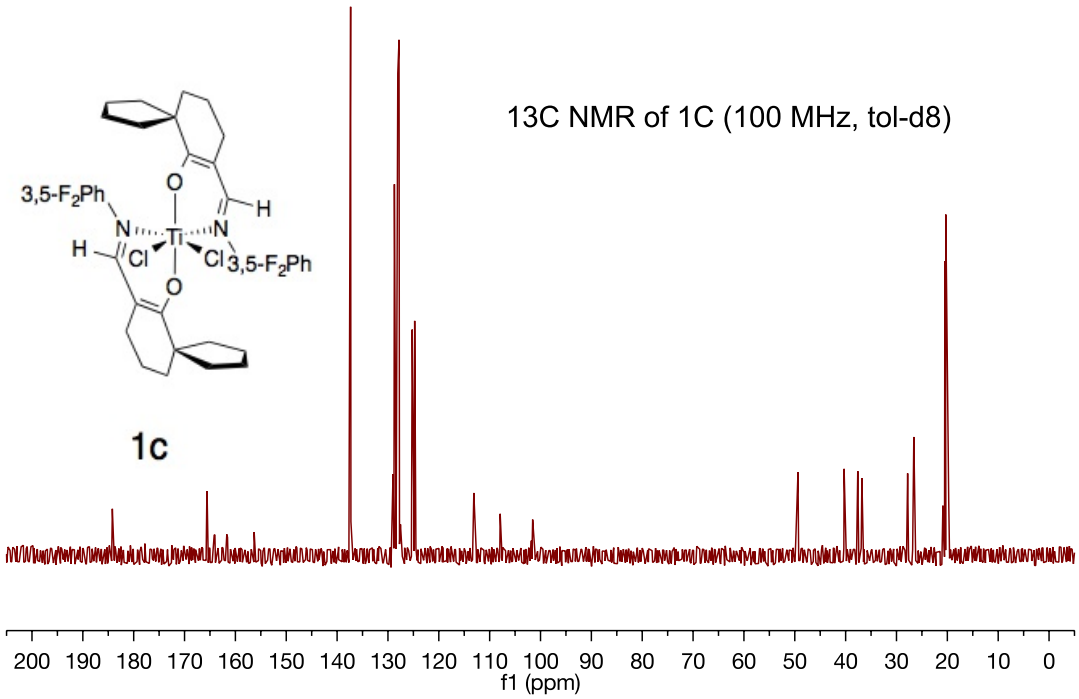


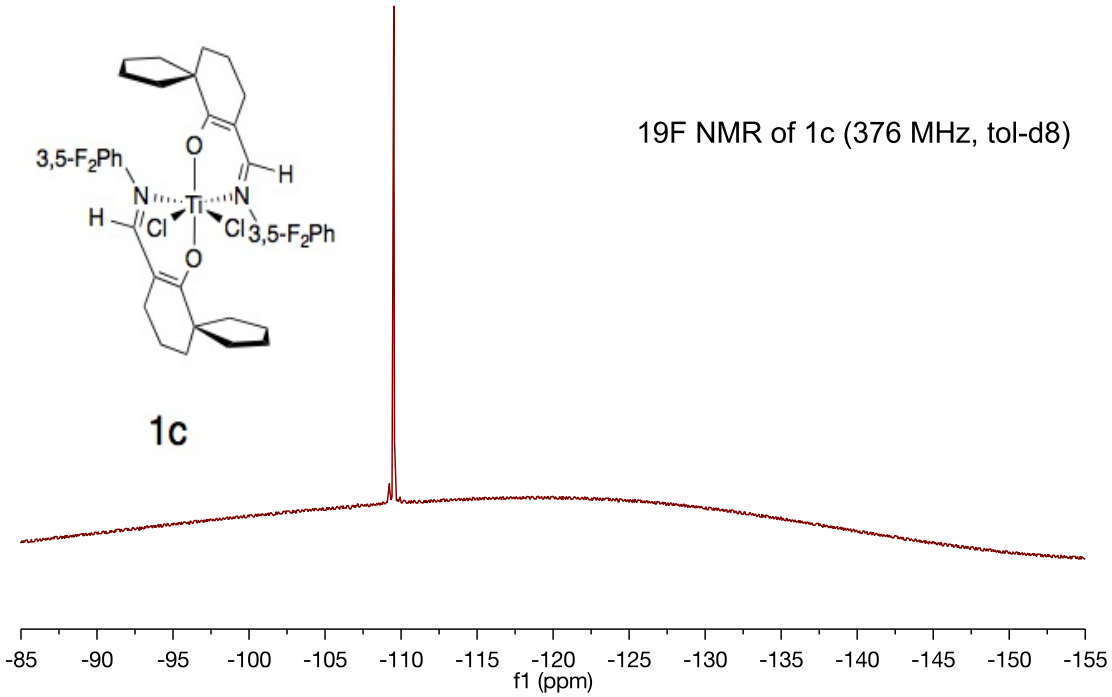
4c

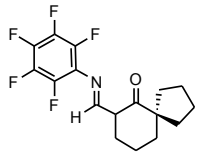


Ti complex 1c The Ti complex **1c** was synthesized following the procedure used to make **1a**. Thus, ligand 7-[(3,5-difluoro-phenylimino)-methyl]-spiro[4,5]decan-6-one (**4c**, 0.68 g, 2.3 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 1.46 mL, 2.33 mmol) and then $TiCl_4$ (1.0 M in toluene, 1.17 mL, 1.17 mmol) to give a deep red powder that was crystallized from toluene to give the desired complex as a deep red crystalline solid (0.088 g, 11%). ^{1}H NMR (toluene-d_8, 400 MHz): δ 6.74 (s, 2H, C*H*N), 6.46 (dd, J = 8.7, 1.9, 4H, Ar*H*), 6.34 (tt, J = 9.0, 2.3, 2H, Ar*H*), 2.36 (m, 2H, CH_2), 2.10-1.76 (m, 8H, CH_2), 1.49-1.13 (m, 16H, CH_2), 0.85 (m, 2H, CH_2).. ^{13}C NMR (toluene-d_8, 100 MHz): δ 184.2, 165.6, 163.4 (dd, J_{CF} = 249.7, 14.4), 156.3 (t, J_{CF} = 12.0), 113.1, 107.8 (d, J_{CF} = 26.3), 101.3 (t, J_{CF} = 25.5), 49.4, 40.3, 37.6, 36.8, 27.8, 26.6. ^{19}F NMR (toluene-d_8, 376 MHz): δ -109.51. MS (EI): 696.3 $(M)^+$.



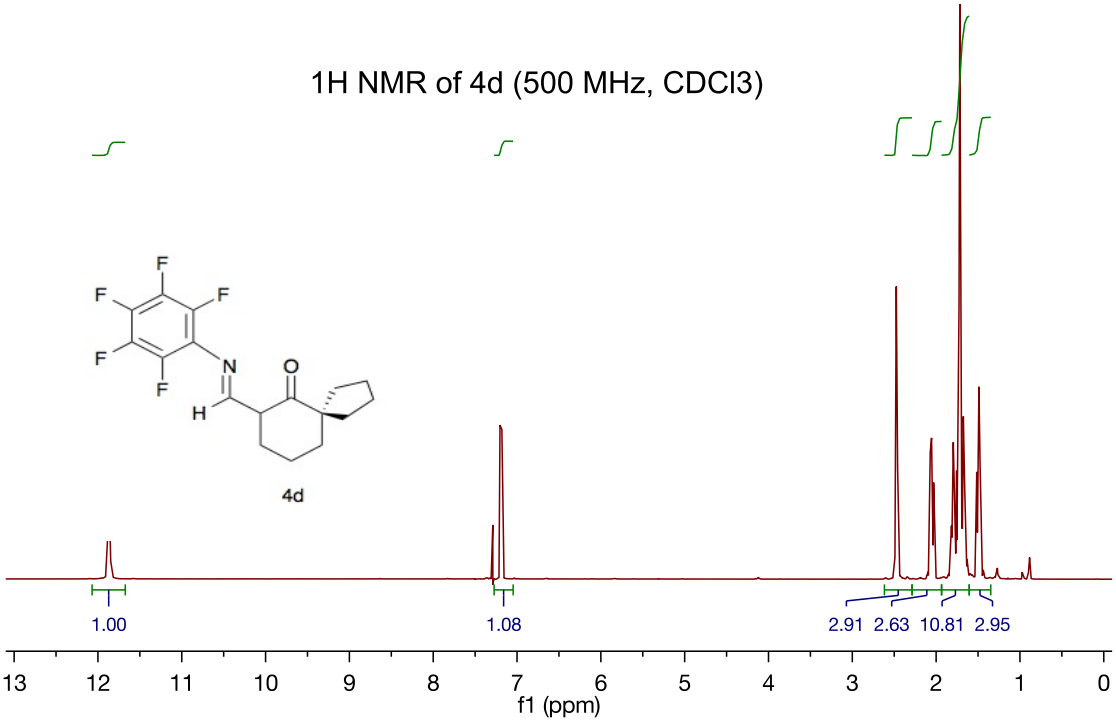

13C NMR of 1C (100 MHz, tol-d8)
3,5-F2Ph
O
H
N
Ti
N
H
Cl
Cl
3,5-F2Ph
O
1c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


19F NMR of 1c (376 MHz, tol-d8)
3,5-F2Ph
O
H
N
Ti
N
H
Cl
Cl
3,5-F2Ph
O
1c
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)

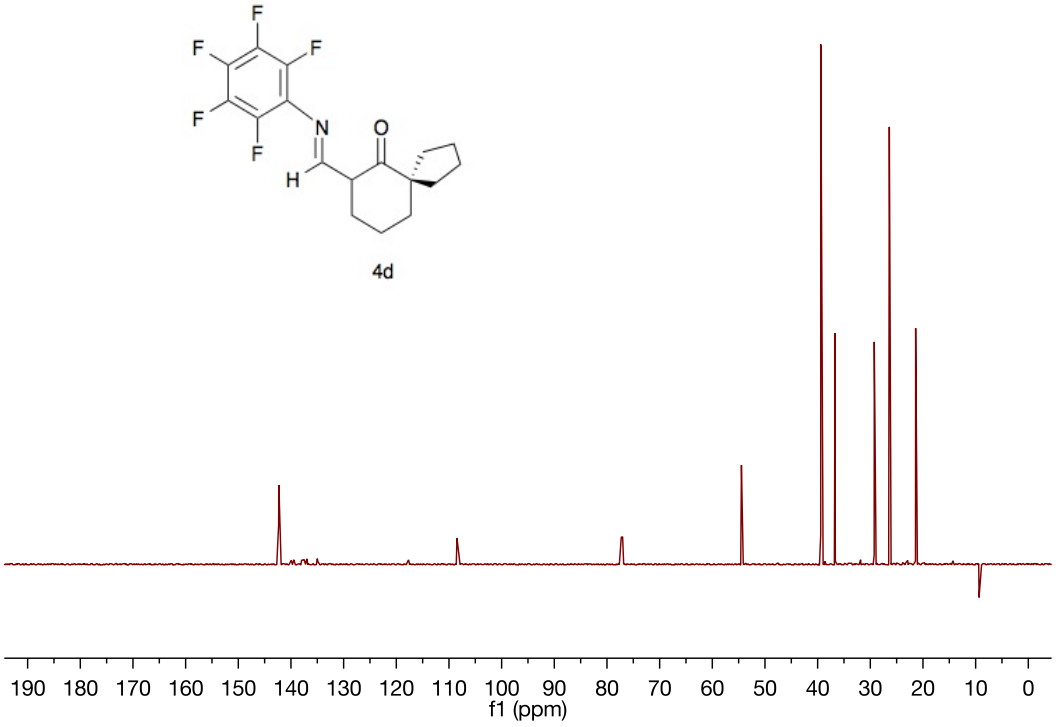


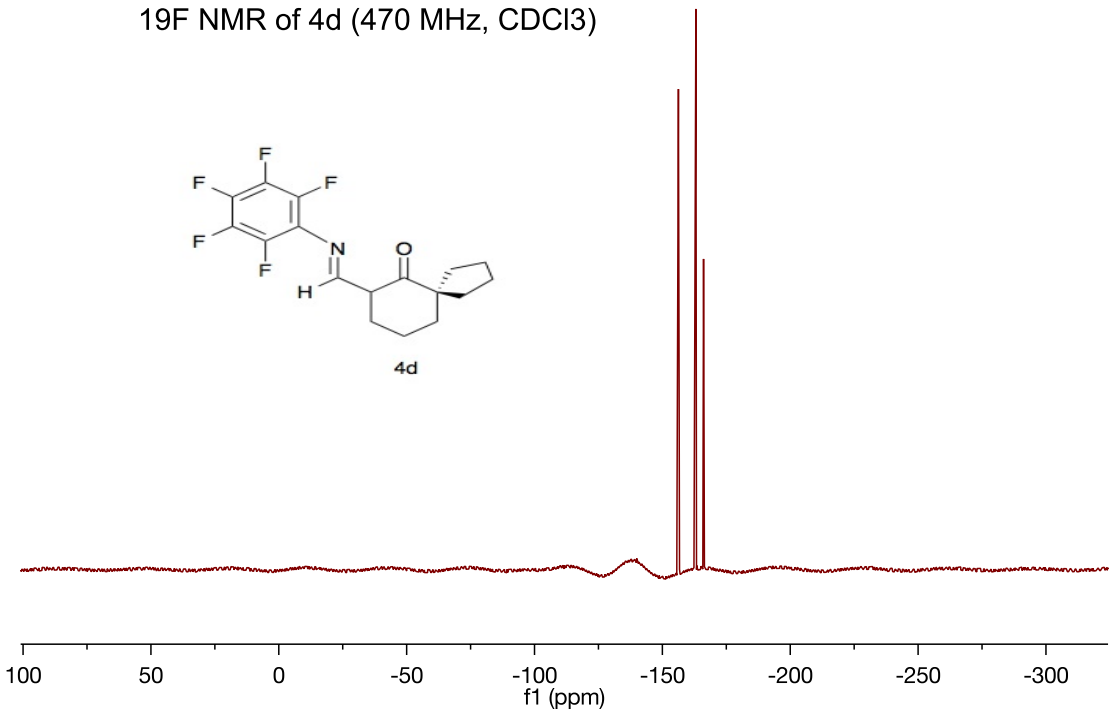
7-(Pentafluorophenylimino-methyl)-spiro[4.5]decan-6-one (4d) The procedure to make *N*-phenyl analogue **4a** was followed. Thus, spiroaldehyde **3** (0.66 g, 3.7 mmol) was reacted with 2,3,4,5,6-pentafluoroaniline (0.81 g, 4.4 mmol) in the presence of *p*-TSA (40 mg) and P_2O_5 (50 mg) to afford 1.10 g (87%) of pure product as light yellow crystals after column chromatography over silica gel (10% (v/v) EtOAc/hexanes). ^{1}H NMR (500 MHz): δ 11.84 (d, J = 11.0, 1H, O*H*/C*H*), 7.16 (d, J = 11.3, 1H, C*H*N), 2.44 (m, 2H, CH_2), 2.06-2.00 (m, 2H, CH_2), 1.78-1.75 (m, 2H, CH_2), 1.73-1.63 (m, 6H, CH_2), 1.49-1.43 (m, 2H, CH_2). ^{13}C NMR (125 MHz): δ 208.2, 142.3 (t, J_{CF} = 6.1), 139.0, 138.5, 136.0 (dtt, J_{CF} = 249.5, 13.7, 4.6), 117.7 (td, J_{CF} = 10.7, 4.1), 108.5, 54.5, 39.4, 36.7, 29.3, 26.4, 21.4. ^{19}F NMR (470 MHz): δ -156.24 (d, J_{FF} = 21.4), -163.07 (td, J_{FF} = 21.4, 4.6), -166.08 (tt, J_{FF} = 21.4, 4.6). ^{1}H NMR (toluene-d_8, 300 MHz): δ 12.07 (d, J = 10.6, 1H, O*H*/C*H*), 6.80 (d, J = 11.0, 1H, C*H*N), 2.19-2.14 (m, 4H, CH_2), 1.86-1.79 (m, 2H, CH_2), 1.59-1.46 (m, 6H, CH_2), 1.36-1.28 (m, 2H, CH_2). ^{13}C NMR (toluene-d_8, 75 MHz): δ 207.5, 142.4 (t, J_{CF} = 5.6), 140.6, 137.1, 134.6, 118.1, 108.4, 54.8, 39.8, 37.2, 29.6, 27.0, 22.0. ^{19}F NMR (282 MHz): δ -157.2 (d, J_{FF} = 21.3), -164.3 (td, J_{FF} = 21.3, 6.1), -167.6 (tt, JFF = 21.4, 6.1). MS (ESI): 346.1 $(M + H)^+$; HRMS (ESI) Calcd for $C_{17}H_{17}F_5NO$: 346.1230, found 346.1214. Anal Calcd for $C_{17}H_{16}F_5NO$: C, 59.13; H, 4.67; N, 4.06. Found: C, 59.18; H, 4.60; N, 3.96.

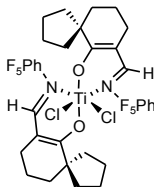
1H NMR of 4d (500 MHz, CDCl3)



13C NMR of 4d (partial spectrum, 125 MHz, tol-d8)

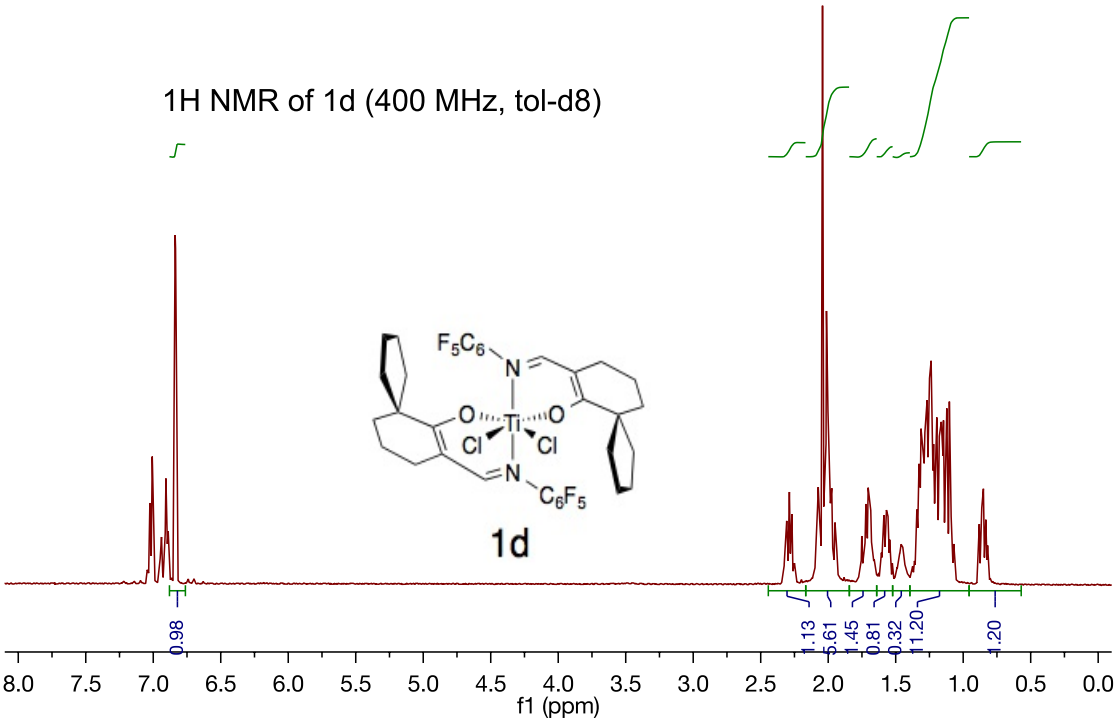




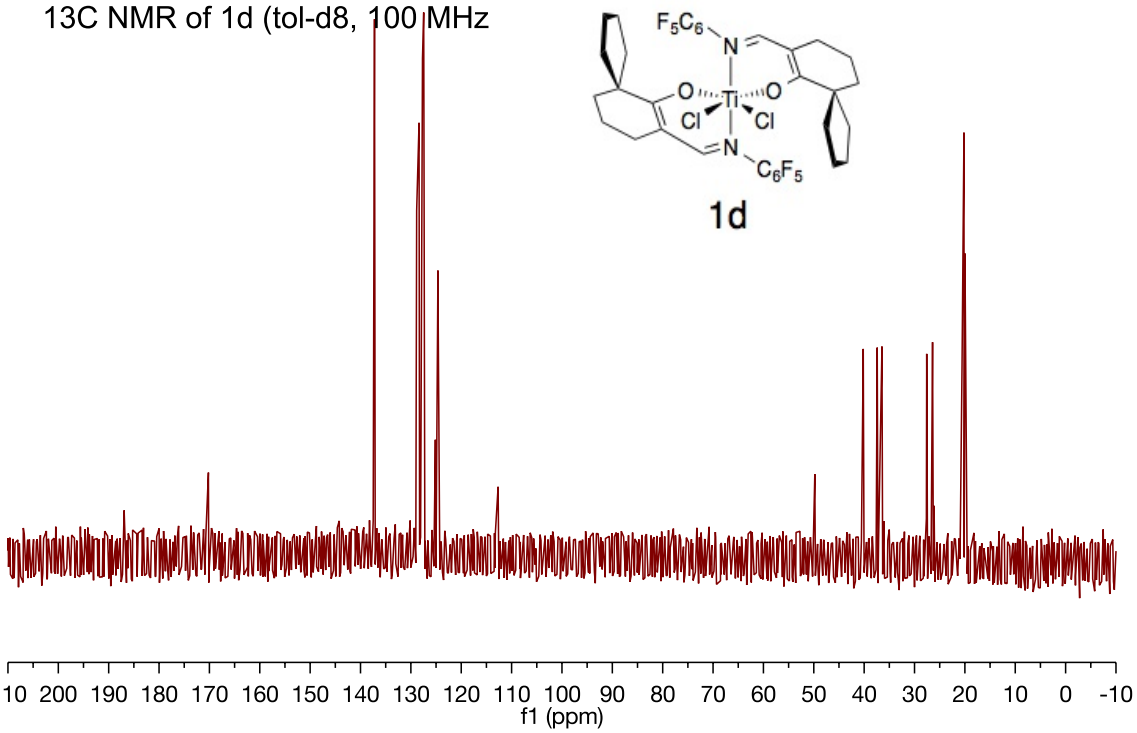


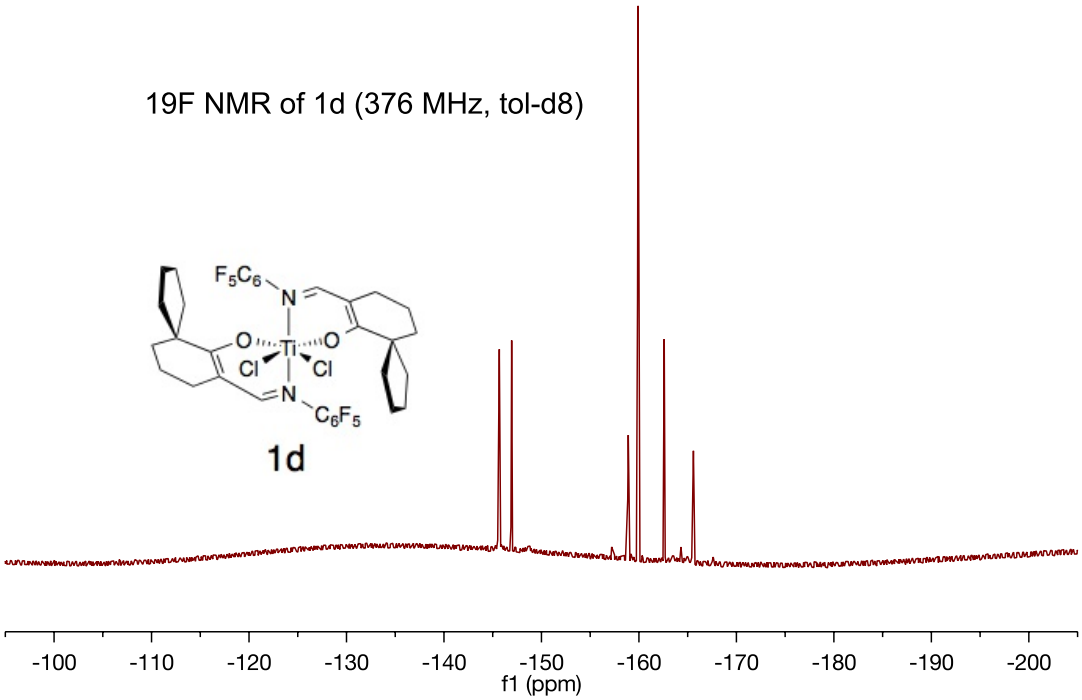
Ti complex 1d The Ti complex **1d** was synthesized following the procedure to make **1a**. Thus, ligand 7-(pentafluorophenylimino-methyl)-spiro[4.5]decan-6-one (**4d**, 1.08 g, 3.13 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 1.96 mL, 3.13 mmol) and then $TiCl_4$ (1.0 M in toluene, 1.57 mL, 1.57 mmol) to give a deep red powder that was crystallized from toluene to give the desired complex as a deep red crystalline solid (0.80 g, 63%). ^{1}H NMR (toluene-d_8, 400 MHz): δ 6.91 (s, 2H, C*H*N), 2.31-2.25 (m, 2H, CH_2), 2.07-1.95 (m, 2H, CH_2), 1.75-1.69 (m, 2H, CH_2), 1.59-1.56 (m, 2H, CH_2), 1.34-1.10 (m, 18H, CH_2), 0.88-0.83 (m, 2H, CH_2). ^{13}C NMR (toluene-d_8, 100 MHz): δ 187.6, 170.9, 169.1, 142.6, 140.7, 137.3, 113.3, 50.4, 40.7, 38.0, 37.1, 28.2, 27.0. ^{19}F NMR (376 MHz): δ -145.6, -146.9, -158.9, -159.9, -162.6. Anal Calcd for $C_{34}H_{30}Cl_2F_{10}N_2O_2Ti$: C, 50.58; H, 3.75; N, 3.47. Found: C, 50.66; H, 3.52; N, 3.21.

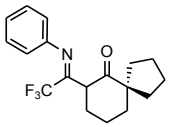
1H NMR of 1d (400 MHz, tol-d8)



13C NMR of 1d (tol-d8, 100 MHz

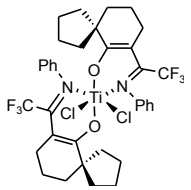




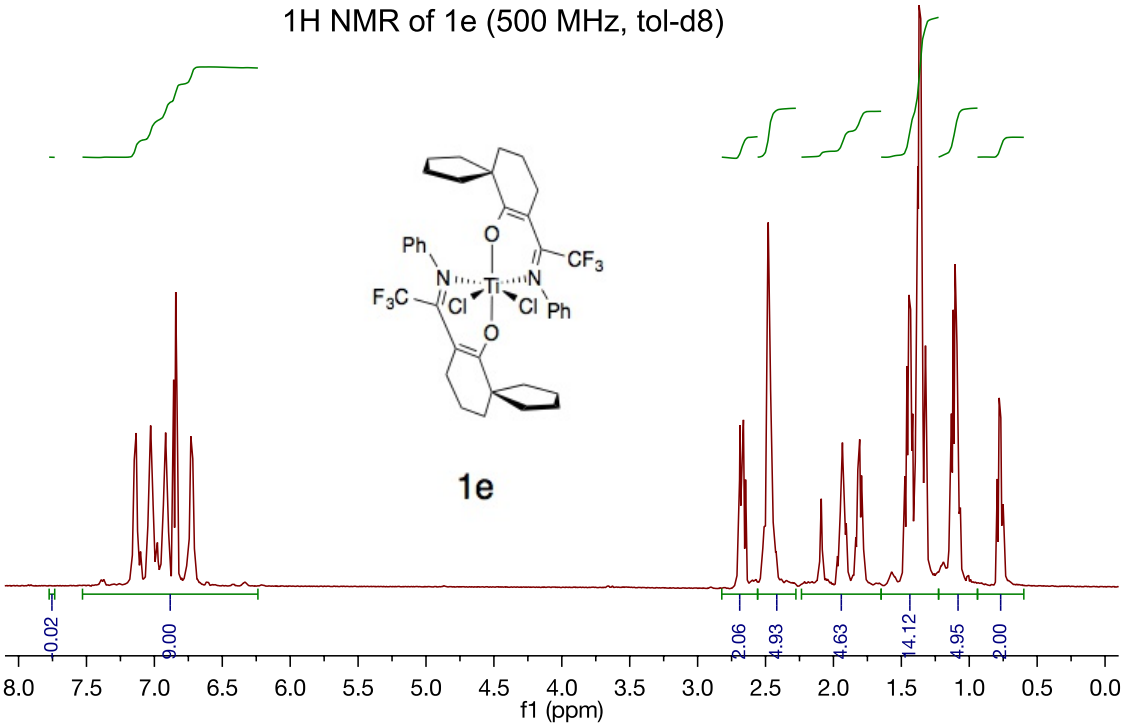


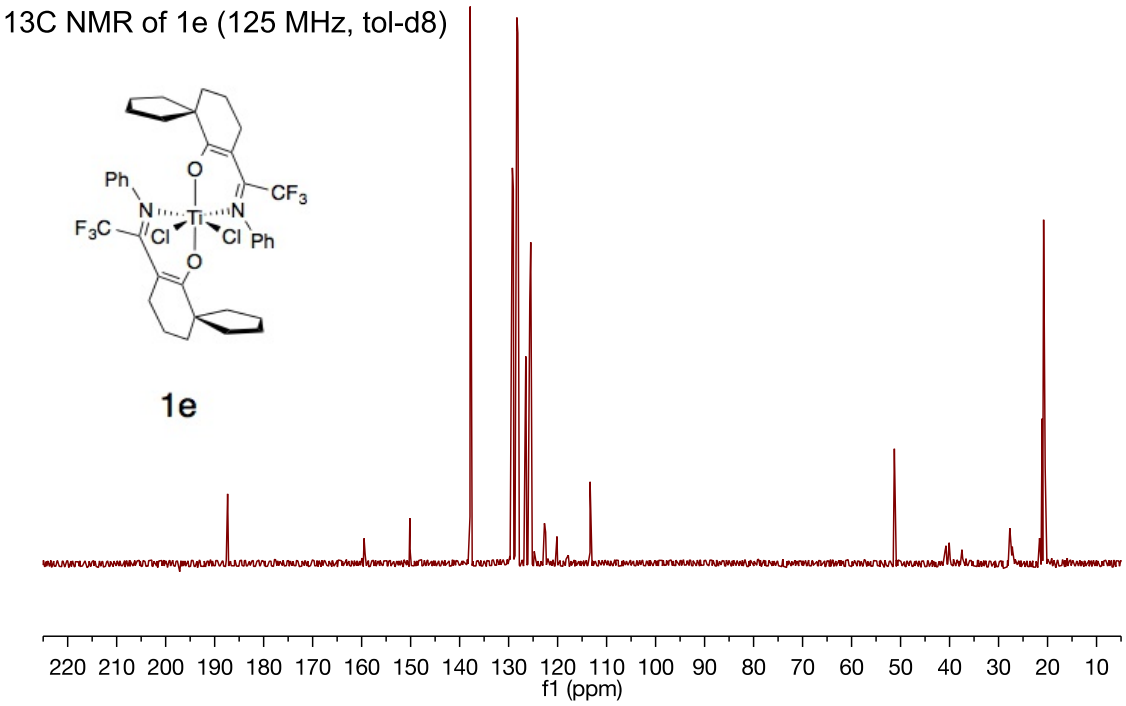
7-(2,2,2-Trifluoro-1-phenylimino-ethyl)-spiro[4.5]decan-6-one (4e) A procedure similar to that used to make a *N*-substituted *β*-enamino acid derivatives from 2-alkyl-2-oxazolines and *N*-arylimidoyl chloride was used.[5] Thus, to a stirred solution of diisopropylamine (2.8 mL, 20 mmol) in THF (15 mL) at 0 ºC was added *n*-BuLi (1.6 M in hexanes, 12.5 mL, 20.0 mmol) dropwise. After being stirred for an additional 30 min, the solution was cooled to –78 ºC and spiro[4,5]-decane-6-one **2** (1.52 g, 10.0 mmol) in THF (15 mL) was added. The reaction mixture was stirred for 2 h, then lifted from the dry ice/acetone bath to warm to room temperature for 20 min. After cooling down to –78 ºC, a solution of the *N*-phenyl-2,2,2-trifluoroacetimidoyl chloride (2.07 g, 10.0 mmol) in THF (15 mL) was slowly added to the reaction mixture. When TLC analysis showed the disappearance of the starting material, the reaction was quenched by saturated ammonium chloride aqueous solution. The aqueous layer was extracted with CH_2Cl_2 (25 mL x 3). The combined organic layers were washed with brine and dried over Na_2SO_4. After filtration, the solvents were removed under reduced pressure to furnish the crude product

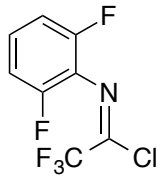
as a brown oil. Purification by column chromatography over silica gel (5-7 % (v/v) ethyl acetate/hexanes, R_f = 0.5) afforded 1.31 g (41%) of pure product as a yellow oil. ^{1}H NMR (300 MHz): δ 10.95 (s, 0.5H, O*H*/CH), 7.24 (m, 2H, Ar*H*), 7.08 (t, J = 7.5, 1H, Ar*H*), 6.95 (d, J = 8.1, 2H, Ar*H*), 5.54 (brs, 0.3H, C*H*/OH), 2.70 (m, 2H, CH_2), 2.31-2.03 (m, 2H, CH_2), 1.86-1.80 (m, 4H, CH_2), 1.73-1.66 (m, 4H, CH_2), 1.51-1.39 (m, 2H, CH_2). ^{13}C NMR (75 MHz): δ 208.5, 142.5, 129.2, 128.0, 124.1, 121.7, 119.7, 116.4, 56.2, 40.2, 38.6, 37.1, 35.2, 26.1, 21.7. ^{19}F NMR (282 MHz): δ -68.3. MS (ESI): 324.1 $(M + H)^+$; HRMS (ESI) Calcd for $C_{11}H_{17}O_2$: 324.1575, found 324.1583.



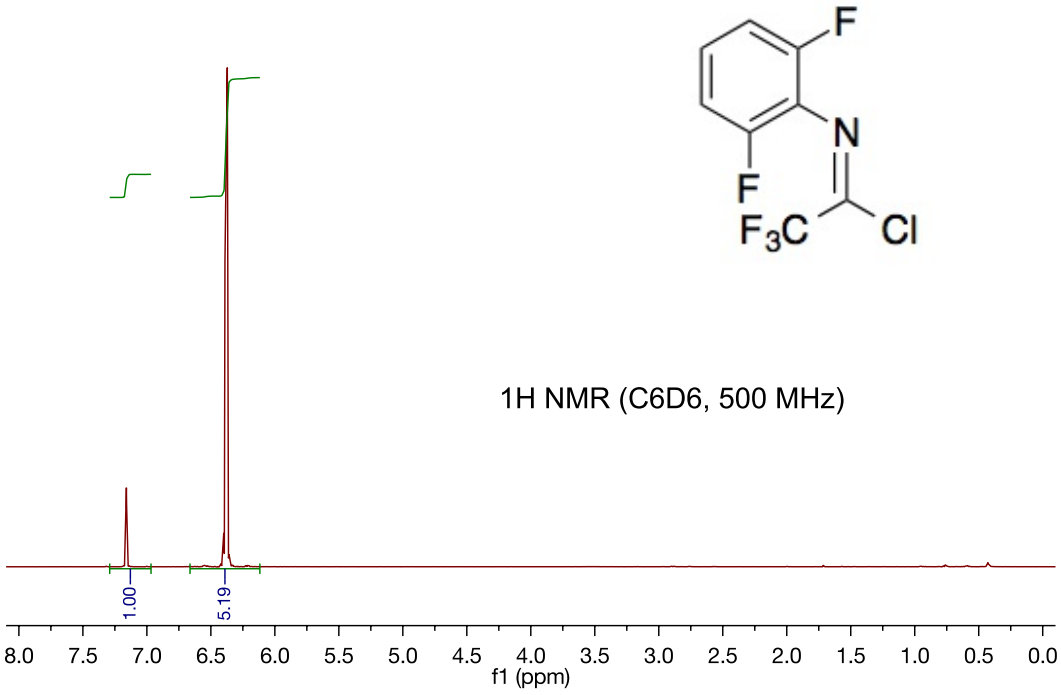
Ti complex 1e. To a stirred solution of ligand 7-(2,2,2-trifluoro-1-phenylimino-ethyl)-spiro[4.5]decan-6-one (**4e**, 1.28 g, 3.98 mmol) in 20 mL of Et_2O at –78 ºC was added *n*-BuLi (1.6 M in hexanes, 2.48 mL, 3.98 mmol) dropwise using a gas tight syringe. This solution was allowed to slowly warm to room temperature and was stirred for an additional half hour. The solution was then added dropwise via cannula to a solution of $TiCl_4$ (1.0 M in toluene, 2.0 mL, 2.0 mmol) in Et_2O (15 mL) at –78 ºC. The resulting deep red solution was allowed to warm to room temperature and was stirred for an additional 16 h. After removal of the solvent under vacuum, the residue was taken up in toluene and the precipitated LiCl was removed by filtration over a Celite plug. Removal of solvent in *vacuo* gave a deep red powder that was crystallized from a mixture of toluene/pentane to give the desired complex as deep red crystalline solid (1.02 g, 67%). ^{1}H NMR (toluene-d_8, 500 MHz): δ 7.14 (d, J = 7.0, 2H, Ar*H*), 7.03 (t, J = 7.8, 2H, Ar*H*), 6.92 (t, J = 7.2, 2H, Ar*H*), 6.84 (t, J = 7.2, 2H, Ar*H*), 6.72 (d, J = 7.0, 2H, Ar*H*), 2.68 (m, 2H, CH_2), 2.48 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.47-1.32 (m, 16H, CH_2), 1.11 (m, 2H, CH_2), 0.77 (m, 2H, CH_2). ^{13}C NMR (toluene-d_8, 125 MHz): δ 187.4, 159.6 (q, J_{CF} = 26.4), 150.2, 126.5, 122.7, 122.5, 120.1, 113.4, 51.3, 40.8, 40.1, 37.5, 27.7, 21.6. ^{19}F NMR (toluene-d_8, 470 MHz): δ -60.0.

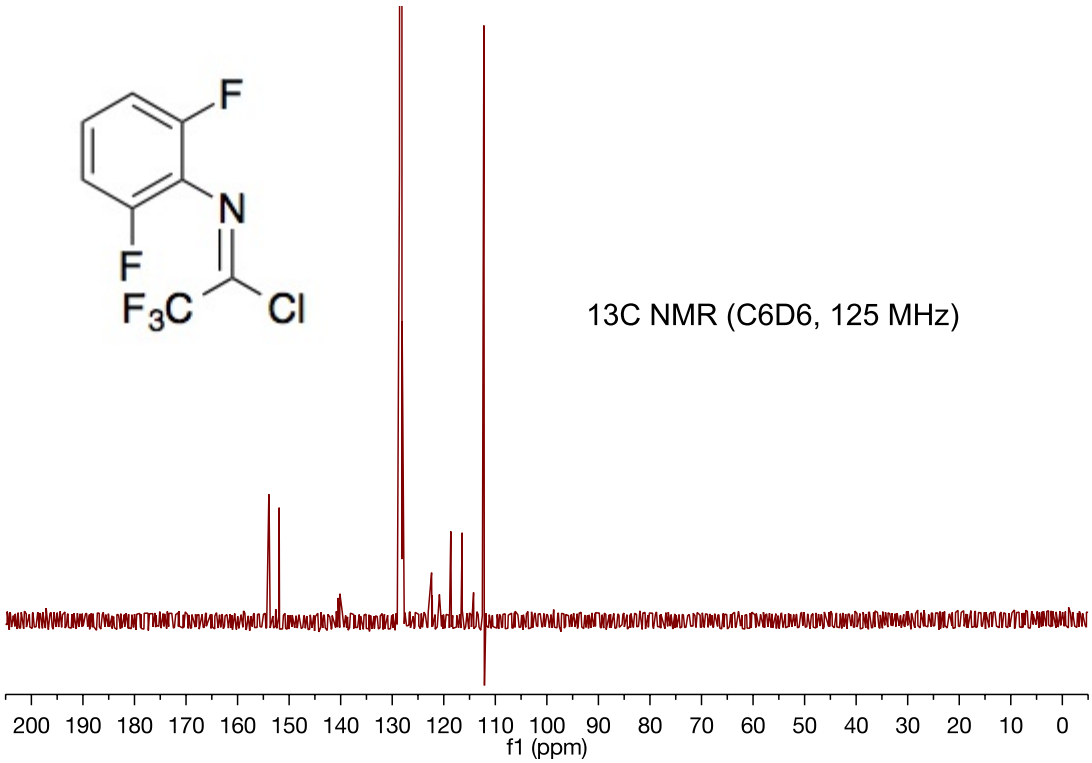

1H NMR of 1e (500 MHz, tol-d8)
Ph
N
F3C
Cl
Ti
O
CF3
N
Cl
Ph
1e
0.02
9.00
2.06
4.93
4.63
14.12
4.95
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

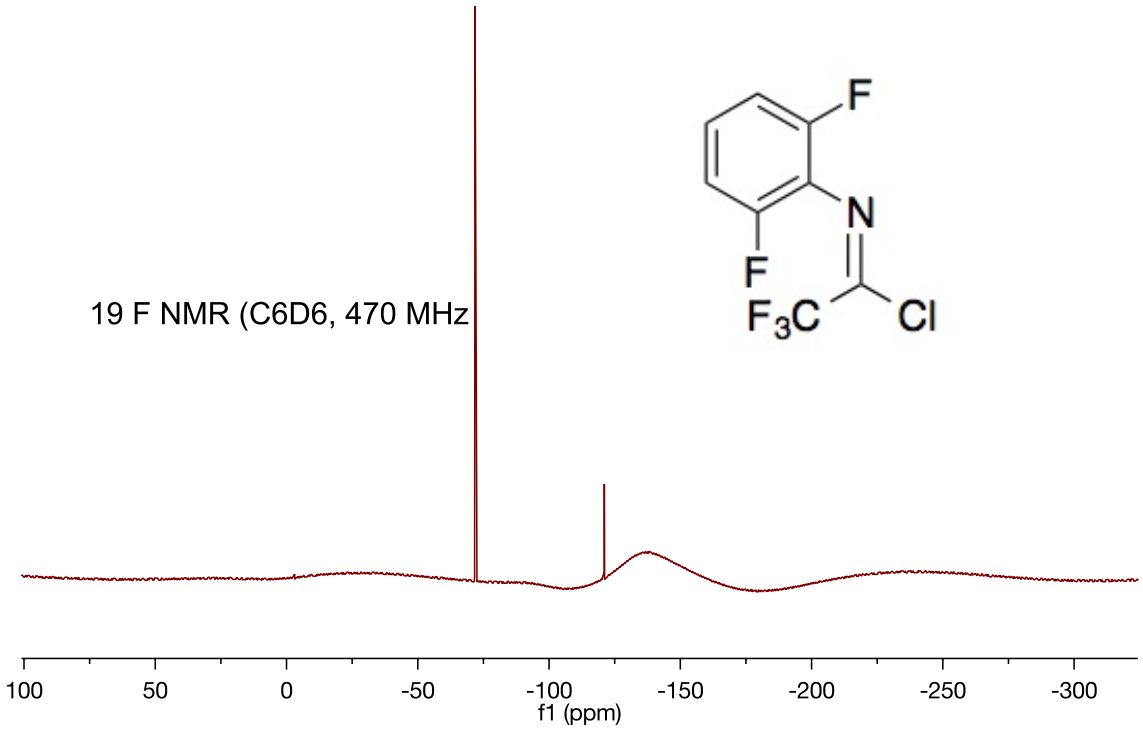

13C NMR of 1e (125 MHz, tol-d8)
Ph
N
F3C
Cl
Ti
O
CF3
N
Cl
Ph
1e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

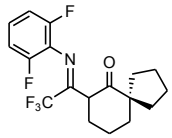


***N*-(2,6-Difluoro-phenyl)-2,2,2-trifluoro-acetimidoyl chloride** The procedure used to make *N*-phenyl analogue was followed. Thus, 2,6-difluoroaniline (5.17 mL, 6.20 g, 48.0 mmol) was reacted with trifluoroacetic acid (TFA, 3.08 mL, 4.56 g, 40.0 mmol) and carbon tetrachloride (CCl_4, 38.6 mL, 61.5 g, 400 mmol) in the presence of triphenylphosphine (Ph_3P, 31.47 g, 120.0 mmol) and triethylamine (Et_3N, 6.70 mL, 4.86 g, 48.0 mmol) under reflux for 6 h afforded 3.70 g (38%) of pure product as a colorless oil after vacuum distillation (54 ºC/240 mTorr). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.35 (d, J = 9.1, 2H, Ar*H*-3,5), 6.33 (t, J = 9.0, 1H, Ar*H*-4). ^{13}C NMR (C_6D_6, 125 MHz): δ 153.0 (dd, $^1J_{CF}$ = 251.7, $^3J_{CF}$ = 4.2, Ar*C*, *ortho*), 140.3 (N=C), 128.2, 122.4 (t, $^3J_{CF}$ = 16.0, Ar*C*, *para*), 117.5 (q, $^1J_{CF}$ = 278.0, *C*F_3), 112.3 (dd, $^2J_{CF}$ = 18.3, $^4J_{CF}$ = 4.6, Ar*C*, *meta*). ^{19}F NMR (C_6D_6, 470 MHz): δ -71.8, -121.0. MS (ESI): 208.0 $(M - Cl)^+$; HRMS (ESI) Calcd for $C_8H_3F_5N$: 208.0186, found 208.018.



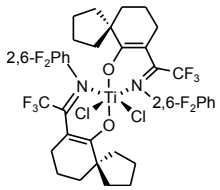

F
N
F
F3C
Cl
13C NMR (C6D6, 125 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


19 F NMR (C6D6, 470 MHz
F
N
F
F3C
Cl
100 50 0 -50 -100 -150 -200 -250 -300
f1 (ppm)



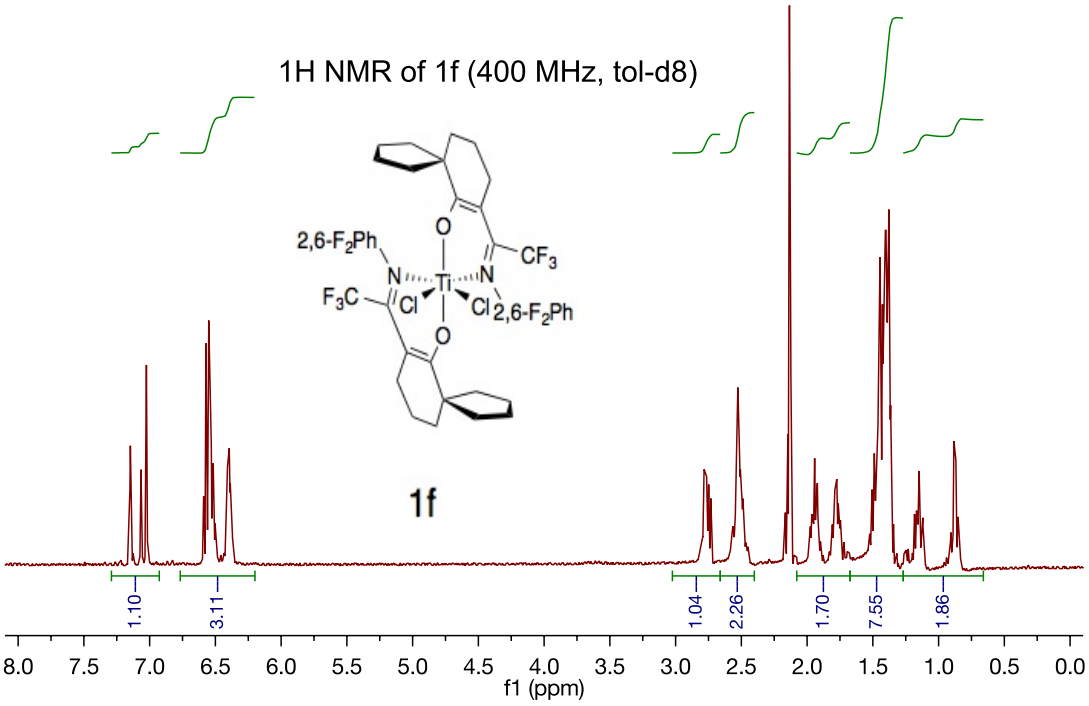
7-[1-(2,6-Difluoro-phenylimino)-2,2,2-trifluoro-ethyl]-spiro[4.5]decan-6-one

(4f) The procedure used to make *N*-phenyl analogue was followed. Thus, spiro[4,5]decan-6-one was reacted with diisopropylamine (2.8 mL, 2.0 g, 20 mmol) and *n*-BuLi (1.6 M in hexane, 12.5 mL, 20.0 mmol) in THF at –78 ºC, and then *N*-(2,6-difluoro-phenyl)-2,2,2-trifluoro-acetimidoyl chloride (2.44 g, 10.0 mmol) to afford 0.51 g (15%) of pure product as a yellow oil. ^{1}H NMR (300 MHz): δ 11.08 (s, 1H, O*H*/CH), 7.03 (m, 1H, Ar*H*), 6.90 (m, 2H, Ar*H*), 2.65 (brs, 2H, CH_2), 2.00-1.42(m, 12H, CH_2). ^{13}C NMR (75 MHz): δ 208.9, 125.1, 125.0, 112.5, 111.8, 111.7, 111.6, 111.5, 56.0, 38.8, 37.0, 27.1, 26.2, 21.4.

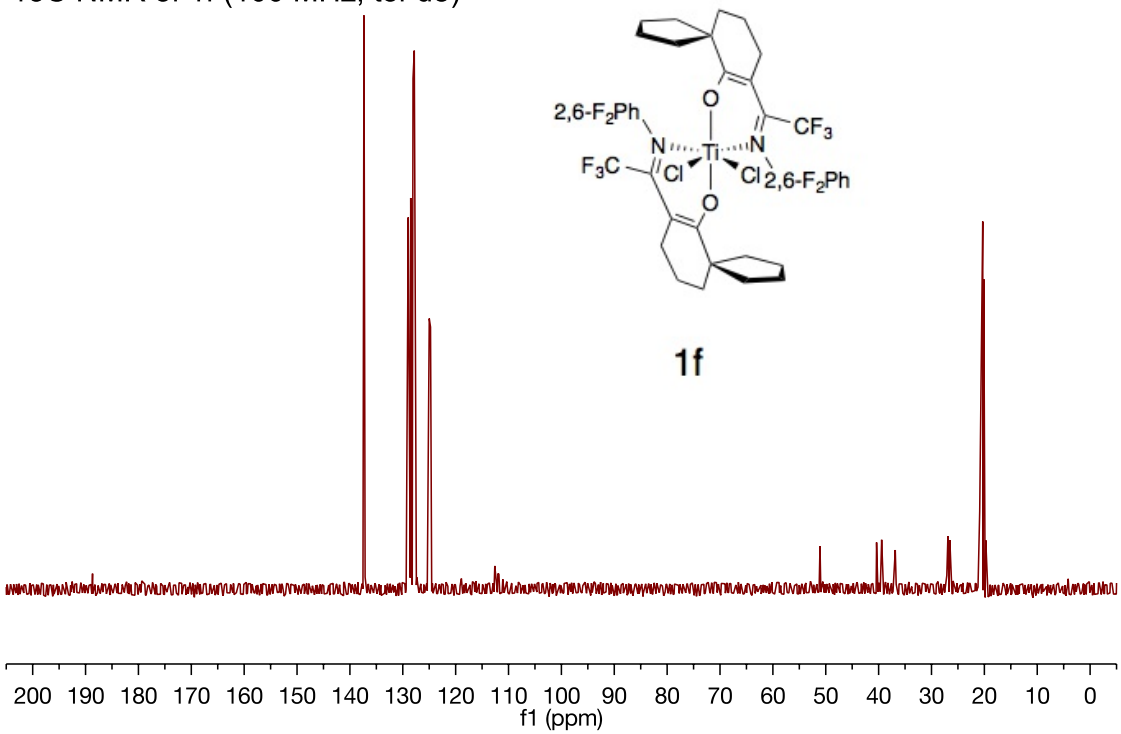


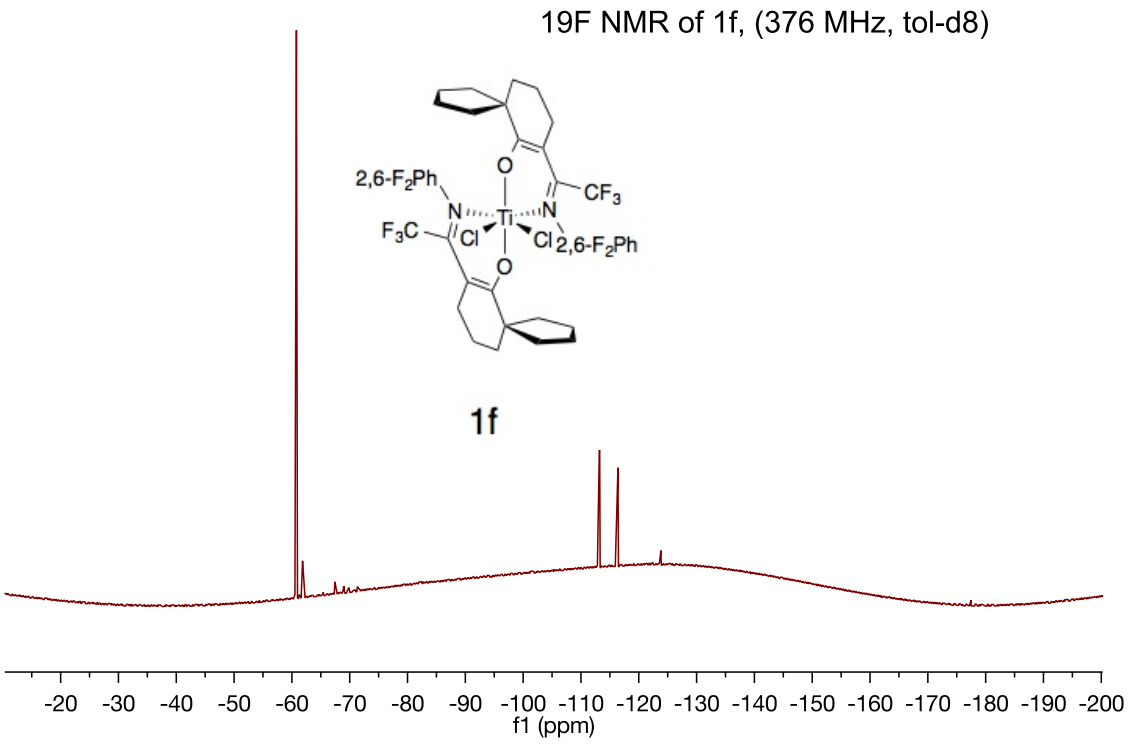
Ti complex 1f. The Ti complex **1f** was synthesized following the procedure to make **1e**. Thus, ligand 7-[1-(2,6-difluoro-phenylimino)-2,2,2-trifluoro-ethyl]-spiro[4,5]decan-6-one (**4f**, 0.57 g, 1.59 mmol) was reacted with *n*-BuLi (1.6 M in hexanes, 0.99 mL, 1.59 mmol) and then $TiCl_4$ (1.0 M in toluene, 0.8 mL, 0.8 mmol) to give a deep red powder that was crystallized from a mixture of toluene/pentane to give the desired complex as a deep red crystalline solid (0.15 g, 23%). ^{1}H NMR (toluene-d_8, 400 MHz): δ 6.52 (m, 4H, Ar*H*), 6.37 (m, 2H, Ar*H*), 2.72 (m, 2H, CH_2), 2.48 (m, 4H, CH_2), 1.89 (m, 2H, CH_2), 1.73 (m, 2H, CH_2), 1.36 (m, 14H, CH_2), 1.11 (m, 2H, CH_2), 0.82 (m, 2H, CH_2). ^{13}C NMR (toluene-d_8, 100 MHz): δ 189.2, 127.8, 122.3, 119.4, 113.1, 112.5, 112.3, 111.6, 51.6, 40.9, 39.9, 37.4, 27.0, 21.4. ^{19}F NMR (toluene-d_8, 376 MHz): δ -60.8, -113.2, -116.4. Anal Calcd for $C_{36}H_{34}Cl_2F_{10}N_2O_2Ti$: C, 51.76; H, 4.10; N, 3.35. Found: C, 51.59; H, 4.17; N, 3.10.

1H NMR of 1f (400 MHz, tol-d8)



13C NMR of 1f (100 MHz, tol-d8)





General Procedure for Ethylene or Propylene Polymerization

A 6-ounce Lab-Crest pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was first conditioned under dynamic vacuum and high temperature, and then taken into a glovebox and charged with a desired amount of dry PMAO and toluene. The reactor was then brought out of the glovebox and equilibrated at the desired polymerization temperature, the atmosphere was exchanged three times with ethylene or propylene, and the solution was saturated under pressure (10 psi for ethylene and 30 psi for propylene). In the glovebox, the titanium catalyst was dissolved in toluene (5 mL), brought out of the glovebox and added to the reactor via gastight syringe to initiate the polymerization. After the desired period of time, the reaction was quenched with methanol (10 mL) and the reactor was vented. The polymer was precipitated in 5% HCl/MeOH, filtered, washed with methanol, and then dried in *vacuo* to constant weight.

References

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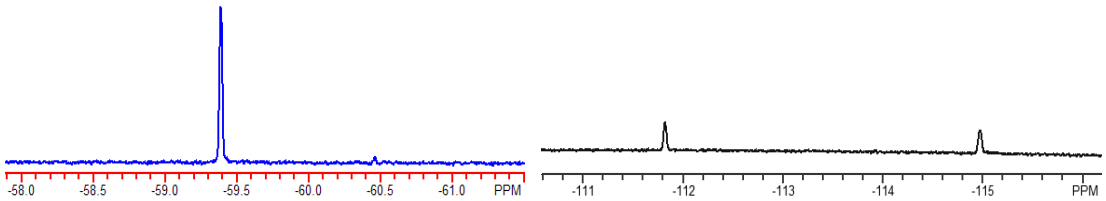
A)



B)

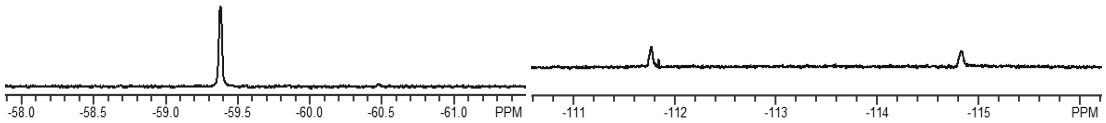


Figure S1. ^{19}F NMR spectra of **1f** in toluene-d_8 at 25 °C (A) and 50 °C (B).

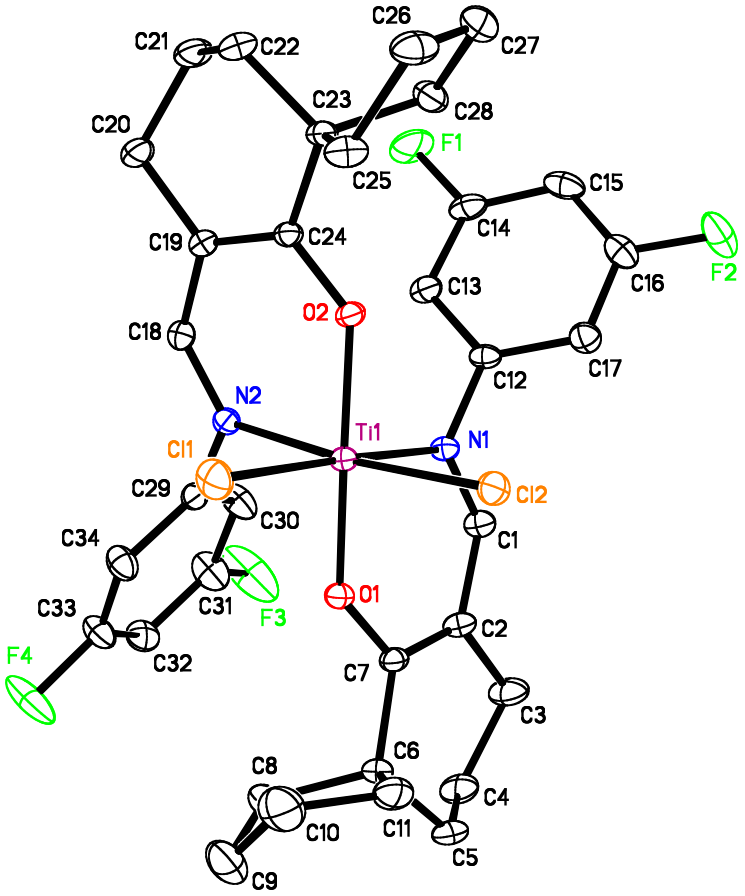


Figure S2. X-ray crystal structure of **1c**. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table S1-1. Crystal data and structure refinement for **1c**.

Identification code	**1c**	
Empirical formula	C_{34} H_{36} Cl_2 F_4 N_2 O_2 Ti	
Formula weight	699.45	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.5330(4) Å	α= 90°.
	b = 19.3123(8) Å	β= 103.3484(8)°.
	c = 16.1038(7) Å	γ = 90°.
Volume	3187.3(2) $Å^3$	
Z	4	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.494 mm^{-1}	
F(000)	1448	
Crystal size	0.40 x 0.30 x 0.15 mm^3	
Theta range for data collection	2.36 to 32.80°.	
Index ranges	-15<=h<=15, -29<=k<=29, -24<=l<=22	
Reflections collected	31576	
Independent reflections	10907 [R(int) = 0.0355]	
Completeness to theta = 32.80°	92.2 %	
Absorption correction	SADABS	
Max. and min. transmission	0.9295 and 0.8268	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10907 / 0 / 550	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1033	
R indices (all data)	R1 = 0.0703, wR2 = 0.1134	
Largest diff. peak and hole	0.466 and -0.405 $e.Å^{-3}$	

Table S1-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	4329(1)	423(1)	2075(1)	15(1)
Cl(1)	4118(1)	-434(1)	1074(1)	29(1)
Cl(2)	2844(1)	14(1)	2804(1)	24(1)
F(1)	3826(1)	3451(1)	1656(1)	44(1)
F(2)	1651(1)	2799(1)	3770(1)	43(1)
F(3)	9604(1)	1763(1)	3283(1)	71(1)
F(4)	9667(1)	-310(1)	1815(1)	54(1)
O(1)	5728(1)	-1(1)	2842(1)	19(1)
O(2)	3140(1)	1022(1)	1383(1)	18(1)
N(1)	4757(1)	1249(1)	3030(1)	17(1)
N(2)	5658(1)	945(1)	1450(1)	17(1)
C(1)	5528(2)	1179(1)	3789(1)	20(1)
C(2)	6309(2)	601(1)	4132(1)	22(1)
C(3)	7129(2)	666(1)	5037(1)	32(1)
C(4)	8183(2)	108(1)	5213(1)	32(1)
C(5)	7552(2)	-591(1)	4973(1)	30(1)
C(6)	6985(2)	-658(1)	4005(1)	22(1)
C(7)	6331(1)	13(1)	3655(1)	18(1)
C(8)	8035(2)	-873(1)	3512(1)	34(1)
C(9)	7730(3)	-1632(1)	3254(2)	52(1)
C(10)	6257(3)	-1661(1)	3064(2)	46(1)
C(11)	5951(2)	-1253(1)	3798(1)	31(1)
C(12)	4041(1)	1888(1)	2903(1)	18(1)
C(13)	4268(2)	2366(1)	2309(1)	22(1)
C(14)	3594(2)	2985(1)	2234(1)	26(1)
C(15)	2700(2)	3155(1)	2708(1)	29(1)
C(16)	2500(2)	2660(1)	3279(1)	27(1)
C(17)	3137(2)	2027(1)	3388(1)	23(1)
C(18)	5319(2)	1304(1)	744(1)	20(1)
C(19)	4030(2)	1480(1)	298(1)	20(1)

C(20)	3870(2)	1882(1)	-528(1)	31(1)
C(21)	2590(2)	2278(1)	-725(1)	29(1)
C(22)	1467(2)	1800(1)	-684(1)	26(1)
C(23)	1575(1)	1507(1)	219(1)	18(1)
C(24)	2977(1)	1333(1)	640(1)	17(1)
C(25)	698(2)	863(1)	192(1)	26(1)
C(26)	-681(2)	1162(1)	12(1)	32(1)
C(27)	-531(2)	1861(1)	483(1)	34(1)
C(28)	957(2)	2006(1)	767(1)	26(1)
C(29)	7034(1)	876(1)	1805(1)	18(1)
C(30)	7666(2)	1371(1)	2369(1)	31(1)
C(31)	8982(2)	1278(1)	2730(1)	34(1)
C(32)	9691(2)	727(1)	2549(1)	27(1)
C(33)	9012(2)	250(1)	1988(1)	28(1)
C(34)	7698(2)	305(1)	1603(1)	26(1)

Table S1-3. Bond lengths [Å] and angles [°] for **1c**.

Ti(1)-O(2)	1.8722(11)	C(18)-C(19)	1.423(2)
Ti(1)-O(1)	1.8777(11)	C(19)-C(24)	1.377(2)
Ti(1)-N(2)	2.1539(12)	C(19)-C(20)	1.515(2)
Ti(1)-N(1)	2.1888(13)	C(20)-C(21)	1.519(2)
Ti(1)-Cl(1)	2.2842(5)	C(21)-C(22)	1.513(3)
Ti(1)-Cl(2)	2.3024(4)	C(22)-C(23)	1.540(2)
F(1)-C(14)	1.357(2)	C(23)-C(24)	1.513(2)
F(2)-C(16)	1.351(2)	C(23)-C(25)	1.544(2)
F(3)-C(31)	1.353(2)	C(23)-C(28)	1.548(2)
F(4)-C(33)	1.345(2)	C(25)-C(26)	1.528(2)
O(1)-C(7)	1.3176(19)	C(26)-C(27)	1.538(3)
O(2)-C(24)	1.3139(18)	C(27)-C(28)	1.553(3)
N(1)-C(1)	1.310(2)	C(29)-C(30)	1.381(2)
N(1)-C(12)	1.4364(19)	C(29)-C(34)	1.384(2)
N(2)-C(18)	1.309(2)	C(30)-C(31)	1.385(3)
N(2)-C(29)	1.4364(18)	C(31)-C(32)	1.368(3)
C(1)-C(2)	1.420(2)	C(32)-C(33)	1.372(3)
C(2)-C(7)	1.373(2)	C(33)-C(34)	1.384(2)
C(2)-C(3)	1.518(2)		
C(3)-C(4)	1.525(3)	O(2)-Ti(1)-O(1)	167.53(5)
C(4)-C(5)	1.516(3)	O(2)-Ti(1)-N(2)	81.35(5)
C(5)-C(6)	1.541(2)	O(1)-Ti(1)-N(2)	90.90(5)
C(6)-C(7)	1.515(2)	O(2)-Ti(1)-N(1)	88.21(5)
C(6)-C(8)	1.559(2)	O(1)-Ti(1)-N(1)	81.53(5)
C(6)-C(11)	1.564(3)	N(2)-Ti(1)-N(1)	86.36(5)
C(8)-C(9)	1.537(3)	O(2)-Ti(1)-Cl(1)	94.86(4)
C(9)-C(10)	1.512(4)	O(1)-Ti(1)-Cl(1)	94.71(4)
C(10)-C(11)	1.516(3)	N(2)-Ti(1)-Cl(1)	88.70(4)
C(12)-C(13)	1.389(2)	N(1)-Ti(1)-Cl(1)	173.73(4)
C(12)-C(17)	1.391(2)	O(2)-Ti(1)-Cl(2)	94.35(3)
C(13)-C(14)	1.381(2)	O(1)-Ti(1)-Cl(2)	92.15(4)
C(14)-C(15)	1.382(3)	N(2)-Ti(1)-Cl(2)	172.11(4)
C(15)-C(16)	1.375(3)	N(1)-Ti(1)-Cl(2)	86.89(3)
C(16)-C(17)	1.386(2)	Cl(1)-Ti(1)-Cl(2)	98.296(18)

C(7)-O(1)-Ti(1)	140.30(10)	F(2)-C(16)-C(15)	118.55(15)
C(24)-O(2)-Ti(1)	138.92(9)	F(2)-C(16)-C(17)	117.78(16)
C(1)-N(1)-C(12)	114.42(13)	C(15)-C(16)-C(17)	123.66(16)
C(1)-N(1)-Ti(1)	124.30(10)	C(16)-C(17)-C(12)	118.19(15)
C(12)-N(1)-Ti(1)	120.66(10)	N(2)-C(18)-C(19)	127.00(14)
C(18)-N(2)-C(29)	116.31(12)	C(24)-C(19)-C(18)	120.81(14)
C(18)-N(2)-Ti(1)	125.30(10)	C(24)-C(19)-C(20)	121.35(14)
C(29)-N(2)-Ti(1)	118.33(9)	C(18)-C(19)-C(20)	117.68(14)
N(1)-C(1)-C(2)	128.48(15)	C(19)-C(20)-C(21)	110.77(14)
C(7)-C(2)-C(1)	121.03(15)	C(22)-C(21)-C(20)	110.40(15)
C(7)-C(2)-C(3)	121.69(14)	C(21)-C(22)-C(23)	112.17(15)
C(1)-C(2)-C(3)	117.27(15)	C(24)-C(23)-C(22)	110.87(13)
C(2)-C(3)-C(4)	110.40(16)	C(24)-C(23)-C(25)	110.43(12)
C(5)-C(4)-C(3)	108.95(16)	C(22)-C(23)-C(25)	110.86(14)
C(4)-C(5)-C(6)	112.17(15)	C(24)-C(23)-C(28)	112.19(13)
C(7)-C(6)-C(5)	109.94(14)	C(22)-C(23)-C(28)	111.17(13)
C(7)-C(6)-C(8)	110.71(13)	C(25)-C(23)-C(28)	100.94(13)
C(5)-C(6)-C(8)	112.49(15)	O(2)-C(24)-C(19)	120.65(14)
C(7)-C(6)-C(11)	108.34(14)	O(2)-C(24)-C(23)	114.75(12)
C(5)-C(6)-C(11)	111.44(14)	C(19)-C(24)-C(23)	124.60(14)
C(8)-C(6)-C(11)	103.71(15)	C(26)-C(25)-C(23)	103.71(14)
O(1)-C(7)-C(2)	120.44(14)	C(25)-C(26)-C(27)	104.66(15)
O(1)-C(7)-C(6)	115.14(14)	C(26)-C(27)-C(28)	106.59(14)
C(2)-C(7)-C(6)	124.39(14)	C(23)-C(28)-C(27)	104.38(14)
C(9)-C(8)-C(6)	105.24(18)	C(30)-C(29)-C(34)	120.88(15)
C(10)-C(9)-C(8)	103.37(17)	C(30)-C(29)-N(2)	119.14(14)
C(9)-C(10)-C(11)	102.4(2)	C(34)-C(29)-N(2)	119.94(14)
C(10)-C(11)-C(6)	106.58(17)	C(29)-C(30)-C(31)	118.03(16)
C(13)-C(12)-C(17)	120.49(14)	F(3)-C(31)-C(32)	118.22(17)
C(13)-C(12)-N(1)	120.05(14)	F(3)-C(31)-C(30)	118.12(17)
C(17)-C(12)-N(1)	119.45(14)	C(32)-C(31)-C(30)	123.65(17)
C(14)-C(13)-C(12)	117.98(15)	C(31)-C(32)-C(33)	115.87(16)
F(1)-C(14)-C(13)	117.65(16)	F(4)-C(33)-C(32)	117.56(15)
F(1)-C(14)-C(15)	118.35(15)	F(4)-C(33)-C(34)	118.51(16)
C(13)-C(14)-C(15)	124.00(16)	C(32)-C(33)-C(34)	123.92(16)
C(16)-C(15)-C(14)	115.65(15)	C(33)-C(34)-C(29)	117.65(16)

Table S1-4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	15(1)	15(1)	14(1)	1(1)	2(1)	1(1)
Cl(1)	32(1)	25(1)	27(1)	-9(1)	5(1)	0(1)
Cl(2)	21(1)	23(1)	29(1)	5(1)	10(1)	0(1)
F(1)	69(1)	24(1)	41(1)	17(1)	14(1)	9(1)
F(2)	36(1)	37(1)	63(1)	-7(1)	26(1)	8(1)
F(3)	29(1)	66(1)	104(1)	-59(1)	-14(1)	2(1)
F(4)	26(1)	48(1)	79(1)	-32(1)	-4(1)	17(1)
O(1)	19(1)	19(1)	18(1)	2(1)	3(1)	3(1)
O(2)	16(1)	21(1)	16(1)	5(1)	2(1)	2(1)
N(1)	18(1)	14(1)	17(1)	2(1)	2(1)	1(1)
N(2)	15(1)	20(1)	17(1)	1(1)	4(1)	1(1)
C(1)	23(1)	17(1)	19(1)	0(1)	1(1)	-1(1)
C(2)	22(1)	22(1)	18(1)	5(1)	0(1)	2(1)
C(3)	38(1)	29(1)	21(1)	2(1)	-6(1)	6(1)
C(4)	28(1)	41(1)	22(1)	6(1)	-5(1)	6(1)
C(5)	34(1)	31(1)	22(1)	11(1)	2(1)	12(1)
C(6)	24(1)	22(1)	21(1)	7(1)	5(1)	8(1)
C(7)	14(1)	20(1)	18(1)	6(1)	3(1)	2(1)
C(8)	31(1)	41(1)	33(1)	8(1)	12(1)	18(1)
C(9)	61(2)	49(1)	47(1)	-7(1)	15(1)	26(1)
C(10)	63(2)	33(1)	41(1)	-7(1)	9(1)	6(1)
C(11)	40(1)	20(1)	32(1)	5(1)	9(1)	3(1)
C(12)	19(1)	13(1)	18(1)	0(1)	-1(1)	0(1)
C(13)	26(1)	19(1)	18(1)	2(1)	2(1)	1(1)
C(14)	36(1)	17(1)	23(1)	4(1)	-1(1)	1(1)
C(15)	29(1)	18(1)	36(1)	-2(1)	-2(1)	7(1)
C(16)	22(1)	25(1)	34(1)	-6(1)	6(1)	2(1)
C(17)	25(1)	19(1)	26(1)	1(1)	7(1)	0(1)
C(18)	21(1)	22(1)	20(1)	2(1)	7(1)	1(1)
C(19)	22(1)	22(1)	17(1)	4(1)	5(1)	4(1)
C(20)	29(1)	41(1)	24(1)	15(1)	11(1)	10(1)

C(21)	29(1)	30(1)	28(1)	14(1)	6(1)	4(1)
C(22)	28(1)	27(1)	21(1)	8(1)	1(1)	3(1)
C(23)	18(1)	17(1)	17(1)	2(1)	1(1)	3(1)
C(24)	19(1)	14(1)	15(1)	1(1)	2(1)	2(1)
C(25)	24(1)	21(1)	28(1)	4(1)	-2(1)	-2(1)
C(26)	21(1)	36(1)	35(1)	11(1)	-2(1)	-3(1)
C(27)	22(1)	49(1)	32(1)	2(1)	6(1)	9(1)
C(28)	22(1)	28(1)	26(1)	-4(1)	2(1)	7(1)
C(29)	15(1)	22(1)	17(1)	2(1)	4(1)	-1(1)
C(30)	21(1)	27(1)	42(1)	-12(1)	3(1)	2(1)
C(31)	23(1)	34(1)	40(1)	-14(1)	0(1)	-3(1)
C(32)	16(1)	33(1)	29(1)	0(1)	1(1)	2(1)
C(33)	21(1)	28(1)	34(1)	-5(1)	5(1)	6(1)
C(34)	20(1)	29(1)	27(1)	-9(1)	3(1)	2(1)

Table S1-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1c**.

	x	y	z	U(eq)
H(28A)	1280(20)	1876(10)	1365(13)	25(5)
H(18)	6040(19)	1477(10)	494(12)	21(5)
H(32)	10530(20)	706(12)	2764(15)	39(6)
H(4B)	8820(20)	216(11)	4871(14)	29(5)
H(11B)	5080(20)	-1061(12)	3656(15)	41(6)
H(20B)	4630(20)	2188(12)	-499(15)	41(6)
H(5B)	8120(20)	-958(11)	5127(13)	25(5)
H(22B)	1490(20)	1412(12)	-1069(15)	37(6)
H(17)	2970(20)	1719(11)	3762(14)	29(5)
H(21B)	2460(20)	2512(13)	-1307(16)	45(7)
H(3B)	6620(20)	602(12)	5445(15)	38(6)
H(28A)	1210(20)	2497(11)	672(14)	28(5)
H(13)	4880(20)	2282(10)	1975(13)	25(5)
H(15)	2250(20)	3560(12)	2660(15)	35(6)
H(5BA)	6900(20)	-638(12)	5249(15)	39(6)
H(26B)	-1310(20)	853(12)	174(15)	41(6)
H(1)	5585(19)	1561(10)	4180(13)	22(5)
H(34)	7240(20)	-38(12)	1232(15)	34(6)
H(22A)	650(20)	2039(11)	-882(14)	31(5)
H(25B)	902(19)	654(10)	764(13)	24(5)
H(4A)	8610(20)	149(11)	5775(15)	32(6)
H(22B)	7970(20)	-588(13)	3019(17)	45(7)
H(11A)	6120(20)	-1546(13)	4311(17)	46(7)
H(25A)	860(20)	512(11)	-224(14)	29(5)
H(31A)	2650(20)	2651(11)	-303(14)	29(5)
H(27B)	-1000(20)	2241(12)	114(15)	36(6)
H(3A)	7520(20)	1121(14)	5112(15)	45(7)
H(27A)	-930(20)	1845(13)	981(17)	50(7)
H(10B)	5860(30)	-2166(18)	3040(20)	82(10)
H(26A)	-1020(20)	1254(12)	-620(16)	38(6)
H(9B)	8090(30)	-1716(15)	2812(18)	57(8)

H(9A)	8120(30)	-1941(16)	3760(20)	70(9)
H(8A)	8950(20)	-795(12)	3878(15)	38(6)
H(20A)	3870(20)	1548(13)	-987(17)	49(7)
H(10A)	5870(30)	-1397(15)	2491(19)	65(8)
H(30)	7240(20)	1747(13)	2499(16)	46(7)

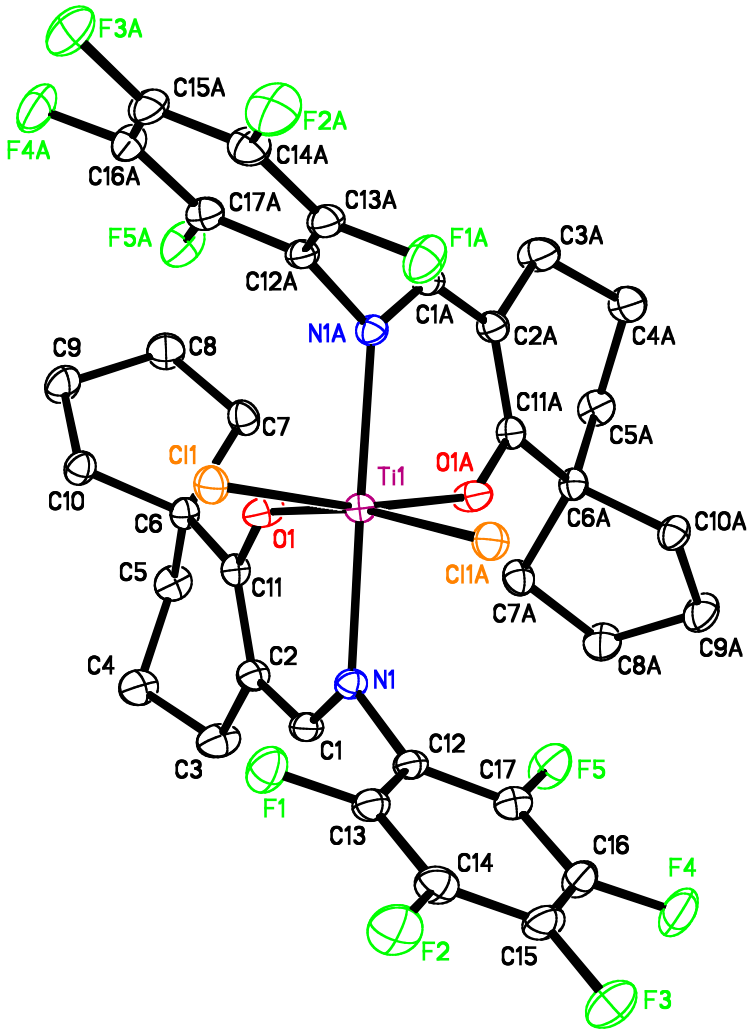


Figure S3. X-ray crystal structure of **1d**. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table S2-1. Crystal data and structure refinement for **1d**.

Identification code	**1d**	
Empirical formula	$C_{34}\ H_{30}\ Cl_2\ F_{10}\ N_2\ O_2\ Ti$ * $1/2(C_7H_8)$	
Formula weight	898.53	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.090(4) Å	α= 90°.
	b = 9.2839(11) Å	β= 107.216(5)°.
	c = 16.883(2) Å	γ = 90°.
Volume	3906.3(9) $Å^3$	
Z	4	
Density (calculated)	1.528 Mg/m^3	
Absorption coefficient	0.443 mm^{-1}	
F(000)	1836	
Crystal size	0.40 x 0.35 x 0.30 mm^3	
Theta range for data collection	2.34 to 31.78°.	
Index ranges	-27<=h<=36, -13<=k<=13, -24<=l<=20	
Reflections collected	16302	
Independent reflections	5881 [R(int) = 0.0347]	
Completeness to theta = 31.78°	88.1 %	
Absorption correction	SADABS	
Max. and min. transmission	0.8785 and 0.8426	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5881 / 0 / 335	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0913	
R indices (all data)	R1 = 0.0593, wR2 = 0.0998	
Largest diff. peak and hole	0.395 and -0.332 $e.Å^{-3}$	

Table S2-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	0	1497(1)	2500	16(1)
Cl(1)	210(1)	3205(1)	1669(1)	24(1)
F(1)	-1107(1)	4070(1)	1252(1)	34(1)
F(2)	-1799(1)	5768(1)	1734(1)	40(1)
F(3)	-2301(1)	4769(1)	2816(1)	45(1)
F(4)	-2097(1)	2052(1)	3438(1)	41(1)
F(5)	-1405(1)	343(1)	2961(1)	36(1)
O(1)	25(1)	35(1)	1736(1)	25(1)
N(1)	-849(1)	1272(1)	1878(1)	18(1)
C(1)	-1070(1)	219(2)	1359(1)	21(1)
C(2)	-813(1)	-902(1)	1060(1)	21(1)
C(3)	-1166(1)	-2013(2)	493(1)	33(1)
C(4)	-858(1)	-2819(2)	-5(1)	31(1)
C(5)	-330(1)	-3372(2)	577(1)	27(1)
C(6)	50(1)	-2150(1)	1003(1)	19(1)
C(7)	515(1)	-2725(2)	1736(1)	25(1)
C(8)	927(1)	-3331(2)	1333(1)	33(1)
C(9)	814(1)	-2606(2)	485(1)	34(1)
C(10)	358(1)	-1530(2)	425(1)	23(1)
C(11)	-263(1)	-975(1)	1276(1)	18(1)
C(12)	-1240(1)	2158(1)	2087(1)	20(1)
C(13)	-1347(1)	3550(2)	1787(1)	22(1)
C(14)	-1701(1)	4423(2)	2033(1)	28(1)
C(15)	-1957(1)	3921(2)	2582(1)	29(1)
C(16)	-1857(1)	2543(2)	2892(1)	28(1)
C(17)	-1503(1)	1679(2)	2641(1)	24(1)
C(1S)	-2278(1)	1524(3)	-420(2)	54(1)
C(2S)	-2235(1)	2959(3)	-545(2)	54(1)
C(3S)	-2451(1)	3967(3)	-129(2)	52(1)
C(4S)	-2395(2)	5433(5)	-255(3)	45(1)

Table S2-3. Bond lengths [Å] and angles [°] for **1d**.

Ti(1)-O(1)#1	1.8874(10)	C(2S)-C(3S)	1.385(4)
Ti(1)-O(1)	1.8875(10)	C(3S)-C(4S)	1.392(5)
Ti(1)-N(1)#1	2.1630(13)	C(3S)-C(1S)#2	1.396(3)
Ti(1)-N(1)	2.1630(13)		
Ti(1)-Cl(1)#1	2.2886(4)	O(1)#1-Ti(1)-O(1)	87.99(7)
Ti(1)-Cl(1)	2.2887(4)	O(1)#1-Ti(1)-N(1)#1	80.60(5)
F(1)-C(13)	1.3325(18)	O(1)-Ti(1)-N(1)#1	91.39(5)
F(2)-C(14)	1.3434(17)	O(1)#1-Ti(1)-N(1)	91.39(5)
F(3)-C(15)	1.3403(17)	O(1)-Ti(1)-N(1)	80.60(5)
F(4)-C(16)	1.3382(19)	N(1)#1-Ti(1)-N(1)	168.92(6)
F(5)-C(17)	1.3461(17)	O(1)#1-Ti(1)-Cl(1)#1	90.94(4)
O(1)-C(11)	1.3039(16)	O(1)-Ti(1)-Cl(1)#1	168.70(3)
N(1)-C(1)	1.3251(18)	N(1)#1-Ti(1)-Cl(1)#1	99.53(3)
N(1)-C(12)	1.4331(18)	N(1)-Ti(1)-Cl(1)#1	88.18(3)
C(1)-C(2)	1.411(2)	O(1)#1-Ti(1)-Cl(1)	168.70(3)
C(2)-C(11)	1.373(2)	O(1)-Ti(1)-Cl(1)	90.94(4)
C(2)-C(3)	1.519(2)	N(1)#1-Ti(1)-Cl(1)	88.18(3)
C(3)-C(4)	1.520(2)	N(1)-Ti(1)-Cl(1)	99.53(3)
C(4)-C(5)	1.526(3)	Cl(1)#1-Ti(1)-Cl(1)	92.27(2)
C(5)-C(6)	1.538(2)	C(11)-O(1)-Ti(1)	142.49(10)
C(6)-C(11)	1.5140(19)	C(1)-N(1)-C(12)	112.57(12)
C(6)-C(10)	1.546(2)	C(1)-N(1)-Ti(1)	125.07(10)
C(6)-C(7)	1.550(2)	C(12)-N(1)-Ti(1)	121.79(9)
C(7)-C(8)	1.539(2)	N(1)-C(1)-C(2)	128.37(15)
C(8)-C(9)	1.530(3)	C(11)-C(2)-C(1)	120.81(13)
C(9)-C(10)	1.534(2)	C(11)-C(2)-C(3)	121.66(13)
C(12)-C(13)	1.3862(19)	C(1)-C(2)-C(3)	117.52(14)
C(12)-C(17)	1.387(2)	C(2)-C(3)-C(4)	111.22(15)
C(13)-C(14)	1.383(2)	C(3)-C(4)-C(5)	109.50(15)
C(14)-C(15)	1.372(3)	C(4)-C(5)-C(6)	112.74(12)
C(15)-C(16)	1.377(2)	C(11)-C(6)-C(5)	110.10(13)
C(16)-C(17)	1.381(2)	C(11)-C(6)-C(10)	110.60(11)
C(1S)-C(2S)	1.359(4)	C(5)-C(6)-C(10)	111.28(13)
C(1S)-C(3S)#2	1.396(3)	C(11)-C(6)-C(7)	111.72(12)

C(5)-C(6)-C(7)	111.29(12)	F(2)-C(14)-C(13)	120.10(15)
C(10)-C(6)-C(7)	101.63(13)	C(15)-C(14)-C(13)	120.35(14)
C(8)-C(7)-C(6)	104.89(13)	F(3)-C(15)-C(14)	120.11(15)
C(9)-C(8)-C(7)	106.63(14)	F(3)-C(15)-C(16)	120.12(16)
C(8)-C(9)-C(10)	106.21(14)	C(14)-C(15)-C(16)	119.78(14)
C(9)-C(10)-C(6)	104.75(13)	F(4)-C(16)-C(15)	120.24(15)
O(1)-C(11)-C(2)	119.70(13)	F(4)-C(16)-C(17)	120.29(15)
O(1)-C(11)-C(6)	115.56(13)	C(15)-C(16)-C(17)	119.46(15)
C(2)-C(11)-C(6)	124.72(13)	F(5)-C(17)-C(16)	118.56(14)
C(13)-C(12)-C(17)	117.36(13)	F(5)-C(17)-C(12)	119.47(13)
C(13)-C(12)-N(1)	121.72(13)	C(16)-C(17)-C(12)	121.95(14)
C(17)-C(12)-N(1)	120.80(13)	C(2S)-C(1S)-C(3S)#2	120.3(3)
F(1)-C(13)-C(14)	118.81(13)	C(1S)-C(2S)-C(3S)	121.3(2)
F(1)-C(13)-C(12)	120.09(13)	C(2S)-C(3S)-C(4S)	120.4(3)
C(14)-C(13)-C(12)	121.10(15)	C(2S)-C(3S)-C(1S)#2	118.5(2)
F(2)-C(14)-C(15)	119.55(14)	C(4S)-C(3S)-C(1S)#2	121.1(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2 #2 -x-1/2,-y+1/2,-z

Table S2-4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	16(1)	14(1)	18(1)	0	5(1)	0
Cl(1)	25(1)	25(1)	23(1)	6(1)	7(1)	-1(1)
F(1)	37(1)	31(1)	39(1)	9(1)	20(1)	8(1)
F(2)	44(1)	27(1)	51(1)	6(1)	17(1)	16(1)
F(3)	40(1)	49(1)	52(1)	-7(1)	23(1)	18(1)
F(4)	39(1)	52(1)	43(1)	1(1)	28(1)	2(1)
F(5)	40(1)	28(1)	47(1)	10(1)	23(1)	6(1)
O(1)	18(1)	21(1)	35(1)	-11(1)	8(1)	-1(1)
N(1)	17(1)	18(1)	20(1)	-1(1)	6(1)	2(1)
C(1)	17(1)	24(1)	22(1)	-3(1)	4(1)	1(1)
C(2)	20(1)	21(1)	22(1)	-5(1)	5(1)	-2(1)
C(3)	24(1)	34(1)	39(1)	-18(1)	7(1)	-4(1)
C(4)	29(1)	30(1)	32(1)	-15(1)	8(1)	-3(1)
C(5)	30(1)	19(1)	34(1)	-8(1)	10(1)	-2(1)
C(6)	23(1)	17(1)	20(1)	-1(1)	8(1)	2(1)
C(7)	29(1)	24(1)	22(1)	2(1)	7(1)	7(1)
C(8)	31(1)	33(1)	35(1)	5(1)	11(1)	13(1)
C(9)	31(1)	39(1)	36(1)	4(1)	17(1)	13(1)
C(10)	25(1)	23(1)	26(1)	2(1)	11(1)	3(1)
C(11)	22(1)	15(1)	18(1)	-1(1)	7(1)	0(1)
C(12)	15(1)	22(1)	21(1)	-5(1)	4(1)	1(1)
C(13)	18(1)	24(1)	25(1)	-1(1)	6(1)	2(1)
C(14)	26(1)	25(1)	30(1)	-2(1)	5(1)	8(1)
C(15)	21(1)	34(1)	32(1)	-9(1)	8(1)	7(1)
C(16)	23(1)	36(1)	27(1)	-4(1)	12(1)	0(1)
C(17)	21(1)	24(1)	27(1)	0(1)	7(1)	2(1)
C(1S)	30(1)	81(2)	46(1)	6(1)	5(1)	8(1)
C(2S)	30(1)	85(2)	48(1)	18(1)	10(1)	3(1)
C(3S)	25(1)	73(1)	47(1)	13(1)	-4(1)	-2(1)
C(4S)	28(2)	63(3)	41(2)	2(2)	7(2)	-8(2)

Table S2-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **1d**.

	x	y	z	U(eq)
H(1)	-1458(8)	193(18)	1157(12)	25(5)
H(3B)	-1482(8)	-1500(20)	121(13)	35(5)
H(3A)	-1301(9)	-2700(20)	835(14)	46(6)
H(4B)	-1088(8)	-3590(20)	-318(13)	30(5)
H(4A)	-797(8)	-2160(20)	-431(12)	30(5)
H(5B)	-404(8)	-3970(20)	979(12)	26(5)
H(5A)	-144(8)	-4010(20)	265(13)	33(5)
H(7B)	418(8)	-3410(20)	2080(12)	28(5)
H(7A)	680(8)	-1913(19)	2126(12)	25(5)
H(8B)	1282(10)	-3170(20)	1712(15)	45(6)
H(8A)	904(11)	-4340(30)	1307(17)	67(8)
H(9B)	1112(9)	-2080(20)	423(13)	40(6)
H(9A)	717(11)	-3370(30)	12(17)	66(8)
H(10B)	514(7)	-590(20)	634(11)	25(5)
H(10A)	112(8)	-1430(20)	-159(13)	29(5)
H(1S)	-2153(11)	850(30)	-720(17)	65(8)
H(2S)	-2044(11)	3240(30)	-889(17)	64(8)
H(4S1)	-2013	5680	-104	67
H(4S2)	-2568	5985	91	67
H(4S3)	-2566	5666	-840	67

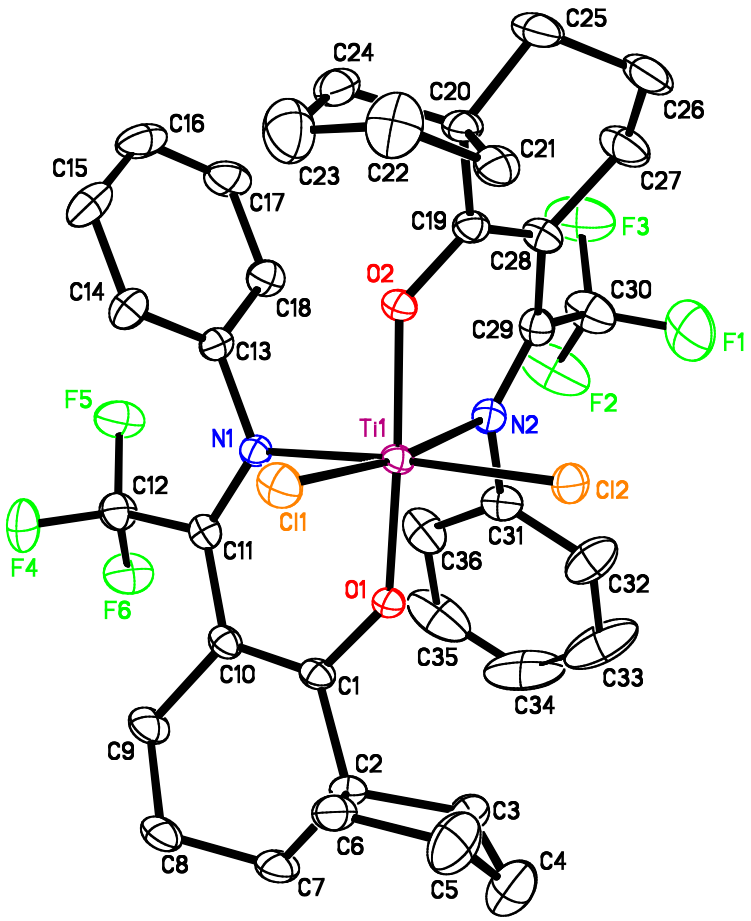


Figure S4. X-ray crystal structure of **1e**. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table S3-1. Crystal data and structure refinement for **1e**.

Identification code	**1e**	
Empirical formula	$C_{36}\ H_{38}\ Cl_2\ F_6\ N_2\ O_2\ Ti * C_7\ H_8$	
Formula weight	855.62	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.5392(15) Å	α= 90°.
	b = 12.9101(17) Å	β= 98.051(4)°.
	c = 29.846(4) Å	γ = 90°.
Volume	4020.9(10) $Å^3$	
Z	4	
Density (calculated)	1.413 Mg/m^3	
Absorption coefficient	0.413 mm^{-1}	
F(000)	1776	
Crystal size	0.40 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.95 to 26.37°.	
Index ranges	-13<=h<=12, -16<=k<=16, -37<=l<=37	
Reflections collected	39319	
Independent reflections	8207 [R(int) = 0.0499]	
Completeness to theta = 26.37°	99.9 %	
Absorption correction	SADABS	
Max. and min. transmission	0.9219 and 0.8522	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8207 / 0 / 676	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.1423	
R indices (all data)	R1 = 0.0776, wR2 = 0.1567	
Largest diff. peak and hole	0.988 and -0.478 $e.Å^{-3}$	

Table S3-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	6985(1)	6170(1)	1593(1)	19(1)
Cl(1)	6612(1)	6321(1)	2322(1)	33(1)
Cl(2)	8828(1)	7126(1)	1636(1)	29(1)
F(1)	7978(2)	7042(1)	-46(1)	67(1)
F(2)	6778(2)	5714(1)	-72(1)	69(1)
F(3)	5943(2)	7182(1)	-203(1)	66(1)
F(4)	3610(1)	3203(1)	1777(1)	46(1)
F(5)	3305(1)	3830(1)	1106(1)	43(1)
F(6)	4495(1)	2521(1)	1239(1)	41(1)
O(1)	7840(1)	4917(1)	1684(1)	22(1)
O(2)	5917(1)	7274(1)	1387(1)	21(1)
N(1)	5367(2)	5091(1)	1464(1)	20(1)
N(2)	7069(2)	6087(1)	852(1)	24(1)
C(1)	7677(2)	3976(1)	1829(1)	22(1)
C(2)	8889(2)	3497(2)	2073(1)	26(1)
C(3)	10074(2)	3721(2)	1836(1)	37(1)
C(4)	11139(3)	3977(3)	2211(1)	64(1)
C(5)	10481(3)	4596(2)	2531(1)	57(1)
C(6)	9202(2)	4071(2)	2541(1)	32(1)
C(7)	8712(2)	2336(2)	2140(1)	34(1)
C(8)	7456(2)	2121(2)	2307(1)	35(1)
C(9)	6350(2)	2423(2)	1948(1)	33(1)
C(10)	6489(2)	3525(1)	1775(1)	23(1)
C(11)	5400(2)	4087(1)	1555(1)	22(1)
C(12)	4188(2)	3414(2)	1421(1)	31(1)
C(13)	4168(2)	5608(1)	1315(1)	22(1)
C(14)	3381(2)	5840(2)	1635(1)	32(1)
C(15)	2225(2)	6344(2)	1500(1)	40(1)
C(16)	1891(2)	6638(2)	1055(1)	42(1)
C(17)	2693(2)	6419(2)	740(1)	38(1)

C(18)	3843(2)	5909(2)	867(1)	29(1)
C(19)	5917(2)	8019(2)	1091(1)	24(1)
C(20)	5395(2)	9028(2)	1251(1)	27(1)
C(21)	6331(2)	9409(2)	1675(1)	32(1)
C(22)	5508(3)	9615(2)	2044(1)	52(1)
C(23)	4434(3)	8857(2)	1951(1)	61(1)
C(24)	4115(2)	8842(2)	1435(1)	36(1)
C(25)	5245(3)	9834(2)	872(1)	42(1)
C(26)	6372(3)	9816(2)	613(1)	48(1)
C(27)	6387(3)	8791(2)	364(1)	45(1)
C(28)	6352(2)	7870(2)	684(1)	29(1)
C(29)	6778(2)	6851(2)	566(1)	26(1)
C(30)	6875(3)	6689(2)	61(1)	43(1)
C(31)	7676(2)	5150(2)	722(1)	28(1)
C(32)	8970(3)	5175(2)	695(1)	48(1)
C(33)	9604(3)	4284(3)	608(1)	76(1)
C(34)	8964(4)	3362(3)	556(1)	79(1)
C(35)	7675(4)	3328(2)	583(1)	64(1)
C(36)	6996(3)	4226(2)	664(1)	40(1)
C(1S)	11257(9)	8978(6)	200(3)	85(3)
C(2S)	11020(6)	9609(4)	628(2)	55(2)
C(2S')	11066(8)	10476(9)	1054(4)	130(4)
C(3S)	11618(3)	10470(3)	678(1)	83(1)
C(4S)	11492(5)	11158(4)	1192(3)	74(3)
C(4S')	11319(9)	9456(8)	313(4)	122(4)
C(5S)	10755(6)	10675(4)	1400(2)	57(2)
C(5S')	10267(9)	8751(6)	403(4)	104(3)
C(6S)	10108(4)	9653(3)	1175(2)	106(2)
C(7S)	10090(6)	9087(4)	837(2)	70(2)

Table S3-3. Bond lengths [Å] and angles [°] for **1e**.

Ti(1)-O(1)	1.8532(13)	C(15)-C(16)	1.379(4)
Ti(1)-O(2)	1.8659(13)	C(16)-C(17)	1.381(4)
Ti(1)-N(1)	2.1935(16)	C(17)-C(18)	1.385(3)
Ti(1)-N(2)	2.2272(18)	C(19)-C(28)	1.372(3)
Ti(1)-Cl(1)	2.2728(7)	C(19)-C(20)	1.516(3)
Ti(1)-Cl(2)	2.2901(6)	C(20)-C(25)	1.529(3)
F(1)-C(30)	1.328(3)	C(20)-C(24)	1.545(3)
F(2)-C(30)	1.320(3)	C(20)-C(21)	1.570(3)
F(3)-C(30)	1.332(3)	C(21)-C(22)	1.517(4)
F(4)-C(12)	1.327(3)	C(22)-C(23)	1.493(4)
F(5)-C(12)	1.339(3)	C(23)-C(24)	1.532(4)
F(6)-C(12)	1.333(3)	C(25)-C(26)	1.504(4)
O(1)-C(1)	1.310(2)	C(26)-C(27)	1.520(4)
O(2)-C(19)	1.306(2)	C(27)-C(28)	1.529(3)
N(1)-C(11)	1.324(2)	C(28)-C(29)	1.449(3)
N(1)-C(13)	1.443(2)	C(29)-C(30)	1.540(3)
N(2)-C(29)	1.313(3)	C(31)-C(32)	1.378(4)
N(2)-C(31)	1.447(3)	C(31)-C(36)	1.390(3)
C(1)-C(10)	1.369(3)	C(32)-C(33)	1.373(4)
C(1)-C(2)	1.512(3)	C(33)-C(34)	1.366(5)
C(2)-C(7)	1.527(3)	C(34)-C(35)	1.373(5)
C(2)-C(3)	1.546(3)	C(35)-C(36)	1.400(4)
C(2)-C(6)	1.576(3)	C(1S)-C(4S')	0.701(14)
C(3)-C(4)	1.506(4)	C(1S)-C(5S')	1.313(14)
C(4)-C(5)	1.489(5)	C(1S)-C(2S)	1.565(10)
C(5)-C(6)	1.513(4)	C(2S)-C(4S')	1.052(14)
C(7)-C(8)	1.503(3)	C(2S)-C(3S)	1.276(7)
C(8)-C(9)	1.518(3)	C(2S)-C(7S)	1.406(9)
C(9)-C(10)	1.528(3)	C(2S)-C(5S')	1.468(10)
C(10)-C(11)	1.437(3)	C(2S)-C(2S')	1.689(13)
C(11)-C(12)	1.550(3)	C(2S')-C(4S)	1.047(12)
C(13)-C(14)	1.382(3)	C(2S')-C(5S)	1.155(12)
C(13)-C(18)	1.388(3)	C(2S')-C(3S)	1.335(11)
C(14)-C(15)	1.390(3)	C(2S')-C(6S)	1.543(11)

C(2S')-C(7S)	2.122(13)	C(1)-C(2)-C(3)	112.67(17)
C(3S)-C(4S)	1.796(9)	C(7)-C(2)-C(3)	111.45(18)
C(3S)-C(4S')	1.704(13)	C(1)-C(2)-C(6)	106.97(16)
C(4S)-C(5S)	1.229(9)	C(7)-C(2)-C(6)	111.08(18)
C(4S')-C(5S')	1.488(14)	C(3)-C(2)-C(6)	103.66(17)
C(5S)-C(6S)	1.590(7)	C(4)-C(3)-C(2)	105.5(2)
C(5S')-C(7S)	1.403(12)	C(5)-C(4)-C(3)	103.2(2)
C(6S)-C(7S)	1.243(7)	C(4)-C(5)-C(6)	105.6(2)
		C(5)-C(6)-C(2)	105.6(2)
O(1)-Ti(1)-O(2)	166.72(6)	C(8)-C(7)-C(2)	110.72(18)
O(1)-Ti(1)-N(1)	79.72(6)	C(7)-C(8)-C(9)	110.2(2)
O(2)-Ti(1)-N(1)	90.51(6)	C(8)-C(9)-C(10)	112.09(18)
O(1)-Ti(1)-N(2)	90.95(6)	C(1)-C(10)-C(11)	119.80(17)
O(2)-Ti(1)-N(2)	79.35(6)	C(1)-C(10)-C(9)	119.05(18)
N(1)-Ti(1)-N(2)	86.16(6)	C(11)-C(10)-C(9)	121.14(18)
O(1)-Ti(1)-Cl(1)	94.64(5)	N(1)-C(11)-C(10)	125.78(18)
O(2)-Ti(1)-Cl(1)	94.20(5)	N(1)-C(11)-C(12)	119.91(17)
N(1)-Ti(1)-Cl(1)	89.33(5)	C(10)-C(11)-C(12)	114.30(17)
N(2)-Ti(1)-Cl(1)	172.09(5)	F(4)-C(12)-F(6)	108.19(18)
O(1)-Ti(1)-Cl(2)	94.05(5)	F(4)-C(12)-F(5)	107.07(18)
O(2)-Ti(1)-Cl(2)	94.29(5)	F(6)-C(12)-F(5)	104.30(17)
N(1)-Ti(1)-Cl(2)	169.89(5)	F(4)-C(12)-C(11)	111.24(18)
N(2)-Ti(1)-Cl(2)	85.99(5)	F(6)-C(12)-C(11)	110.58(18)
Cl(1)-Ti(1)-Cl(2)	99.17(2)	F(5)-C(12)-C(11)	115.02(17)
C(1)-O(1)-Ti(1)	140.76(13)	C(14)-C(13)-C(18)	120.92(19)
C(19)-O(2)-Ti(1)	136.80(13)	C(14)-C(13)-N(1)	118.18(18)
C(11)-N(1)-C(13)	120.83(16)	C(18)-C(13)-N(1)	120.83(19)
C(11)-N(1)-Ti(1)	126.04(13)	C(13)-C(14)-C(15)	119.2(2)
C(13)-N(1)-Ti(1)	112.72(11)	C(16)-C(15)-C(14)	120.1(2)
C(29)-N(2)-C(31)	121.64(18)	C(15)-C(16)-C(17)	120.2(2)
C(29)-N(2)-Ti(1)	124.85(14)	C(16)-C(17)-C(18)	120.4(2)
C(31)-N(2)-Ti(1)	112.84(12)	C(17)-C(18)-C(13)	119.1(2)
O(1)-C(1)-C(10)	121.07(17)	O(2)-C(19)-C(28)	121.77(18)
O(1)-C(1)-C(2)	113.42(17)	O(2)-C(19)-C(20)	112.74(18)
C(10)-C(1)-C(2)	125.44(17)	C(28)-C(19)-C(20)	125.48(18)
C(1)-C(2)-C(7)	110.72(17)	C(19)-C(20)-C(25)	110.88(19)

C(19)-C(20)-C(24)	110.62(17)	C(4S')-C(2S)-C(7S)	128.5(8)
C(25)-C(20)-C(24)	111.30(19)	C(3S)-C(2S)-C(7S)	136.9(6)
C(19)-C(20)-C(21)	107.94(16)	C(4S')-C(2S)-C(5S')	70.2(8)
C(25)-C(20)-C(21)	111.77(17)	C(3S)-C(2S)-C(5S')	159.5(6)
C(24)-C(20)-C(21)	104.10(19)	C(7S)-C(2S)-C(5S')	58.4(6)
C(22)-C(21)-C(20)	106.4(2)	C(4S')-C(2S)-C(1S)	21.5(7)
C(23)-C(22)-C(21)	104.3(2)	C(3S)-C(2S)-C(1S)	114.5(6)
C(22)-C(23)-C(24)	104.4(2)	C(7S)-C(2S)-C(1S)	108.4(6)
C(20)-C(24)-C(23)	106.0(2)	C(5S')-C(2S)-C(1S)	51.2(6)
C(26)-C(25)-C(20)	111.2(2)	C(4S')-C(2S)-C(2S')	144.8(9)
C(25)-C(26)-C(27)	109.2(2)	C(3S)-C(2S)-C(2S')	51.2(4)
C(26)-C(27)-C(28)	111.5(2)	C(7S)-C(2S)-C(2S')	86.1(5)
C(19)-C(28)-C(29)	119.72(18)	C(5S')-C(2S)-C(2S')	143.1(7)
C(19)-C(28)-C(27)	119.02(19)	C(1S)-C(2S)-C(2S')	165.5(7)
C(29)-C(28)-C(27)	121.3(2)	C(4S)-C(2S')-C(5S)	67.7(9)
N(2)-C(29)-C(28)	125.20(19)	C(4S)-C(2S')-C(3S)	97.1(9)
N(2)-C(29)-C(30)	119.59(19)	C(5S)-C(2S')-C(3S)	164.7(11)
C(28)-C(29)-C(30)	115.21(18)	C(4S)-C(2S')-C(6S)	138.2(11)
F(2)-C(30)-F(1)	106.8(2)	C(5S)-C(2S')-C(6S)	70.5(6)
F(2)-C(30)-F(3)	104.9(2)	C(3S)-C(2S')-C(6S)	124.7(9)
F(1)-C(30)-F(3)	107.0(2)	C(4S)-C(2S')-C(2S)	145.1(10)
F(2)-C(30)-C(29)	114.3(2)	C(5S)-C(2S')-C(2S)	146.9(10)
F(1)-C(30)-C(29)	111.6(2)	C(3S)-C(2S')-C(2S)	48.2(5)
F(3)-C(30)-C(29)	111.7(2)	C(6S)-C(2S')-C(2S)	76.7(6)
C(32)-C(31)-C(36)	120.6(2)	C(4S)-C(2S')-C(7S)	173.6(10)
C(32)-C(31)-N(2)	118.4(2)	C(5S)-C(2S')-C(7S)	105.9(7)
C(36)-C(31)-N(2)	120.8(2)	C(3S)-C(2S')-C(7S)	89.3(7)
C(33)-C(32)-C(31)	120.2(3)	C(6S)-C(2S')-C(7S)	35.4(4)
C(34)-C(33)-C(32)	120.4(3)	C(2S)-C(2S')-C(7S)	41.4(4)
C(33)-C(34)-C(35)	119.9(3)	C(2S')-C(3S)-C(2S)	80.6(6)
C(34)-C(35)-C(36)	121.2(3)	C(2S')-C(3S)-C(4S)	35.4(5)
C(31)-C(36)-C(35)	117.7(3)	C(2S)-C(3S)-C(4S)	115.8(4)
C(4S')-C(1S)-C(5S')	90.0(15)	C(2S')-C(3S)-C(4S')	118.6(7)
C(4S')-C(1S)-C(2S)	33.4(12)	C(2S)-C(3S)-C(4S')	38.1(5)
C(5S')-C(1S)-C(2S)	60.6(6)	C(4S)-C(3S)-C(4S')	153.9(5)
C(4S')-C(2S)-C(3S)	93.6(8)	C(2S')-C(4S)-C(5S)	60.3(7)

C(2S')-C(4S)-C(3S)	47.6(7)	C(7S)-C(5S')-C(2S)	58.6(5)
C(5S)-C(4S)-C(3S)	107.9(5)	C(1S)-C(5S')-C(4S')	28.1(6)
C(1S)-C(4S')-C(2S)	125.2(17)	C(7S)-C(5S')-C(4S')	100.2(8)
C(1S)-C(4S')-C(5S')	61.9(12)	C(2S)-C(5S')-C(4S')	41.7(6)
C(2S)-C(4S')-C(5S')	68.1(8)	C(7S)-C(6S)-C(2S')	98.7(6)
C(1S)-C(4S')-C(3S)	168.3(15)	C(7S)-C(6S)-C(5S)	141.9(5)
C(2S)-C(4S')-C(3S)	48.4(6)	C(2S')-C(6S)-C(5S)	43.2(5)
C(5S')-C(4S')-C(3S)	115.4(9)	C(6S)-C(7S)-C(5S')	160.3(7)
C(2S')-C(5S)-C(4S)	52.0(7)	C(6S)-C(7S)-C(2S)	98.4(5)
C(2S')-C(5S)-C(6S)	66.2(6)	C(5S')-C(7S)-C(2S)	63.1(5)
C(4S)-C(5S)-C(6S)	118.2(6)	C(6S)-C(7S)-C(2S')	45.9(4)
C(1S)-C(5S')-C(7S)	125.1(8)	C(5S')-C(7S)-C(2S')	114.9(6)
C(1S)-C(5S')-C(2S)	68.2(6)	C(2S)-C(7S)-C(2S')	52.6(4)

Table S3-4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	21(1)	15(1)	21(1)	0(1)	2(1)	1(1)
Cl(1)	42(1)	35(1)	22(1)	-2(1)	7(1)	2(1)
Cl(2)	24(1)	24(1)	37(1)	-1(1)	1(1)	-5(1)
F(1)	85(1)	78(1)	46(1)	3(1)	38(1)	2(1)
F(2)	137(2)	43(1)	23(1)	-10(1)	-1(1)	9(1)
F(3)	98(1)	69(1)	25(1)	1(1)	-10(1)	27(1)
F(4)	36(1)	52(1)	52(1)	2(1)	15(1)	-17(1)
F(5)	35(1)	30(1)	56(1)	2(1)	-17(1)	-6(1)
F(6)	45(1)	23(1)	52(1)	-12(1)	-6(1)	-4(1)
O(1)	20(1)	18(1)	29(1)	3(1)	3(1)	1(1)
O(2)	24(1)	18(1)	22(1)	1(1)	3(1)	2(1)
N(1)	21(1)	18(1)	22(1)	-1(1)	3(1)	0(1)
N(2)	25(1)	21(1)	25(1)	-3(1)	5(1)	-1(1)
C(1)	28(1)	16(1)	23(1)	-1(1)	5(1)	4(1)
C(2)	25(1)	22(1)	30(1)	5(1)	3(1)	5(1)
C(3)	31(1)	35(1)	47(1)	9(1)	15(1)	11(1)
C(4)	35(2)	72(2)	86(2)	6(2)	9(2)	-1(1)
C(5)	38(2)	59(2)	72(2)	-15(2)	1(1)	-14(1)
C(6)	29(1)	29(1)	35(1)	3(1)	-2(1)	4(1)
C(7)	36(1)	20(1)	45(1)	6(1)	1(1)	6(1)
C(8)	39(1)	22(1)	43(1)	11(1)	3(1)	0(1)
C(9)	38(1)	18(1)	42(1)	4(1)	2(1)	-4(1)
C(10)	29(1)	18(1)	23(1)	1(1)	6(1)	1(1)
C(11)	26(1)	21(1)	20(1)	-2(1)	4(1)	-2(1)
C(12)	30(1)	25(1)	37(1)	-1(1)	2(1)	-5(1)
C(13)	19(1)	18(1)	28(1)	-4(1)	0(1)	-2(1)
C(14)	24(1)	36(1)	35(1)	-4(1)	3(1)	-1(1)
C(15)	23(1)	46(1)	53(2)	-13(1)	6(1)	4(1)
C(16)	24(1)	34(1)	64(2)	-3(1)	-10(1)	5(1)
C(17)	34(1)	37(1)	38(1)	7(1)	-13(1)	1(1)
C(18)	28(1)	29(1)	29(1)	-1(1)	-1(1)	-2(1)

C(19)	22(1)	22(1)	26(1)	1(1)	-2(1)	1(1)
C(20)	27(1)	18(1)	35(1)	1(1)	3(1)	4(1)
C(21)	33(1)	19(1)	43(1)	-4(1)	2(1)	-2(1)
C(22)	56(2)	56(2)	46(2)	-18(1)	11(1)	-8(1)
C(23)	69(2)	54(2)	67(2)	-5(1)	31(2)	-5(2)
C(24)	27(1)	28(1)	52(2)	-3(1)	5(1)	5(1)
C(25)	51(2)	25(1)	49(2)	8(1)	5(1)	12(1)
C(26)	67(2)	27(1)	52(2)	17(1)	16(1)	8(1)
C(27)	66(2)	36(1)	36(1)	14(1)	15(1)	11(1)
C(28)	36(1)	25(1)	25(1)	4(1)	3(1)	3(1)
C(29)	28(1)	30(1)	21(1)	0(1)	4(1)	-1(1)
C(30)	69(2)	36(1)	24(1)	-1(1)	9(1)	7(1)
C(31)	36(1)	29(1)	20(1)	-4(1)	4(1)	6(1)
C(32)	36(1)	67(2)	41(1)	-17(1)	5(1)	12(1)
C(33)	54(2)	110(2)	59(2)	-37(2)	-2(2)	45(2)
C(34)	108(2)	81(2)	46(2)	-21(2)	0(2)	67(2)
C(35)	129(3)	28(1)	37(1)	-7(1)	19(2)	10(2)
C(36)	65(2)	28(1)	32(1)	-6(1)	19(1)	0(1)
C(1S)	111(6)	65(4)	70(5)	-15(4)	-16(5)	15(4)
C(2S)	69(3)	48(3)	40(3)	-3(2)	-17(3)	37(3)
C(2S')	53(4)	202(8)	133(7)	92(6)	8(5)	53(5)
C(3S)	54(2)	110(3)	88(2)	50(2)	16(2)	25(2)
C(4S)	20(2)	13(2)	187(8)	8(3)	7(3)	-3(2)
C(4S')	75(5)	116(7)	157(9)	68(6)	-53(6)	-36(5)
C(5S)	76(3)	57(3)	46(3)	5(2)	34(3)	37(3)
C(5S')	87(5)	74(5)	135(8)	28(5)	-42(5)	9(4)
C(6S)	58(2)	73(2)	183(4)	63(2)	0(3)	-2(2)
C(7S)	97(3)	82(3)	41(3)	44(2)	46(2)	80(3)

Table S3-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **1e**.

	x	y	z	U(eq)
H(3B)	9970(30)	4260(20)	1646(9)	47(7)
H(3A)	10290(30)	3190(20)	1641(10)	58(9)
H(4B)	11660(40)	3300(40)	2411(16)	129(16)
H(4A)	11890(30)	4460(30)	2056(12)	88(11)
H(9B)	10950(30)	4640(20)	2811(11)	68(10)
H(5A)	10470(50)	5140(40)	2263(16)	143(18)
H(6B)	8610(20)	4590(20)	2587(8)	40(7)
H(6B)	9330(20)	3552(19)	2796(8)	38(7)
H(7B)	9450(20)	2107(19)	2361(9)	41(7)
H(7A)	8670(20)	1951(17)	1845(8)	30(6)
H(8B)	7420(20)	1343(19)	2389(8)	36(7)
H(8A)	7410(20)	2499(19)	2587(8)	36(7)
H(9B)	6280(20)	1945(19)	1694(9)	38(7)
H(9A)	5520(20)	2409(17)	2058(8)	27(6)
H(14)	3580(20)	5584(18)	1949(9)	37(7)
H(15)	1640(30)	6540(30)	1736(11)	73(10)
H(16)	1170(30)	6950(20)	969(9)	51(8)
H(17)	2510(20)	6597(18)	466(8)	30(6)
H(18)	4440(20)	5760(20)	649(9)	40(7)
H(21B)	6980(20)	8826(19)	1816(9)	42(7)
H(21A)	6770(30)	9970(20)	1606(9)	47(7)
H(22B)	6020(30)	9570(20)	2326(11)	65(9)
H(22A)	5060(40)	10230(30)	1991(13)	101(13)
H(23A)	3685	9084	2093	73
H(23B)	4704	8162	2068	73
H(24B)	3700(30)	8160(20)	1297(10)	61(9)
H(24A)	3560(30)	9400(20)	1328(9)	53(8)
H(25B)	4500(20)	9655(19)	676(8)	38(7)
H(25A)	5170(20)	10518(19)	1020(9)	40(7)
H(26B)	7170(20)	9861(18)	816(8)	33(6)
H(26A)	6300(30)	10320(20)	411(9)	50(8)

H(27B)	7120(30)	8750(20)	235(9)	45(7)
H(27A)	5650(20)	8752(19)	126(9)	40(7)
H(32)	9480(30)	5790(20)	729(10)	57(9)
H(33)	10450(30)	4400(20)	594(11)	65(9)
H(34)	9450(30)	2770(20)	506(11)	67(9)
H(35)	7260(30)	2820(30)	590(12)	74(11)
H(36)	6070(20)	4222(18)	687(8)	30(6)

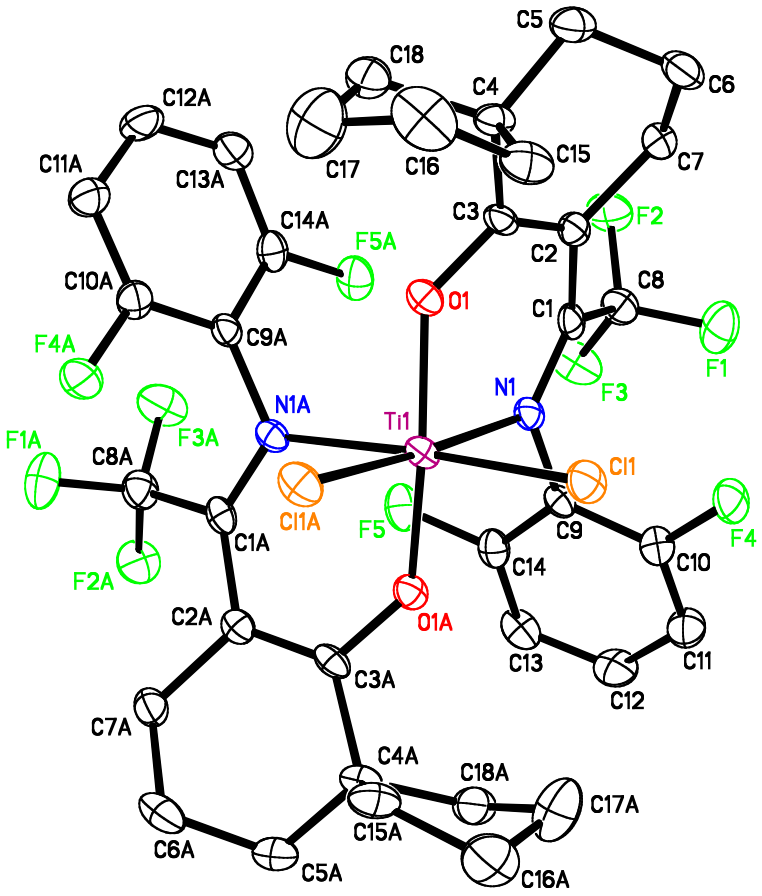


Figure S5. X-ray crystal structure of **1f**. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table S4-1. Crystal data and structure refinement for **1f**.

Identification code	**1f**	
Empirical formula	$C_{36}\ H_{34}\ Cl_2\ F_{10}\ N_2\ O_2\ Ti$	
Formula weight	835.45	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P6(1)22	
Unit cell dimensions	a = 13.5188(16) Å	α= 90°.
	b = 13.5188(16) Å	β= 90°.
	c = 33.888(6) Å	γ = 120°.
Volume	5363.6(13) $Å^3$	
Z	6	
Density (calculated)	1.552 Mg/m^3	
Absorption coefficient	0.478 mm^{-1}	
F(000)	2556	
Crystal size	0.30 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.51 to 24.63°.	
Index ranges	-15<=h<=15, -8<=k<=15, -39<=l<=37	
Reflections collected	17307	
Independent reflections	2819 [R(int) = 0.0616]	
Completeness to theta = 24.63°	95.5 %	
Absorption correction	SADABS	
Max. and min. transmission	0.9765 and 0.8699	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2819 / 0 / 300	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0744	
R indices (all data)	R1 = 0.0615, wR2 = 0.0796	
Absolute structure parameter	-0.04(4)	
Largest diff. peak and hole	0.305 and -0.258 $e.Å^{-3}$	

Table S4-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1f**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	91(1)	5046(1)	833	21(1)
Cl(1)	-1220(1)	5306(1)	500(1)	31(1)
F(1)	2485(2)	8161(2)	-264(1)	47(1)
F(2)	3334(2)	7185(2)	-301(1)	39(1)
F(3)	3528(2)	8151(2)	216(1)	44(1)
F(4)	602(2)	7918(2)	198(1)	38(1)
F(5)	2965(2)	7450(2)	1098(1)	35(1)
O(1)	360(2)	4280(2)	428(1)	23(1)
N(1)	1389(2)	6521(2)	480(1)	21(1)
C(1)	1713(3)	6443(3)	121(1)	23(1)
C(2)	1170(3)	5443(3)	-124(1)	23(1)
C(3)	502(3)	4398(3)	42(1)	22(1)
C(4)	-148(3)	3276(3)	-183(1)	25(1)
C(5)	205(4)	3450(3)	-615(1)	32(1)
C(6)	319(4)	4533(4)	-778(1)	38(1)
C(7)	1294(3)	5548(4)	-573(1)	31(1)
C(8)	2766(3)	7496(3)	-57(1)	32(1)
C(9)	1762(3)	7634(3)	644(1)	21(1)
C(10)	1331(3)	8304(3)	511(1)	27(1)
C(11)	1619(3)	9347(3)	667(1)	35(1)
C(12)	2368(3)	9742(3)	982(1)	37(1)
C(13)	2814(3)	9103(3)	1134(1)	32(1)
C(14)	2508(3)	8070(3)	963(1)	27(1)
C(15)	-1452(3)	2817(3)	-134(1)	36(1)
C(16)	-1961(3)	1585(4)	3(1)	54(1)
C(17)	-1035(4)	1581(4)	248(2)	66(2)
C(18)	35(4)	2340(4)	11(1)	36(1)

Table S4-3. Bond lengths [Å] and angles [°] for **1f**.

Ti(1)-O(1)	1.862(2)	O(1)-Ti(1)-O(1)#1	160.56(14)
Ti(1)-O(1)#1	1.862(2)	O(1)-Ti(1)-N(1)#1	87.38(9)
Ti(1)-N(1)#1	2.234(3)	O(1)#1-Ti(1)-N(1)#1	79.40(9)
Ti(1)-N(1)	2.234(3)	O(1)-Ti(1)-N(1)	79.40(9)
Ti(1)-Cl(1)#1	2.2731(10)	O(1)#1-Ti(1)-N(1)	87.38(9)
Ti(1)-Cl(1)	2.2731(10)	N(1)#1-Ti(1)-N(1)	94.29(13)
F(1)-C(8)	1.336(4)	O(1)-Ti(1)-Cl(1)#1	97.17(7)
F(2)-C(8)	1.331(4)	O(1)#1-Ti(1)-Cl(1)#1	95.92(7)
F(3)-C(8)	1.336(4)	N(1)#1-Ti(1)-Cl(1)#1	85.44(7)
F(4)-C(10)	1.361(4)	N(1)-Ti(1)-Cl(1)#1	176.57(7)
F(5)-C(14)	1.346(4)	O(1)-Ti(1)-Cl(1)	95.92(7)
O(1)-C(3)	1.319(4)	O(1)#1-Ti(1)-Cl(1)	97.17(7)
N(1)-C(1)	1.315(4)	N(1)#1-Ti(1)-Cl(1)	176.57(7)
N(1)-C(9)	1.439(4)	N(1)-Ti(1)-Cl(1)	85.44(7)
C(1)-C(2)	1.436(5)	Cl(1)#1-Ti(1)-Cl(1)	95.04(5)
C(1)-C(8)	1.546(5)	C(3)-O(1)-Ti(1)	136.1(2)
C(2)-C(3)	1.361(4)	C(1)-N(1)-C(9)	119.0(3)
C(2)-C(7)	1.530(5)	C(1)-N(1)-Ti(1)	124.7(2)
C(3)-C(4)	1.524(5)	C(9)-N(1)-Ti(1)	115.72(19)
C(4)-C(5)	1.519(5)	N(1)-C(1)-C(2)	125.2(3)
C(4)-C(18)	1.552(5)	N(1)-C(1)-C(8)	118.5(3)
C(4)-C(15)	1.558(5)	C(2)-C(1)-C(8)	116.3(3)
C(5)-C(6)	1.500(5)	C(3)-C(2)-C(1)	119.9(3)
C(6)-C(7)	1.514(6)	C(3)-C(2)-C(7)	119.5(3)
C(9)-C(10)	1.376(5)	C(1)-C(2)-C(7)	120.5(3)
C(9)-C(14)	1.392(4)	O(1)-C(3)-C(2)	121.1(3)
C(10)-C(11)	1.366(5)	O(1)-C(3)-C(4)	113.5(3)
C(11)-C(12)	1.382(5)	C(2)-C(3)-C(4)	125.4(3)
C(12)-C(13)	1.377(5)	C(5)-C(4)-C(3)	110.4(3)
C(13)-C(14)	1.371(5)	C(5)-C(4)-C(18)	111.7(3)
C(15)-C(16)	1.521(6)	C(3)-C(4)-C(18)	110.6(3)
C(16)-C(17)	1.506(6)	C(5)-C(4)-C(15)	111.7(3)
C(17)-C(18)	1.518(6)	C(3)-C(4)-C(15)	108.5(3)
		C(18)-C(4)-C(15)	103.8(3)

C(6)-C(5)-C(4)	112.2(3)	F(4)-C(10)-C(9)	117.8(3)
C(5)-C(6)-C(7)	109.5(3)	C(11)-C(10)-C(9)	123.8(3)
C(6)-C(7)-C(2)	111.5(3)	C(10)-C(11)-C(12)	118.3(4)
F(2)-C(8)-F(1)	106.9(3)	C(13)-C(12)-C(11)	120.8(4)
F(2)-C(8)-F(3)	105.3(3)	C(14)-C(13)-C(12)	118.6(3)
F(1)-C(8)-F(3)	107.5(3)	F(5)-C(14)-C(13)	119.5(3)
F(2)-C(8)-C(1)	111.2(3)	F(5)-C(14)-C(9)	117.4(3)
F(1)-C(8)-C(1)	112.5(3)	C(13)-C(14)-C(9)	123.0(3)
F(3)-C(8)-C(1)	113.0(3)	C(16)-C(15)-C(4)	105.7(3)
C(10)-C(9)-C(14)	115.5(3)	C(17)-C(16)-C(15)	104.5(3)
C(10)-C(9)-N(1)	121.3(3)	C(16)-C(17)-C(18)	102.6(4)
C(14)-C(9)-N(1)	123.0(3)	C(17)-C(18)-C(4)	106.8(4)
F(4)-C(10)-C(11)	118.3(3)		

Symmetry transformations used to generate equivalent atoms: #1 x,x-y+1,-z+1/6

Table S4-4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1f**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	19(1)	25(1)	16(1)	-1(1)	0	9(1)
Cl(1)	26(1)	42(1)	28(1)	-1(1)	-4(1)	19(1)
F(1)	47(1)	40(1)	55(2)	22(1)	12(1)	23(1)
F(2)	32(1)	44(1)	37(1)	5(1)	15(1)	16(1)
F(3)	26(1)	44(1)	38(1)	-5(1)	3(1)	-1(1)
F(4)	46(1)	40(1)	33(1)	-8(1)	-19(1)	24(1)
F(5)	28(1)	35(1)	36(1)	3(1)	-11(1)	11(1)
O(1)	20(1)	24(1)	21(1)	1(1)	2(1)	8(1)
N(1)	21(2)	27(2)	18(2)	-1(1)	-4(1)	13(1)
C(1)	21(2)	32(2)	20(2)	4(2)	-3(2)	16(2)
C(2)	21(2)	28(2)	21(2)	0(2)	-1(2)	14(2)
C(3)	22(2)	36(2)	15(2)	-1(2)	2(2)	19(2)
C(4)	23(2)	31(2)	23(2)	-9(2)	-4(2)	16(2)
C(5)	33(2)	35(2)	30(2)	-11(2)	-4(2)	18(2)
C(6)	44(3)	58(3)	21(2)	-7(2)	-4(2)	33(2)
C(7)	40(2)	35(2)	23(2)	3(2)	3(2)	23(2)
C(8)	34(2)	35(2)	28(2)	4(2)	6(2)	17(2)
C(9)	22(2)	21(2)	17(2)	2(2)	2(2)	7(2)
C(10)	25(2)	24(2)	28(2)	1(2)	-3(2)	9(2)
C(11)	40(2)	29(2)	35(2)	-5(2)	-7(2)	17(2)
C(12)	44(3)	20(2)	39(2)	-6(2)	2(2)	10(2)
C(13)	27(2)	26(2)	27(2)	-2(2)	-3(2)	2(2)
C(14)	22(2)	27(2)	27(2)	9(2)	4(2)	9(2)
C(15)	28(2)	37(2)	34(3)	-13(2)	-7(2)	11(2)
C(16)	33(2)	52(3)	51(3)	-1(2)	-1(2)	2(2)
C(17)	62(3)	39(3)	82(4)	15(3)	8(3)	15(3)
C(18)	40(3)	35(2)	33(3)	-6(2)	-6(2)	19(2)

Table S4-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1f**.

	x	y	z	U(eq)
H(5B)	980(30)	3500(20)	-651(8)	18(8)
H(5A)	-350(30)	2810(30)	-750(8)	15(8)
H(6B)	-320(30)	4540(20)	-736(9)	21(9)
H(6A)	410(30)	4580(30)	-1044(11)	42(11)
H(7B)	2070(30)	5620(30)	-662(8)	20(8)
H(7A)	1350(20)	6210(30)	-657(8)	15(9)
H(11)	1300(30)	9820(30)	542(10)	55(12)
H(12)	2570(30)	10470(30)	1095(10)	44(11)
H(13)	3390(30)	9280(30)	1326(10)	39(11)
H(15B)	-1590(30)	3320(30)	73(11)	52(11)
H(15A)	-1810(30)	2840(20)	-382(9)	24(9)
H(16A)	-2658	1349	162	64
H(16B)	-2157	1063	-226	64
H(17A)	-1180(40)	800(50)	253(14)	98(18)
H(17B)	-860(40)	2080(40)	552(15)	97(18)
H(18B)	-50(40)	1810(40)	-204(13)	72(14)
H(18A)	610(30)	2520(30)	135(10)	24(12)