Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for Paper Entitled:

"The titanium *tris*-anilide cation $[Ti(N[^tBu]Ar)_3]^+$ stabilized as its perfluoro-*tetra*-phenylborate salt: structural characterization and synthesis in connection with redox activity of 4,4′-bipyridine dititanium complexes"

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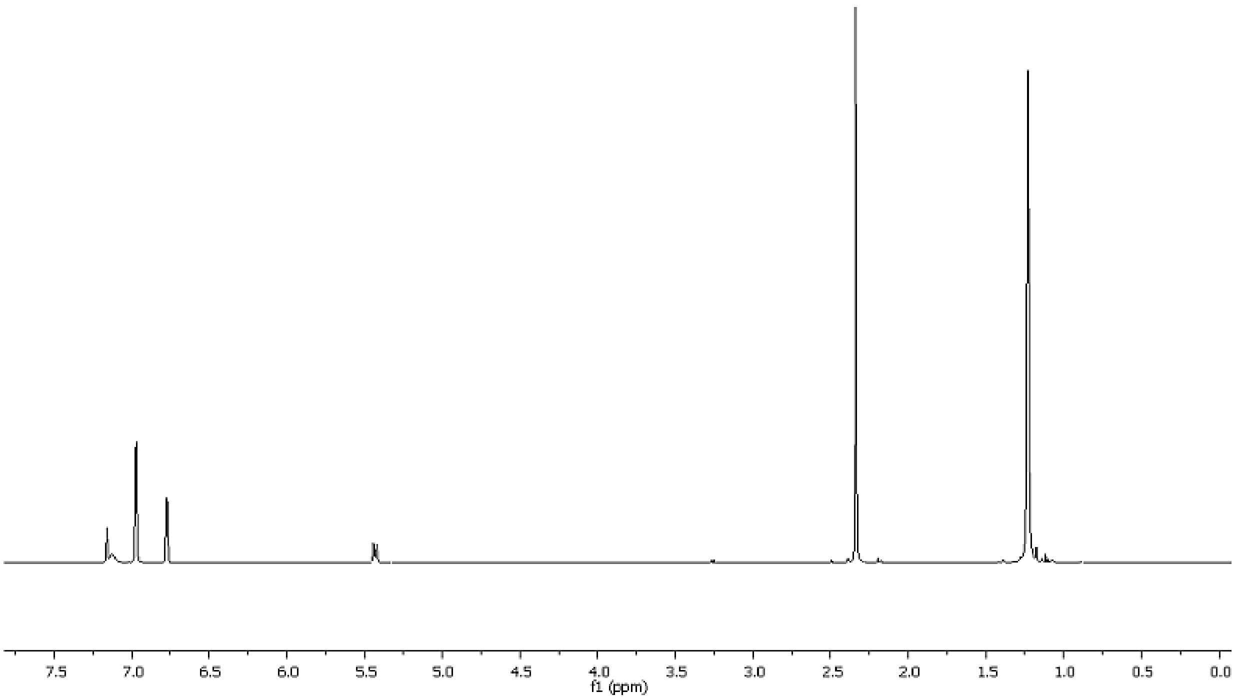

Figure S1. ^{1}H NMR spectrum of (4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$ in C_6D_6.

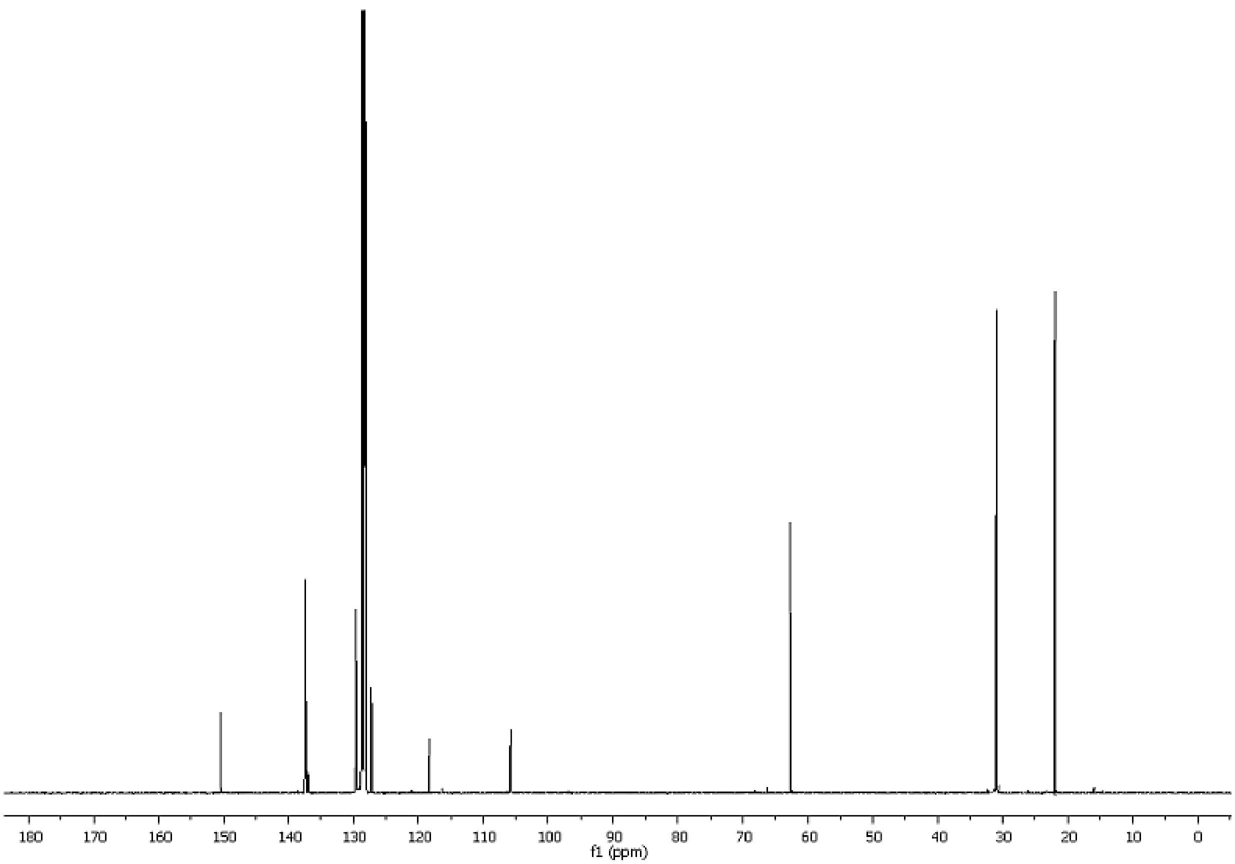

Figure S2. ^{13}C NMR spectrum of (4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$ in C_6D_6.

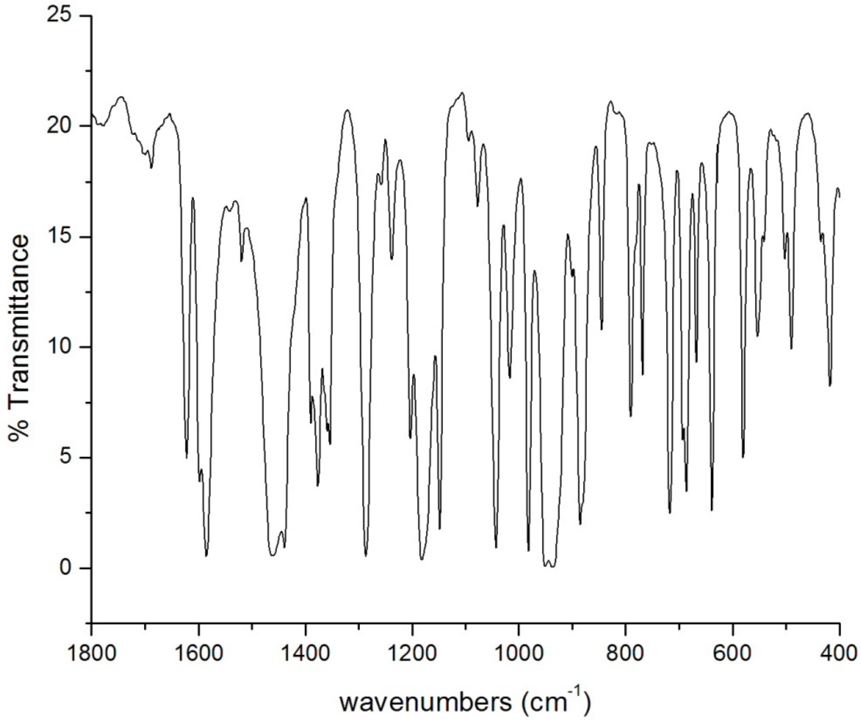

Figure S3. Ir spectrum (nujol mull) of (4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$.

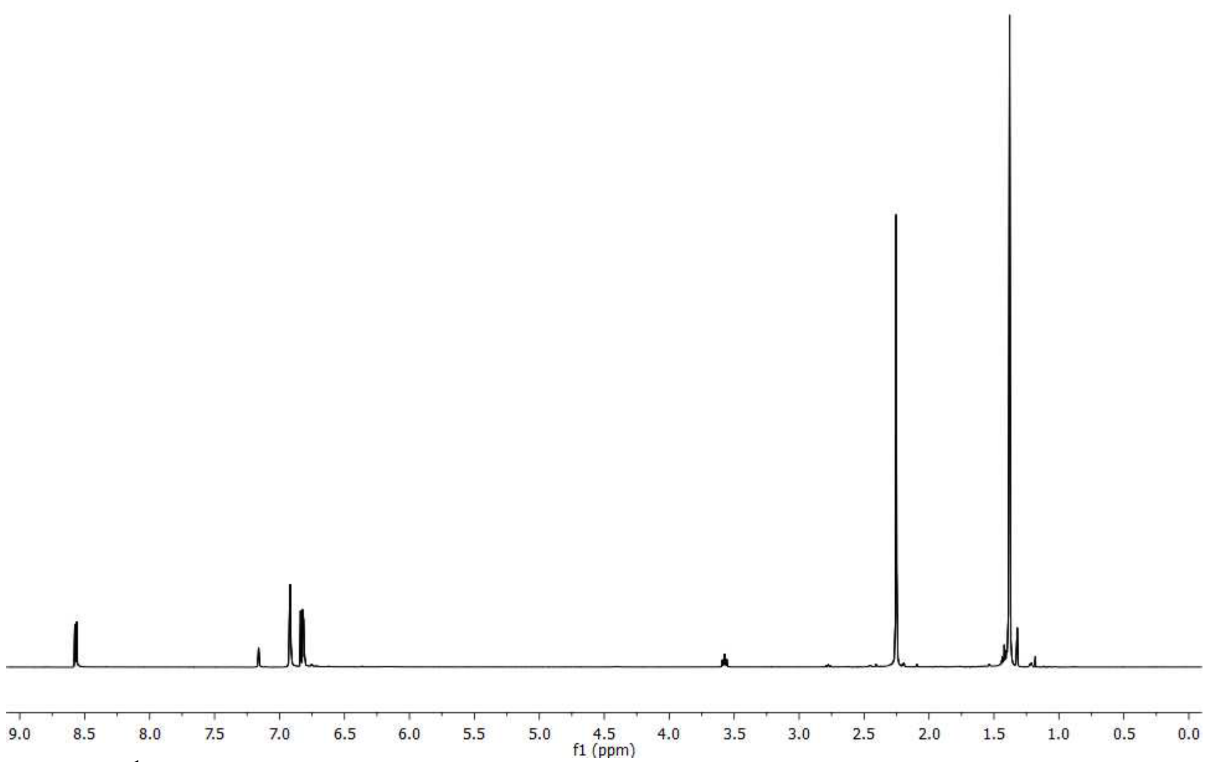

Figure S4. ^{1}H NMR spectrum of mixture of ITi(N[^{t}Bu]Ar)$_3$ and 4,4′-bipyridine, resulting from treatment of (4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$ with I_2.

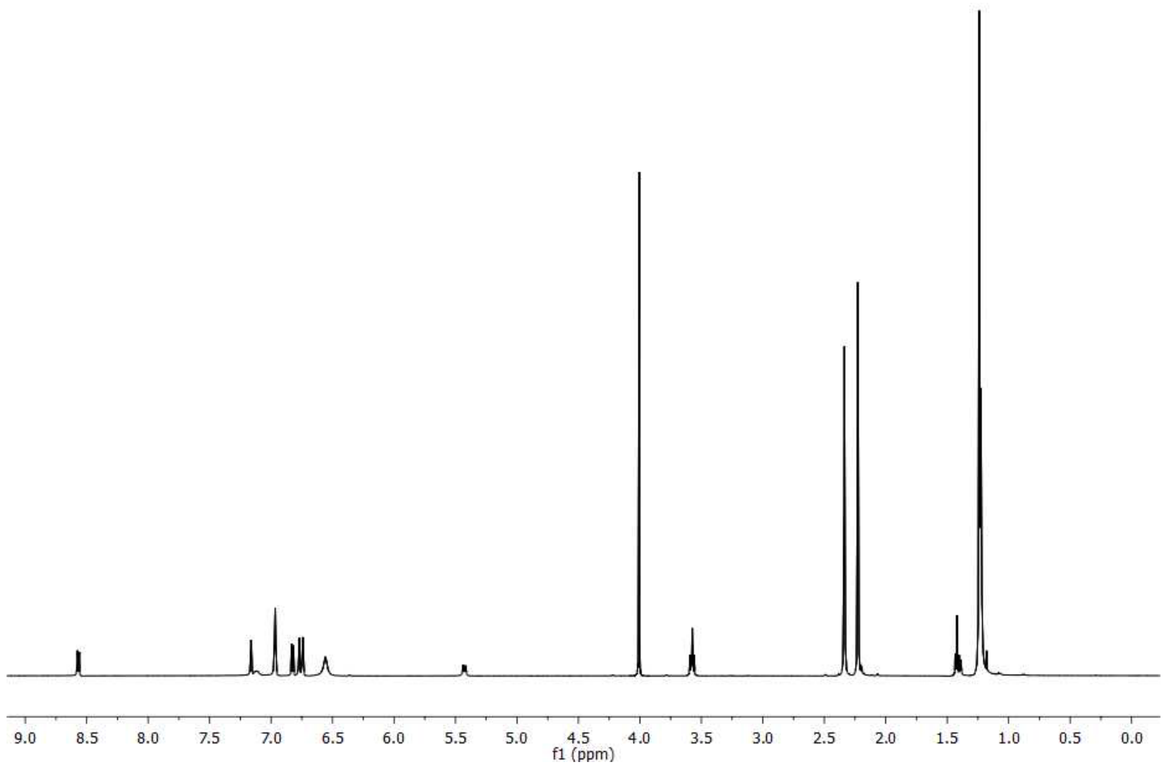

Figure S5. ^{1}H NMR spectrum of mixture of (4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$, TfOTi(N[^{t}Bu]Ar)$_3$, 4,4′-bipyridine, and ferrocene.

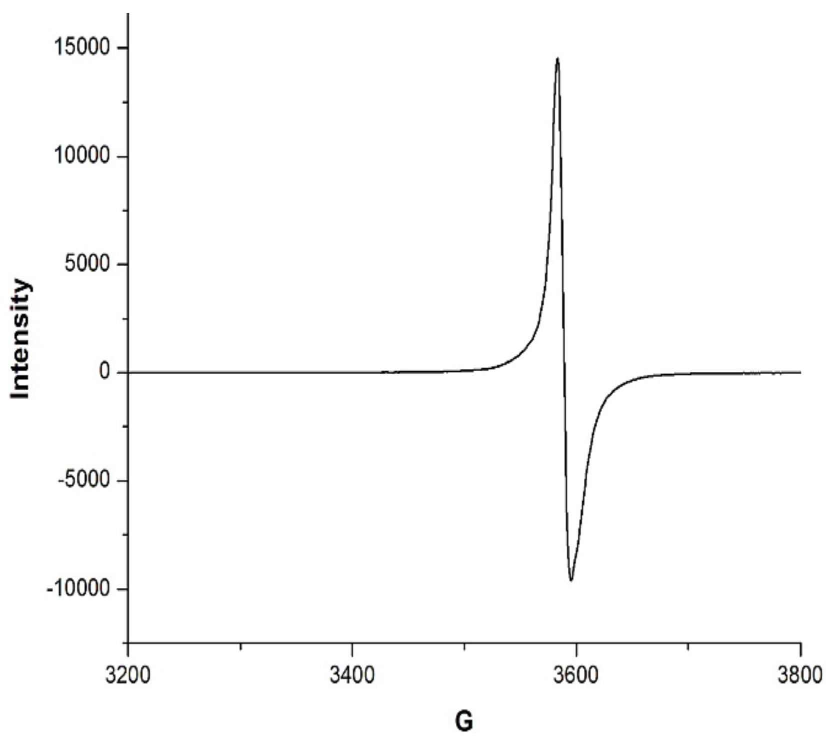

Figure S6. EPR spectrum of material isolated form treatment of (4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$ with excess 1% Na/Hg (C_6D_6).

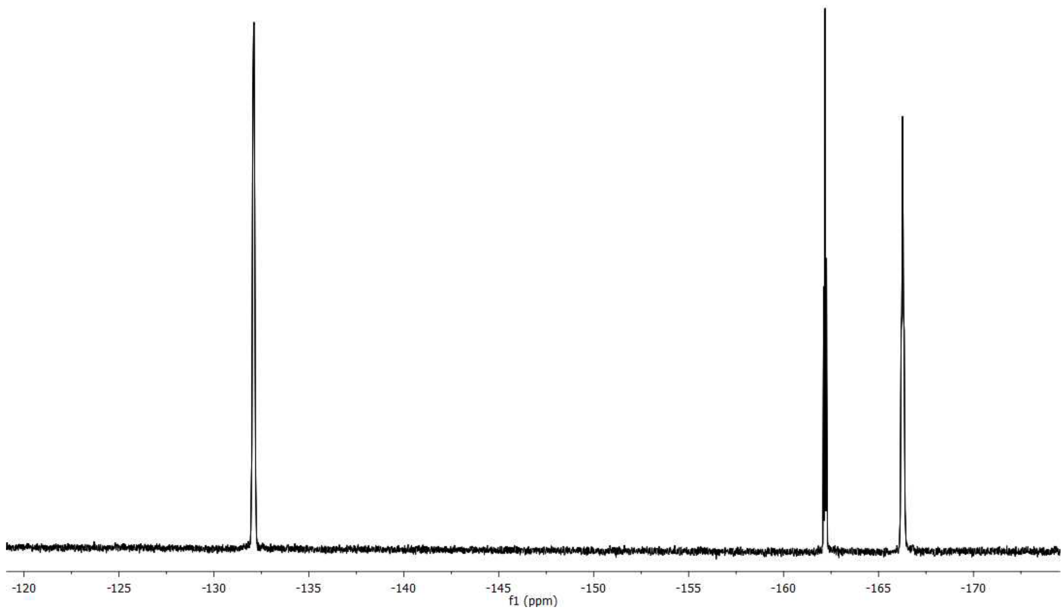

Figure S7. $^{19}F\{^1H\}$ NMR spectrum of $FcB(C_6F_5)_4$ in THF.

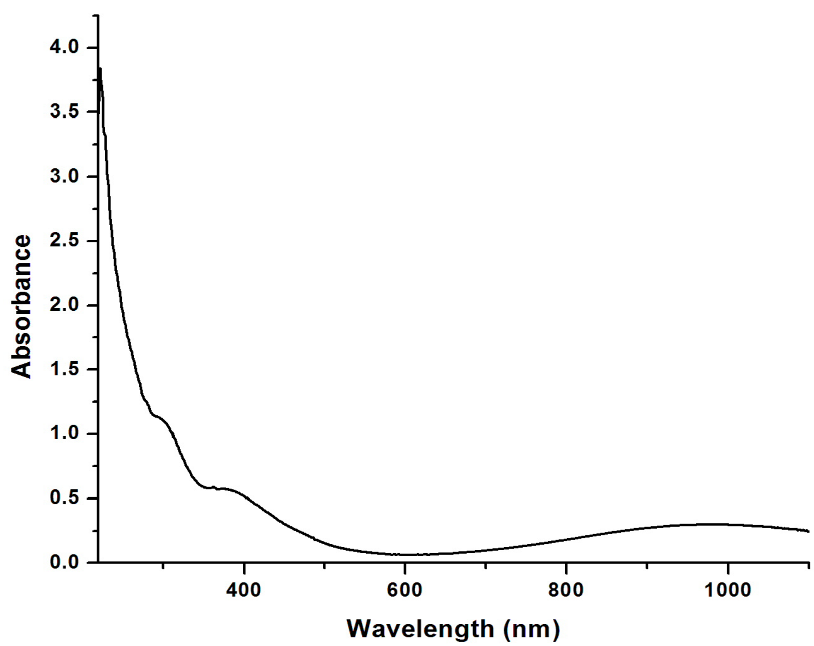

Figure S8. UV/Visible absorbance spectrum of [(4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$][$B(C_6F_5)_4$] in THF solution.

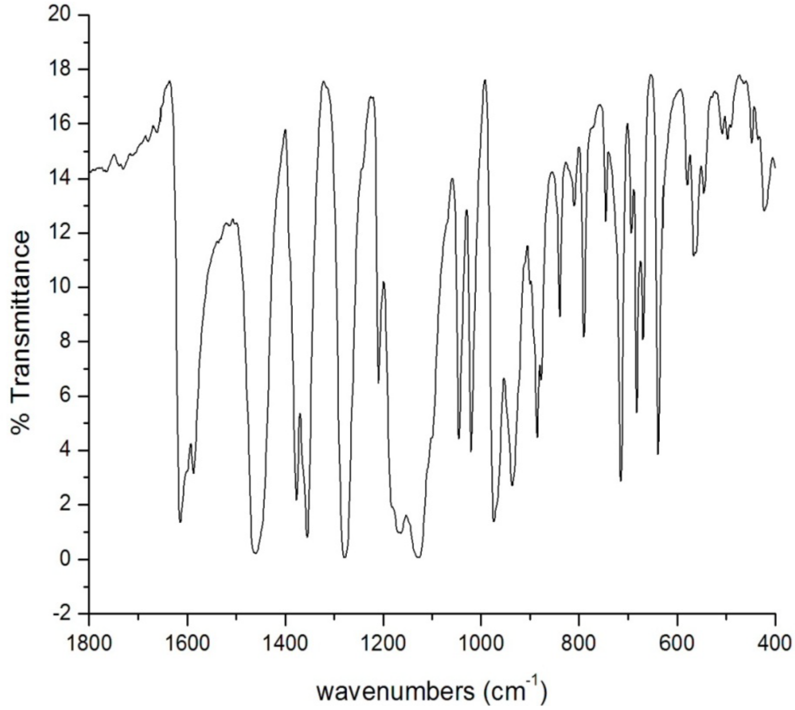

Figure S9. Ir spectrum (nujol mull) of [(4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$][B(C_6F_5)$_4$].

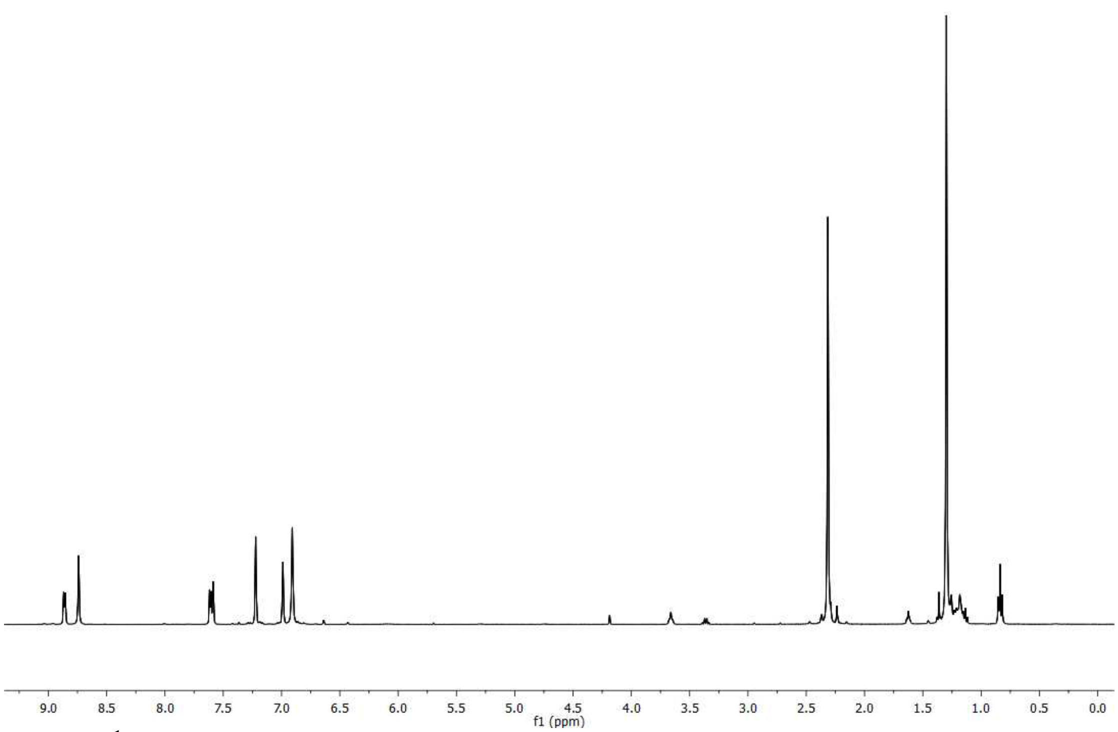

Figure S10. ^{1}H NMR spectrum of [(4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$][B(C_6F_5)$_4$]$_2$ in pyridine-d_5.

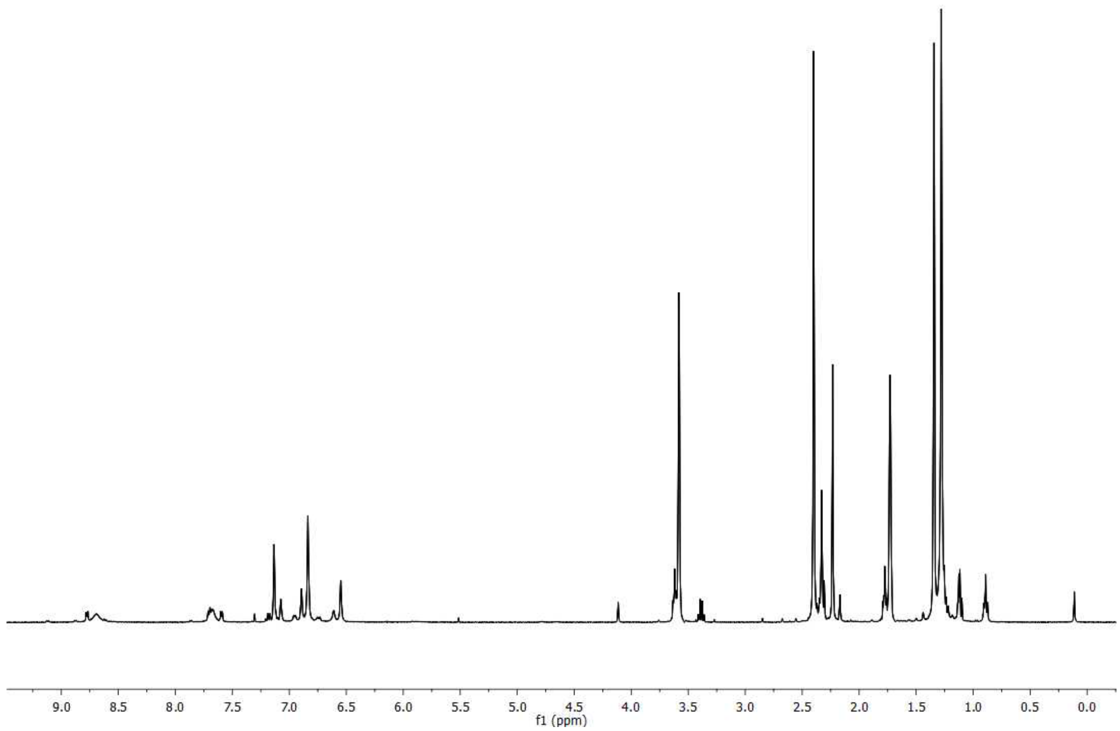

Figure S11. ^{1}H NMR spectrum of $[(4,4'\text{-bipy})\{Ti(N[^{t}Bu]Ar)_3\}_2][B(C_6F_5)_4]_2$ in THF-d_8.

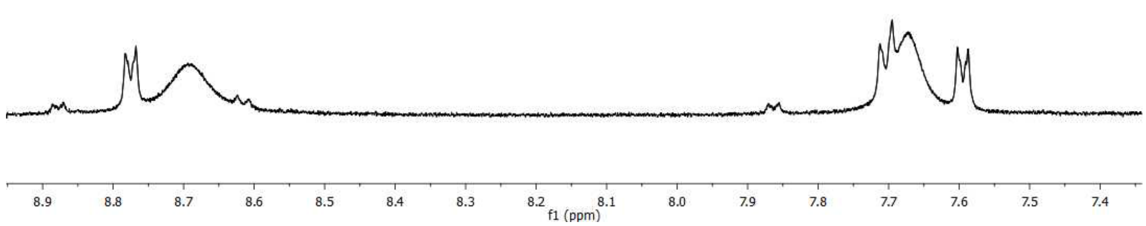

Figure S12. Blow up of 4,4′-bipyridine region of spectrum in Figure S11.

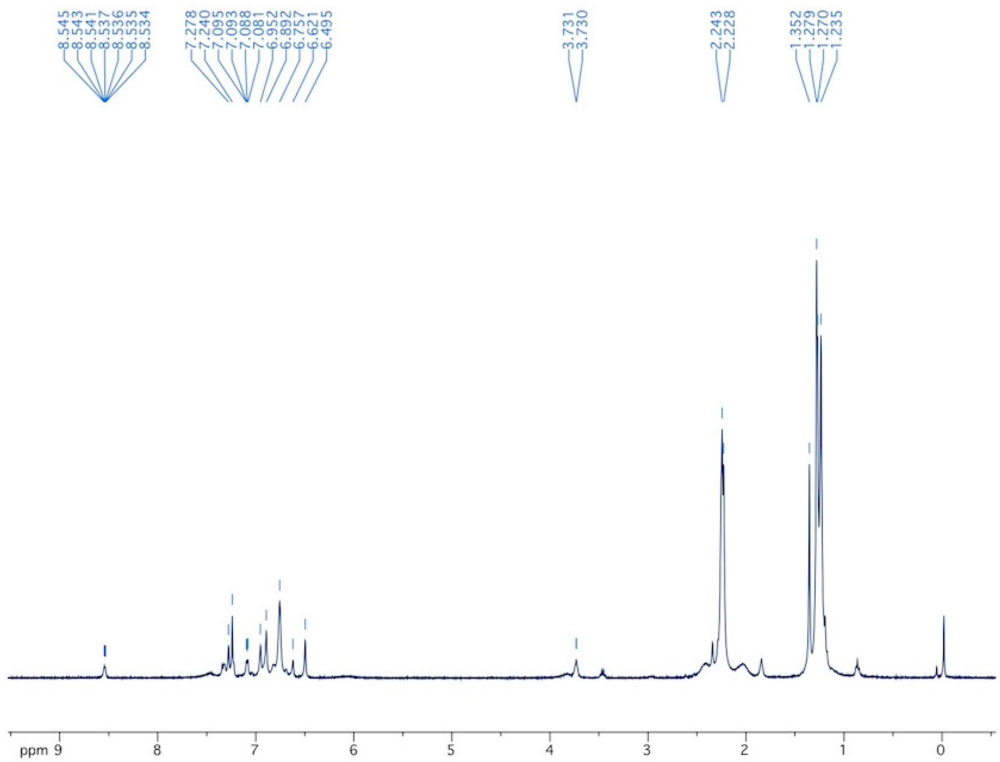

Figure S13. ^{1}H NMR spectrum of [(4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$][B(C$_6$F$_5$)$_4$]$_2$ in CDCl$_3$.

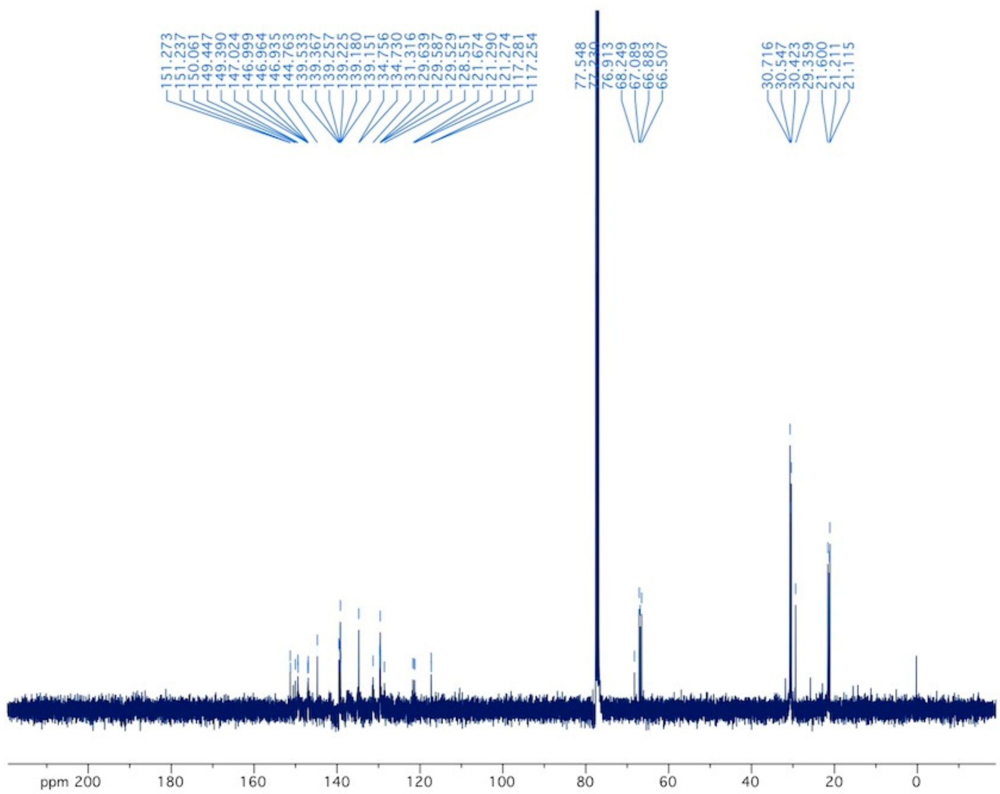

Figure S14. ^{13}C{^{1}H} NMR spectrum of [(4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$][B(C$_6$F$_5$)$_4$]$_2$ in CDCl$_3$.

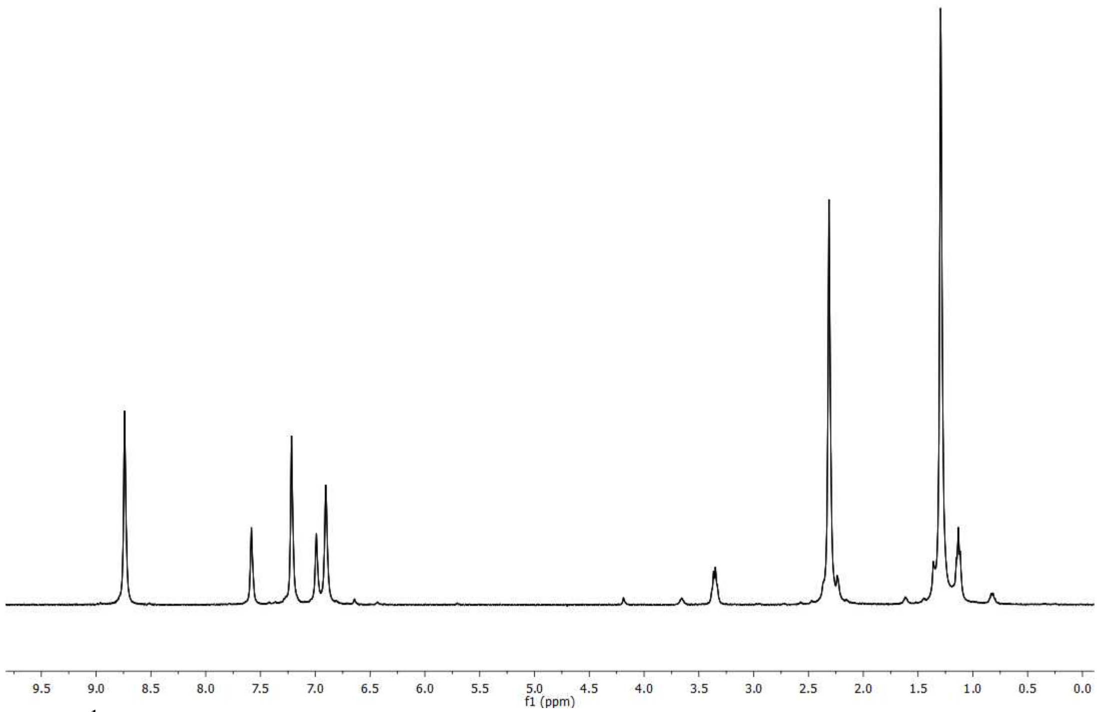

Figure S15. [1]H NMR spectrum of [Ti(N[^{t}Bu]Ar)$_3$][B(C_6F_5)$_4$] in pyridine-d_5.

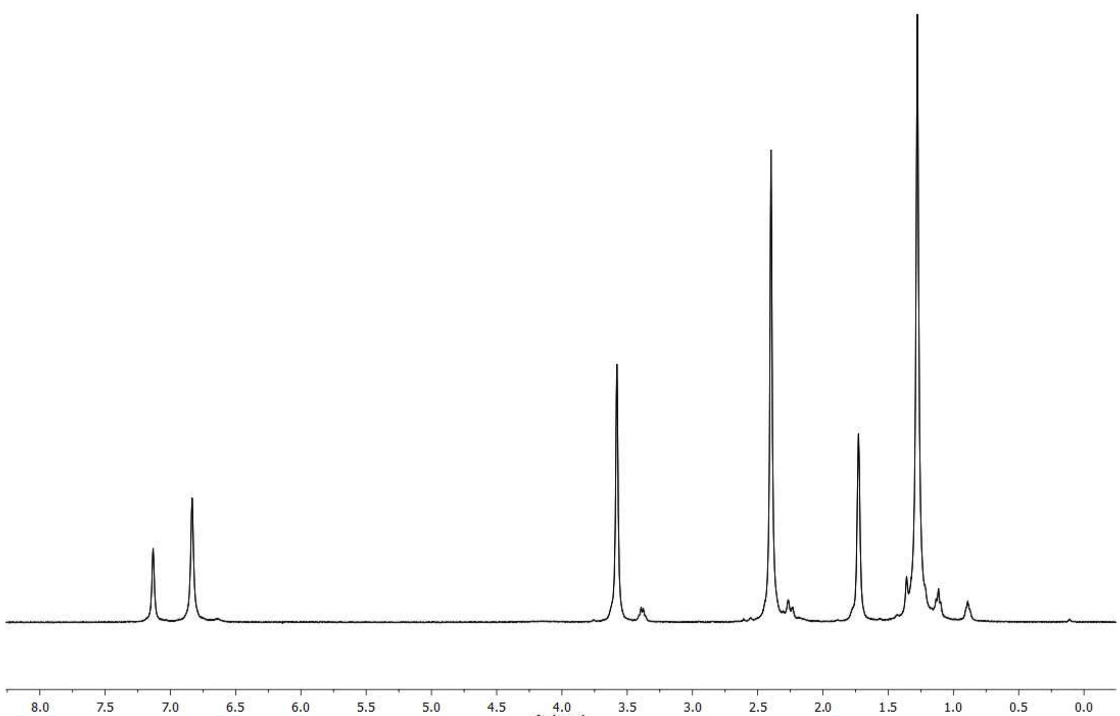

Figure S16. [1]H NMR spectrum of [Ti(N[^{t}Bu]Ar)$_3$][B(C_6F_5)$_4$] in THF-d_8.

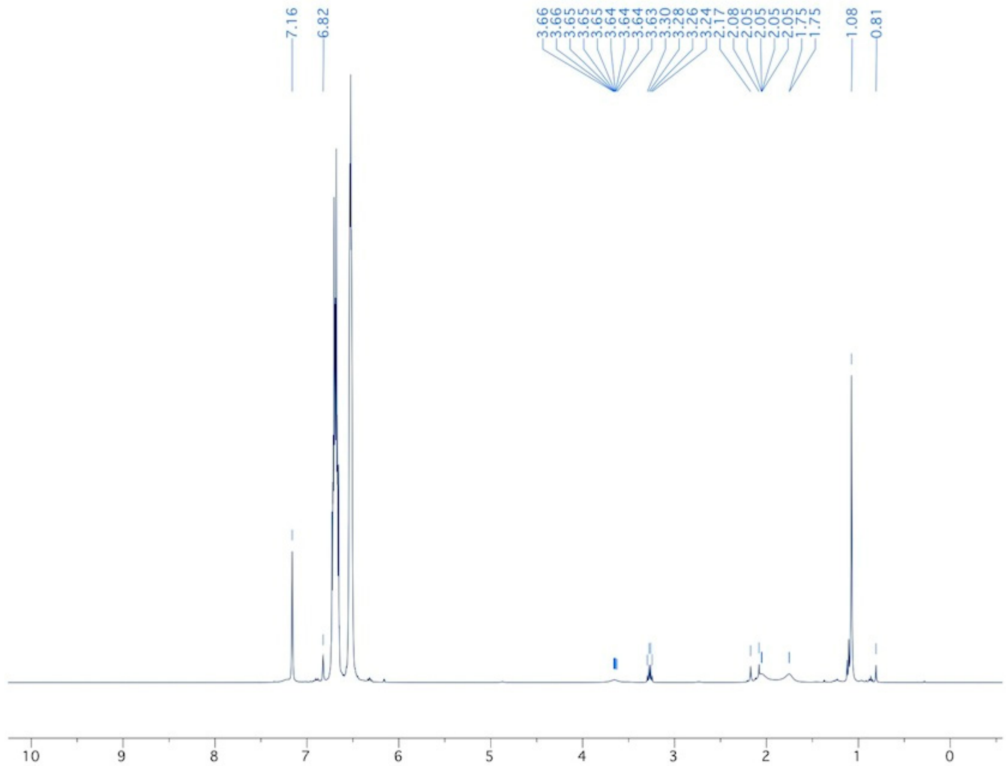

Figure S17. ^{1}H NMR spectrum of [Ti(N[^{t}Bu]Ar)$_3$][B(C_6F_5)$_4$] in C_6D_6/*o*-difluorobenzene.

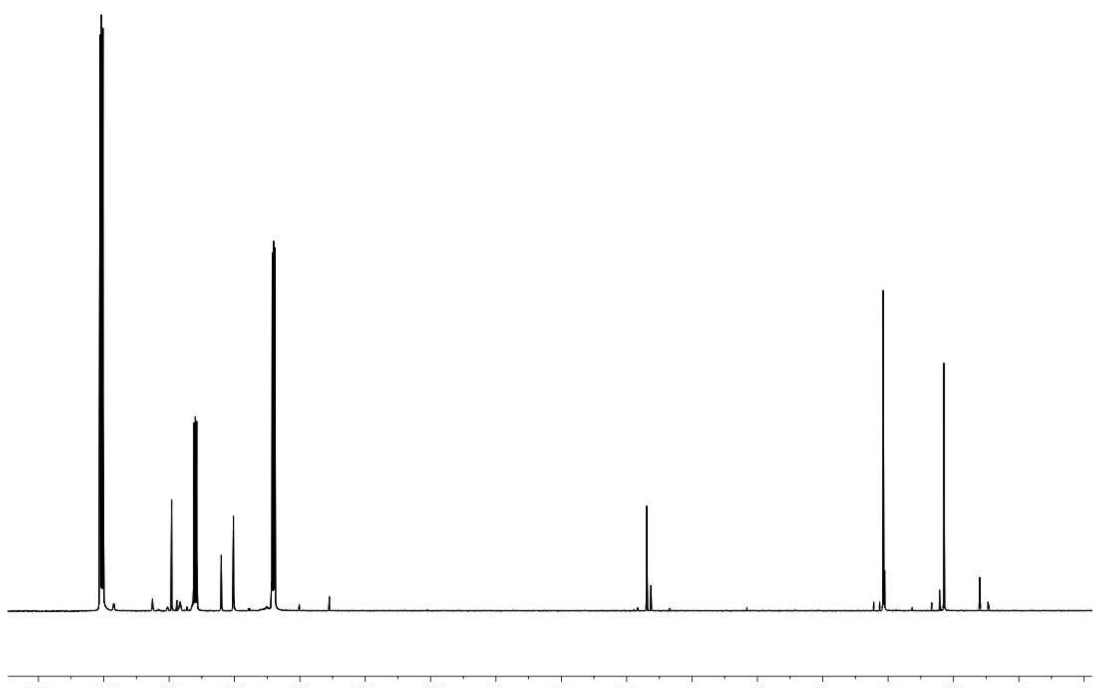

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of [Ti(N[^{t}Bu]Ar)$_3$][B(C_6F_5)$_4$] in pyridine-d_5.

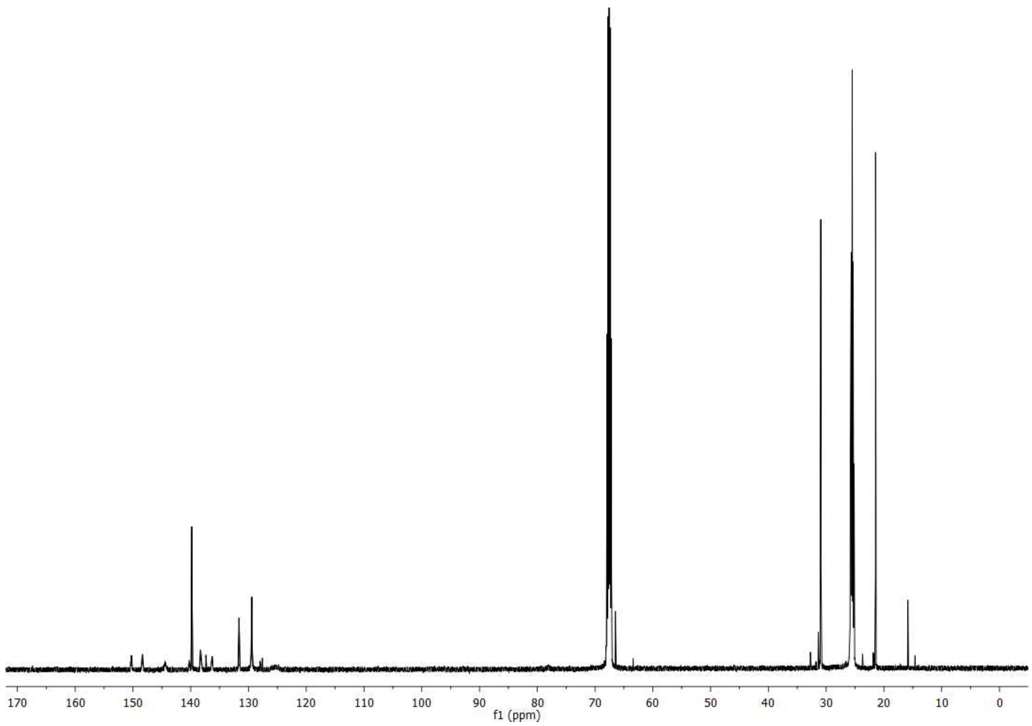

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of $[Ti(N[^tBu]Ar)_3][B(C_6F_5)_4]$ in THF-d_8.

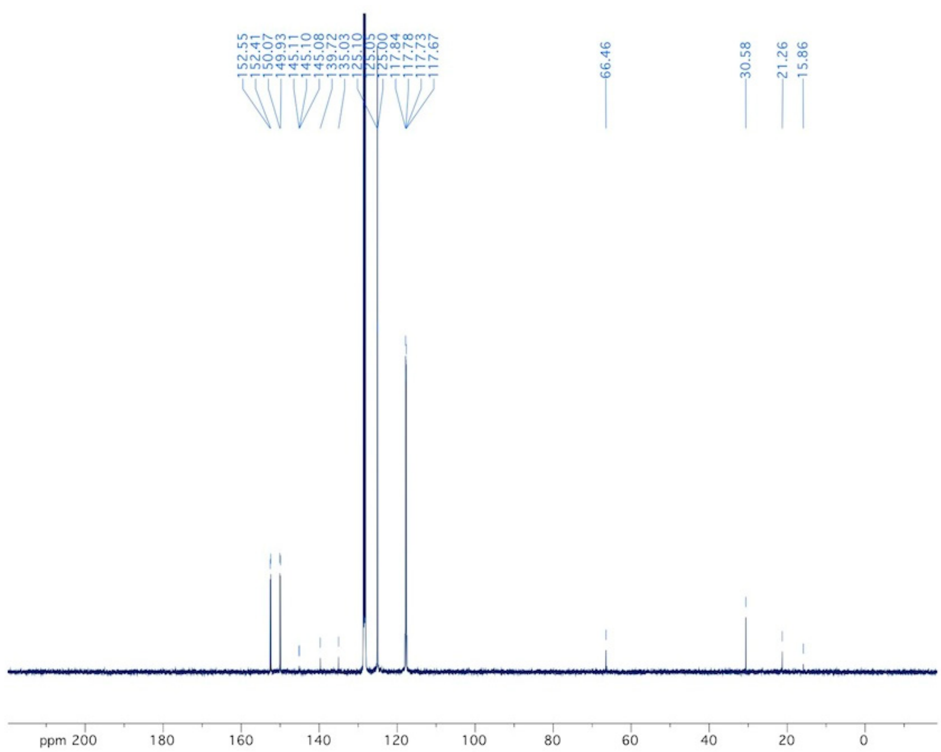

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of $[Ti(N[^tBu]Ar)_3][B(C_6F_5)_4]$ in C_6D_6/*o*-difluorobenzene.

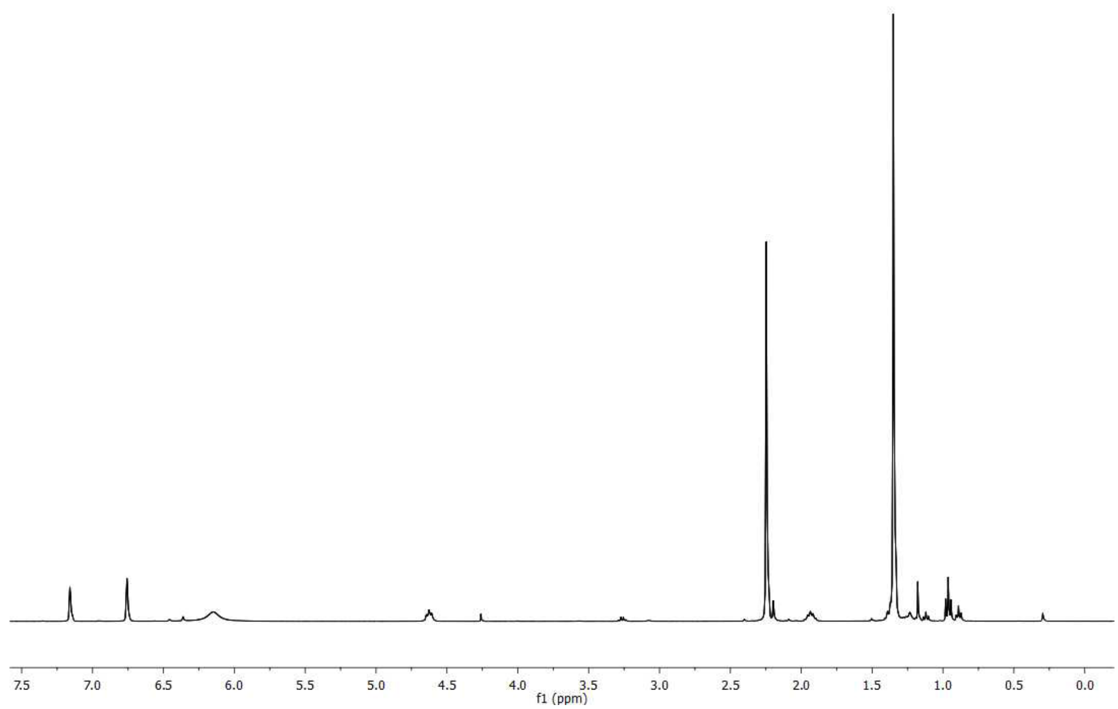

Figure S22. [1]H NMR spectrum of ^{n}BuOTi(N[^{t}Bu]Ar)$_3$ in C_6D_6.

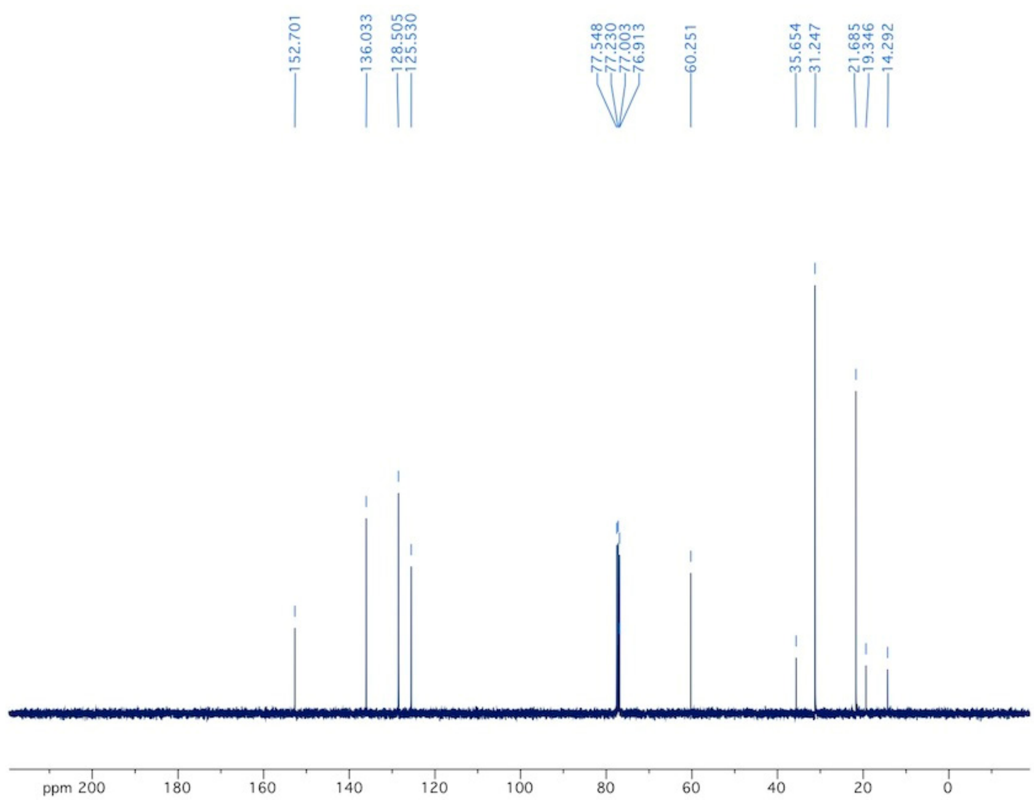

Figure S23. [13]C{[1]H} NMR spectrum of ^{n}BuOTi(N[^{t}Bu]Ar)$_3$ in $CDCl_3$.

Table S1: Crystallographic Data for **2**, **4·(*o*-$F_2C_6H_4$)**, and **5·(THF)(Et_2O)** where **2** = (4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$, **4** = [(4,4′-bipy){Ti(N[^{t}Bu]Ar)$_3$}$_2$][B(C_6F_5)$_4$]$_2$, and **5·(THF)** = [(THF)Ti(N[^{t}Bu]Ar)$_3$][B(C_6F_5)$_4$].

	2·(C_7H_8)$_2$(C_5H_{12})	**4·(*o*-$F_2C_6H_4$)**	**5·(THF)(Et_2O)**
CCDC No.	893531	893532	893533
Formula	$C_{101}H_{144}N_8Ti_2$	$C_{136}H_{120}B_2N_8F_{42}Ti_2$	$C_{68}H_{72}BN_3O_2F_{20}Ti$
Color	orange	orange	orange
Morphology	block	shard	block
Size, mm^3	0.50 × 0.50 × 0.35	0.44 × 0.15 × 0.06	0.36 × 0.21 × 0.10
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	*P*−1	*P*−1	*P*−1
Wavelength, Å	0.71073	0.71073	0.71073
Temperature, K	100(2)	100(2)	100(2)
a, Å	11.7441 (10)	12.9999(16)	13.3000(11)
b, Å	14.5289 (12)	14.4638(18)	13.5930(11)
c, Å	15.3188 (13)	35.939(5)	19.2817(15)
α, deg	80.1400(10)	82.097(2)	107.9740(10)
β, deg	69.8540 (10)	80.086(2)	95.3190(10)
γ, deg	71.3520(10)	83.947(2)	95.813(2)
V, Å^3	2319.6(3)	6570.2(14)	3270.3(5)
Z	1	2	2
D_χ, g cm^{-3}	1.121	1.406	1.424
F(000)	850	2848	1448
μ, (Mo *Kα*), mm^{-1}	0.221	0.234	0.235
No. Reflections	60016	137441	77101
No. Ind. Reflections	12435	20905	15001
R_{int}	0.0353	0.0805	0.0505
$\theta_{max}/\theta_{min}$	29.13 / 1.42	24.11 / 0.58	27.48 / 1.55
Completeness, %	99.7	100.0	100.0
Goodness of Fit	1.058	1.041	1.030
$R(F)^a$ (I > 2σ)	0.0528	0.0457	0.0399
$WR(F^2)^a$	0.1595	0.1034	0.0984
Largest difference peak/hole (e/ Å^3)	+ 1.402 / − 0.857	+ 0.284 / − 0.1034	+ 0.348 / − 0.378

[a] Quantity minimized = $wR(F^2) = (\sum[w(F_o^2\text{-}F_c^2)^2] / \sum[(wF_o^2)^2])^{1/2}$; $R = \sum\Delta / \sum(F_o)$, $\Delta = |F_o\text{-}F_c|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = 2F_c^2 + \text{Max}(F_o, 0)/3$

Table S2: Crystallographic Data for **5** and **6**. Where **5** = $[Ti(N[^tBu]Ar)_3][B(C_6F_5)_4]$ and **6** = $^nBuOTi(N[^tBu]Ar)_3$.

	5	**6**
CCDC No.	893534	893535
Formula	$C_{63}H_{59.90}BN_3F_{20.22}$ Ti	$C_{40}H_{63}N_3OTi$
Color	orange	yellow
Morphology	block	block
Size, mm^3	0.40 × 0.40 × 0.10	0.30 × 0.30 × 0.21
Crystal System	Monoclinic	Cubic
Space Group	$P2_1/n$	$Pa-3$
Wavelength, Å	0.71073	0.71073
Temperature, K	100(2)	100(2)
a, Å	16.8241(15)	19.7299(9)
b, Å	20.9559(19)	19.7299(9)
c, Å	17.3595(15)	19.7299(9)
α, deg	90	90
β, deg	99.905(2)	90
γ, deg	90	90
V, Å^3	6029.1(9)	7680.2(6)
Z	4	8
D_χ, g cm^{-3}	1.434	1.125
$F(000)$	2672	2832
μ, (Mo $K\alpha$), mm^{-1}	0.247	0.255
No. Reflections	121467	166583
No. Ind. Reflections	14973	3187
R_{int}	0.0796	0.0635
$\theta_{max}/\theta_{min}$	28.28 / 1.54	28.26 / 1.79
Completeness, %	100.0	100.0
Goodness of Fit	1.006	1.076
$R(F)^a$ (I > 2σ)	0.0424	0.0532
$WR(F^2)^a$	0.0998	0.1626
Largest difference peak/hole (e/ Å ^{3})	+ 0.346 / − 0.418	+ 0.954 / − 0.463

[a] Quantity minimized = $wR(F^2) = (\sum[w(F_o^2-F_c^2)^2] / \sum[(wF_o^2)^2])^{1/2}$; $R = \sum\Delta / \sum(F_o)$, $\Delta = |F_o-F_c|$, $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = 2F_c^2 + \mathrm{Max}(F_o, 0) / 3$

Optimized Geometries in Cartesian Coordinates (Å)

Truncated Model Version of **2**, (4,4′-bipy){Ti(N[Me]Ph)$_3$}$_2$

C	-0.127856	-0.019634	0.692230
C	0.867200	-0.345028	1.678584
C	0.595316	-0.364073	3.012997
N	-0.645226	-0.071071	3.559384
C	-1.623071	0.227791	2.619120
C	-1.413577	0.257900	1.276618
Ti	-1.136518	-0.038298	5.500526
N	0.345444	-0.799950	6.478909
C	1.519383	0.042700	6.726929
C	0.454887	-2.092782	7.070219
C	0.833405	-3.203043	6.300953
C	0.965231	-4.464568	6.883927
C	0.723854	-4.640785	8.246916
C	0.346620	-3.542595	9.023069
C	0.216208	-2.282430	8.441443
N	-2.748194	-1.068594	5.743180
C	-2.889486	-2.322077	4.992015
C	-3.871860	-0.781186	6.568759
C	-3.828185	-1.035460	7.947827
C	-4.936809	-0.783687	8.757344
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H	1.710095	0.186340	7.800443
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H	0.826418	-5.623132	8.700339
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H	-2.036556	-2.468723	4.322518
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H	-1.119234	1.295931	8.071945
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H	-2.814671	5.695699	2.695404
H	-0.438851	4.969489	2.865359
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C	-0.595316	0.364073	-3.012997
N	0.645226	0.071071	-3.559384
C	1.623071	-0.227791	-2.619120
C	1.413577	-0.257900	-1.276618
Ti	1.136518	0.038298	-5.500526
N	-0.345444	0.799950	-6.478909
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C	3.871860	0.781186	-6.568759
C	3.828185	1.035460	-7.947827
C	4.936809	0.783687	-8.757344
C	6.113213	0.277746	-8.205021
C	6.169298	0.021495	-6.832881
C	5.061908	0.270543	-6.023427
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