Electronic Supplementary information

Titanium imido complexes stabilised by bis(iminophosphoranyl)methanide ligands: influence of N-substituents on solution dynamics and reactivity †

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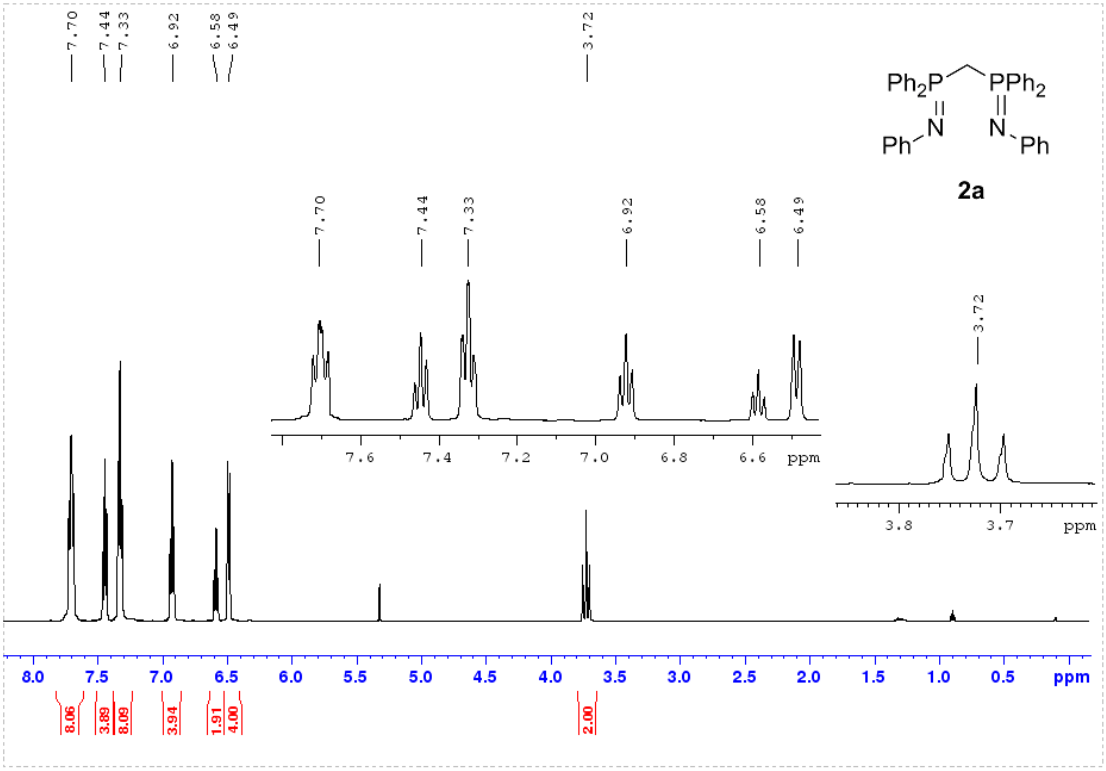
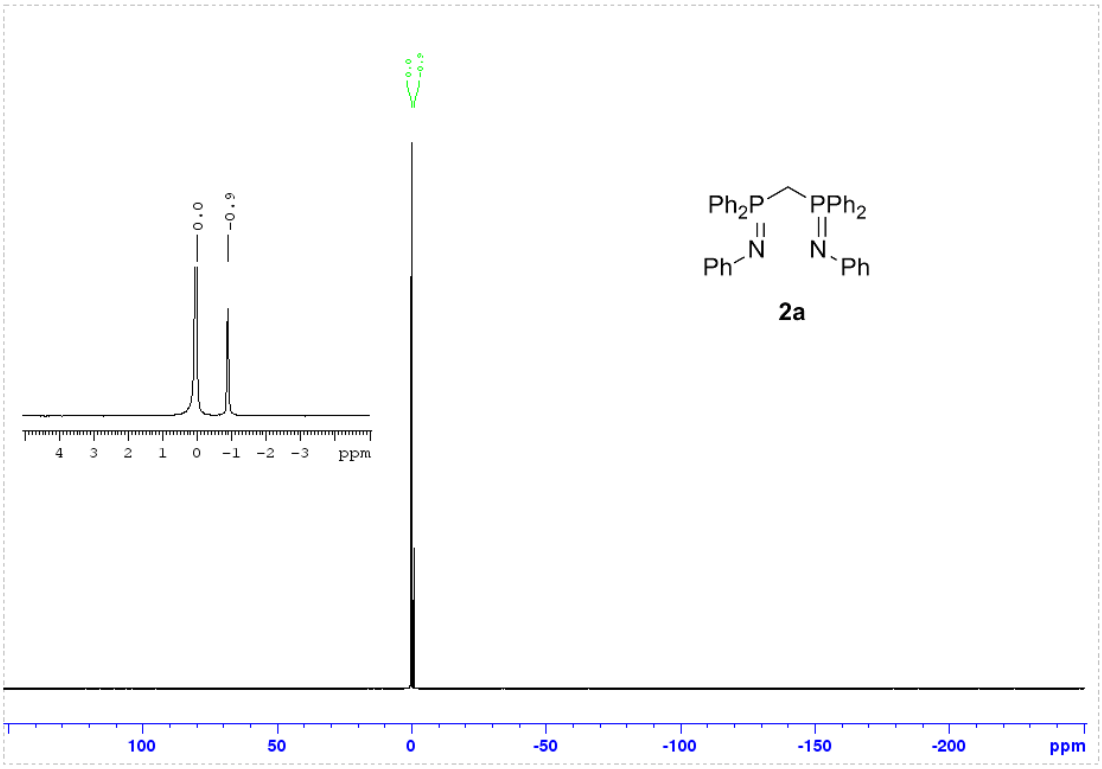
1. *Preparation of compounds*

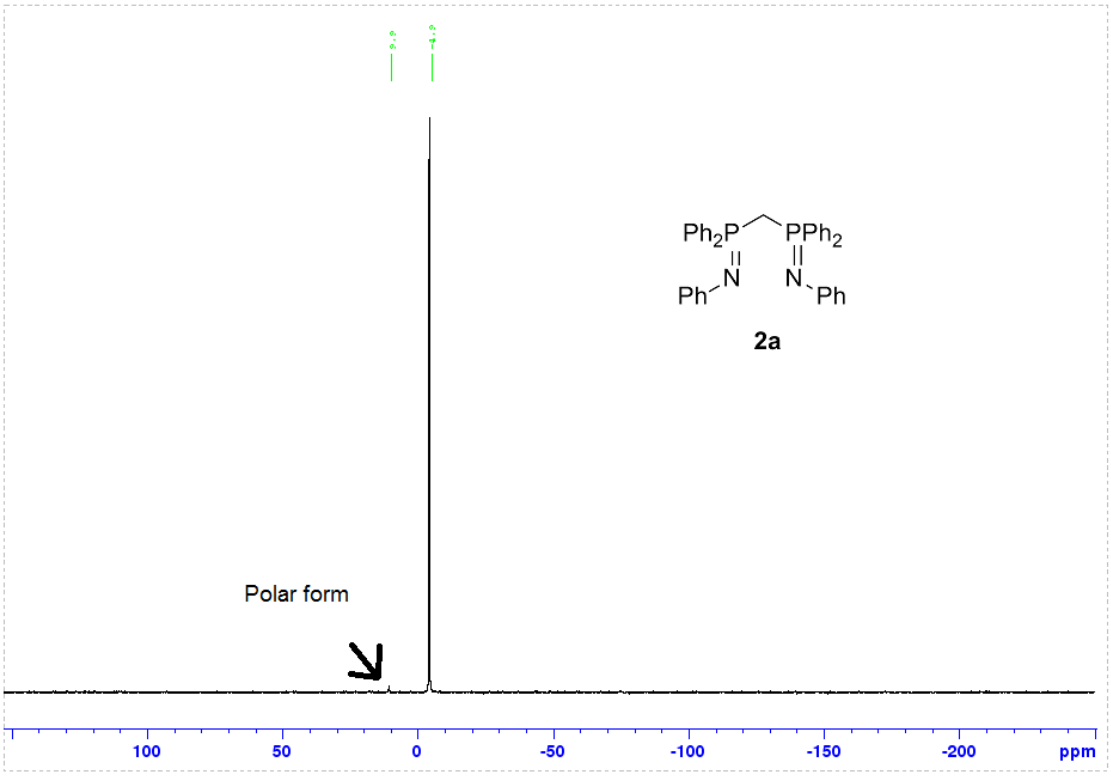
*Preparation of ligand **2a***



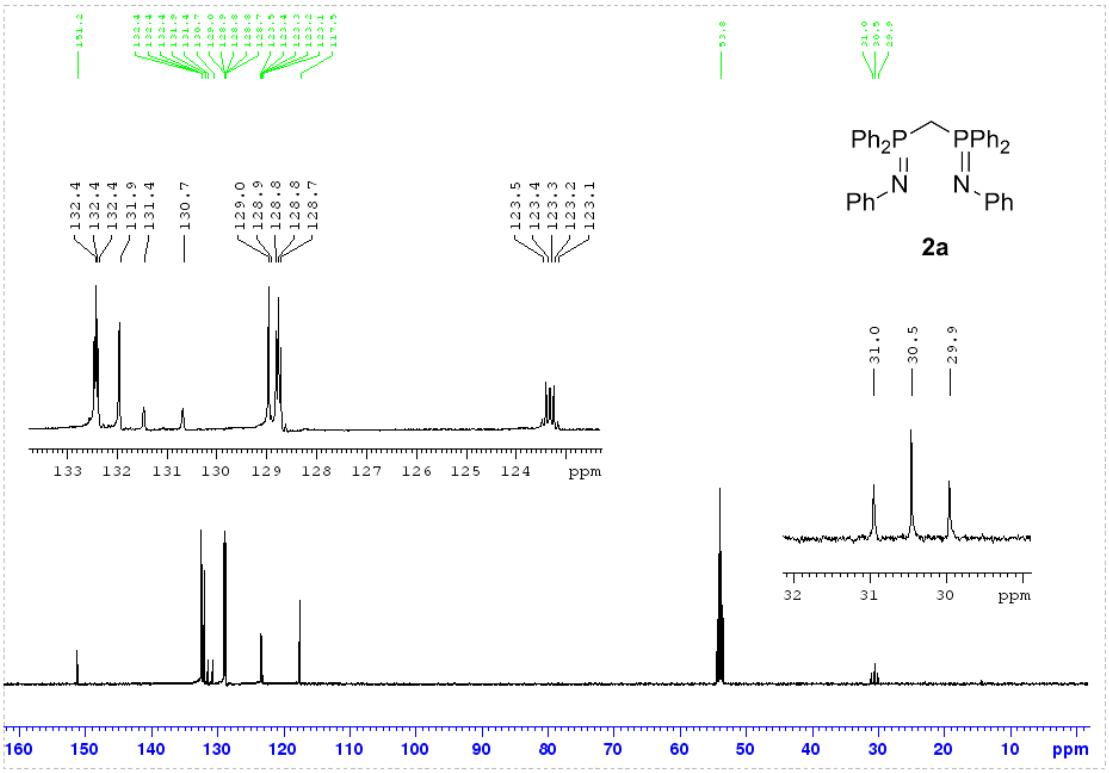
^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)



$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 300 K)

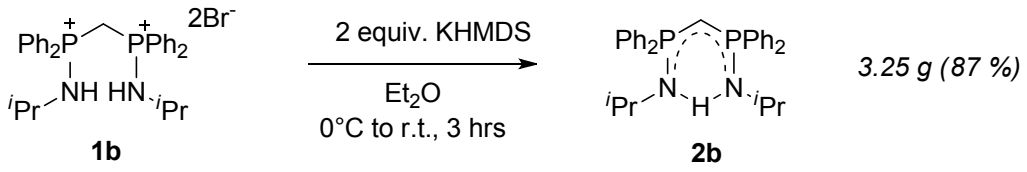


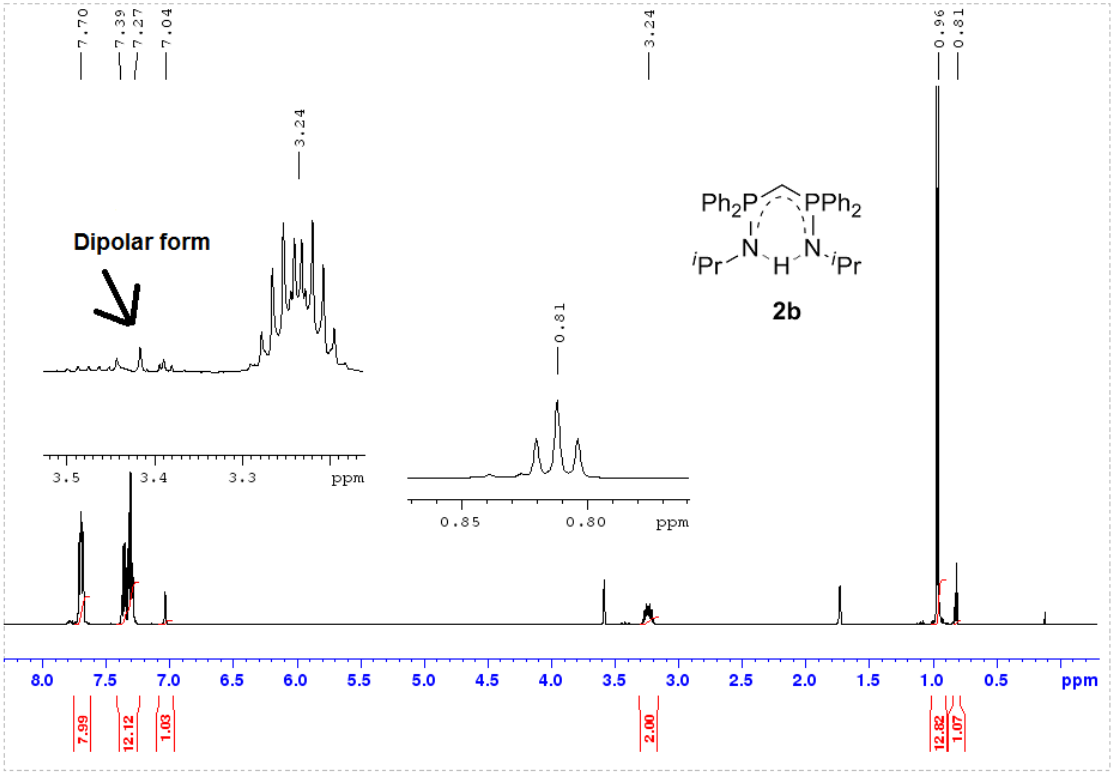
$^{31}P\{^{1}H\}$ NMR (202 MHz, d_8-THF, 300 K)



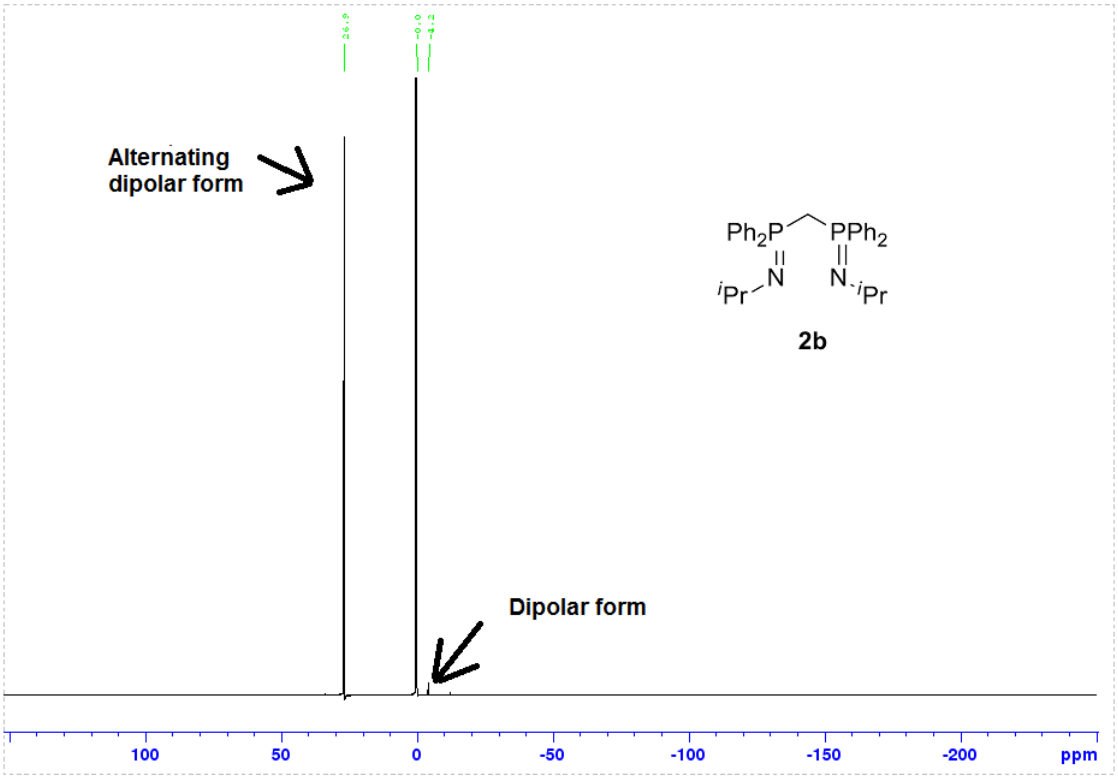
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 300 K)

*Preparation of ligand **2b***

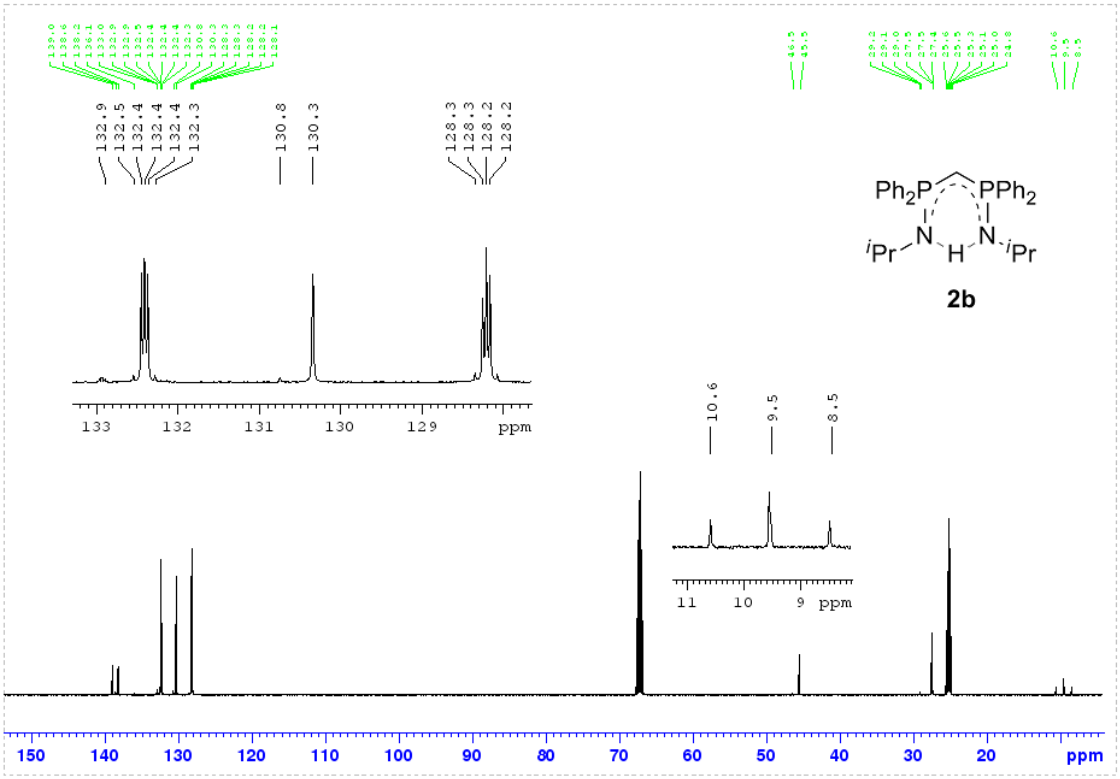




^{1}H NMR (500 MHz, d_8-THF, 300 K)

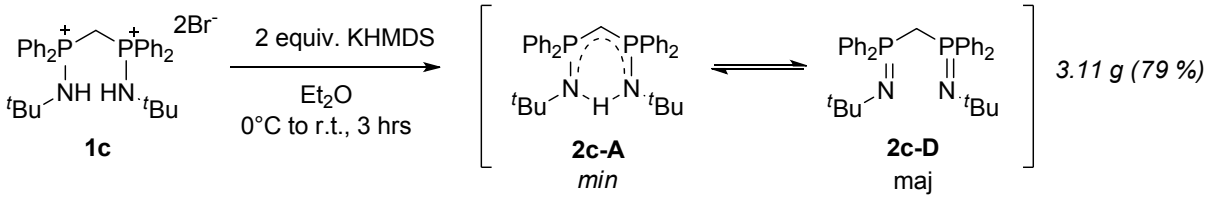


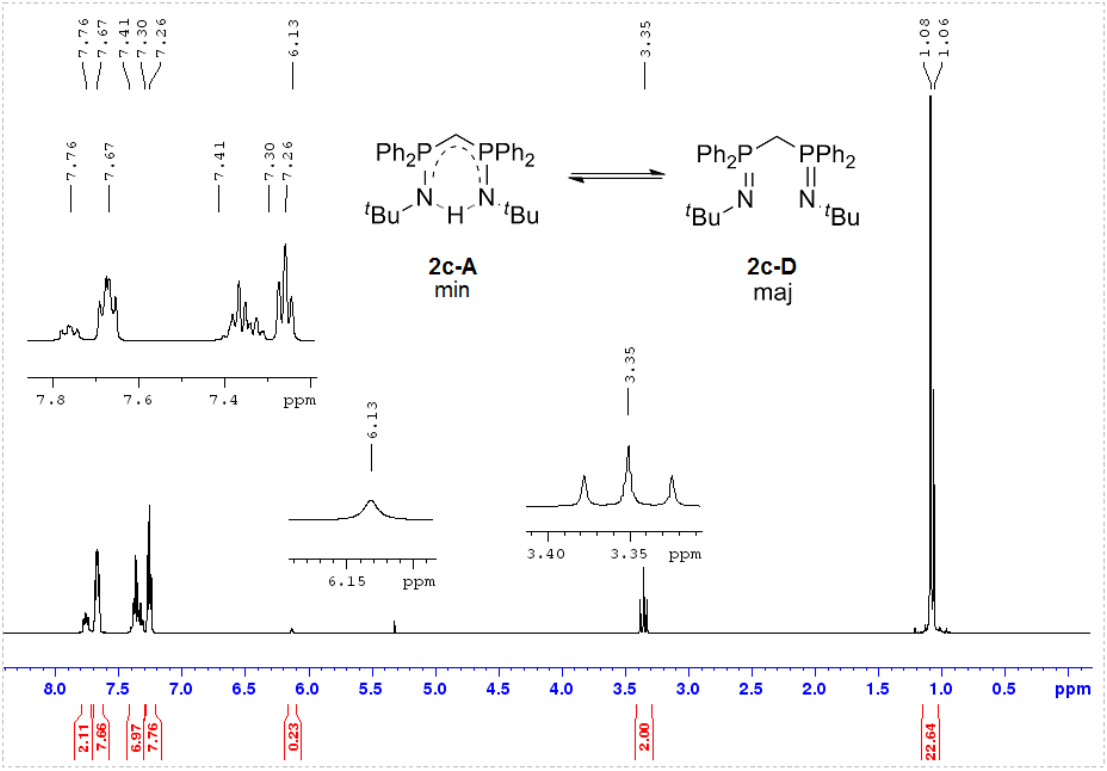
^{31}P{^{1}H} NMR (202 MHz, d_8-THF, 300 K)



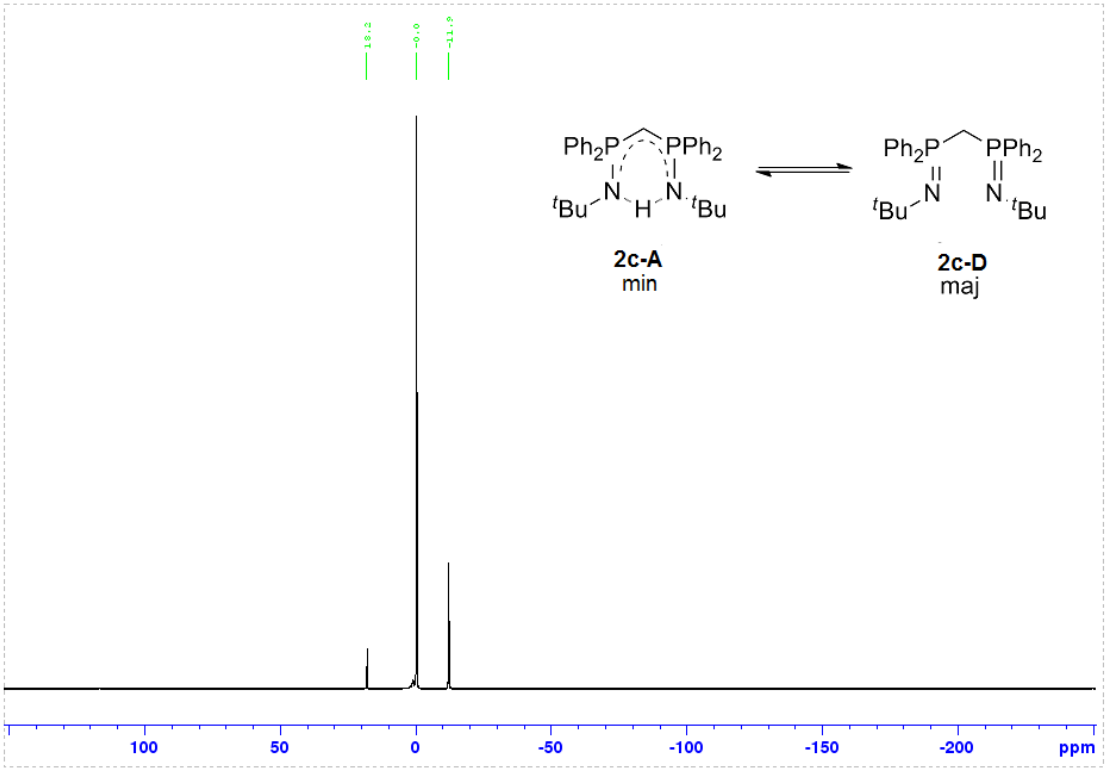
$^{13}C\{^{1}H\}$ NMR (126 MHz, d_8-THF, 300 K)

*Preparation of ligand **2c***

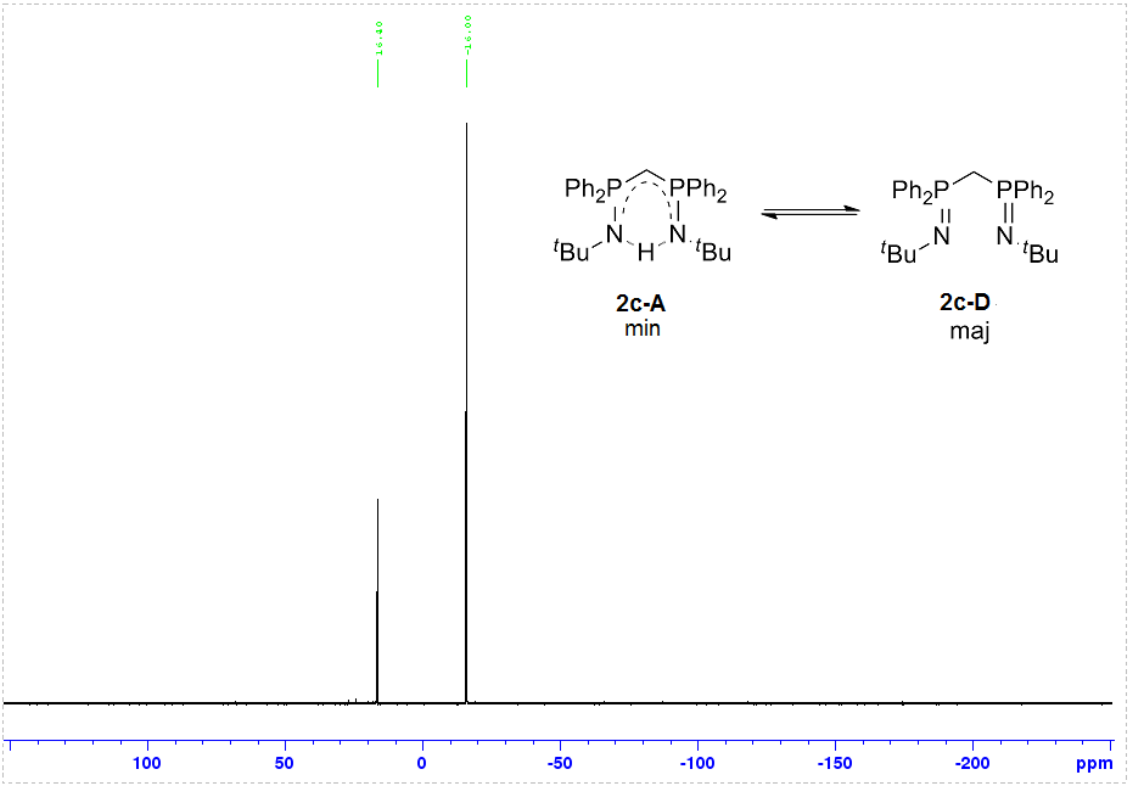




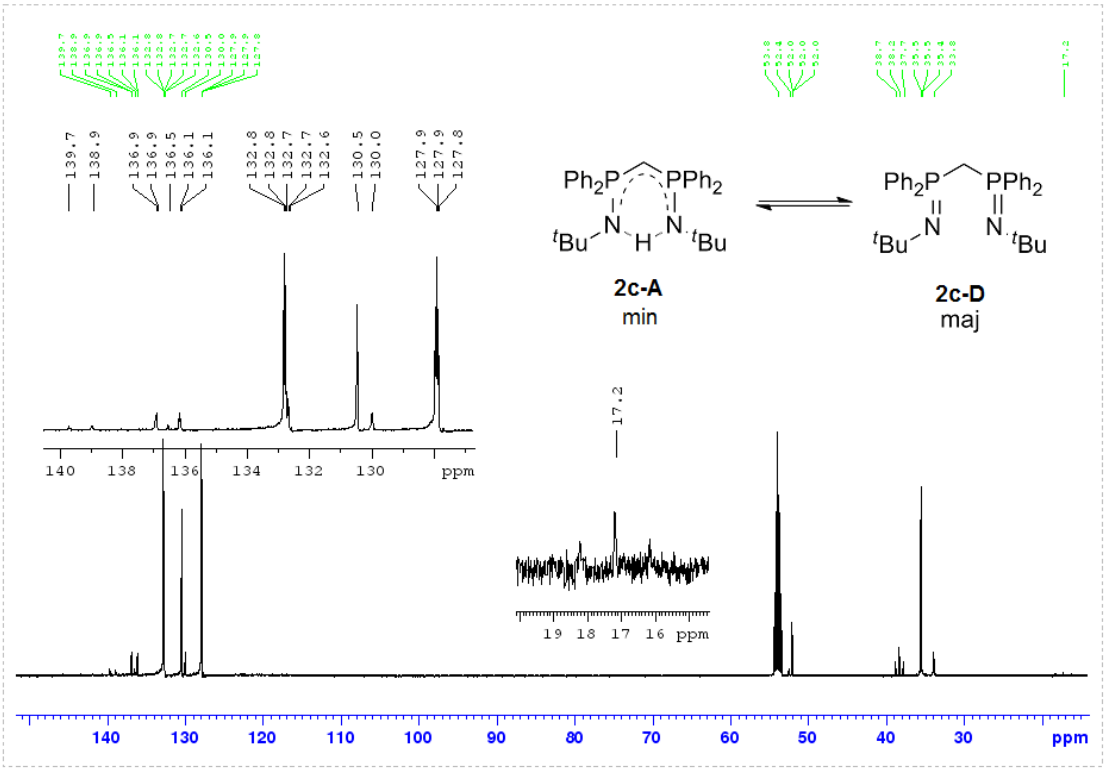
^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)



^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 300 K)

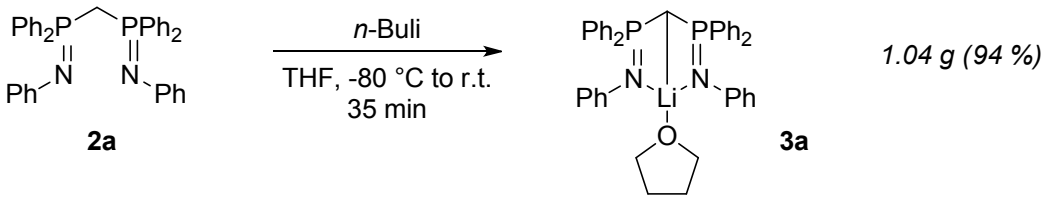


$^{31}P\{^{1}H\}$ NMR (202 MHz, d_8-THF, 300 K)

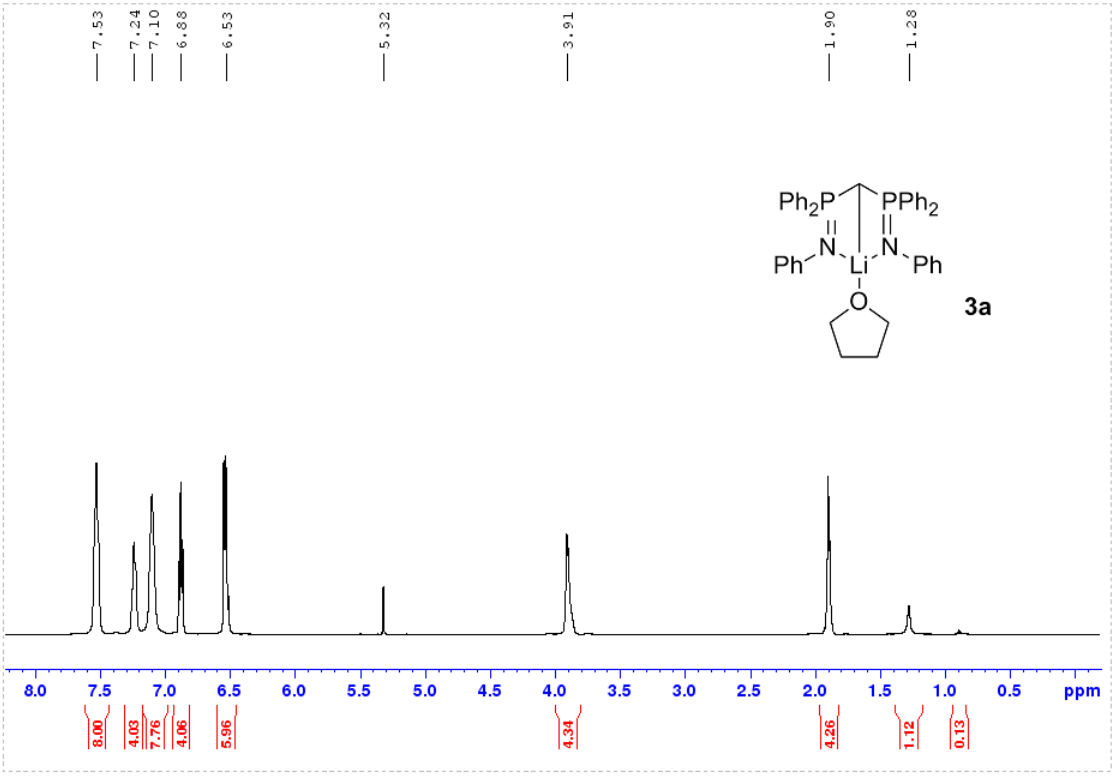


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 300 K)

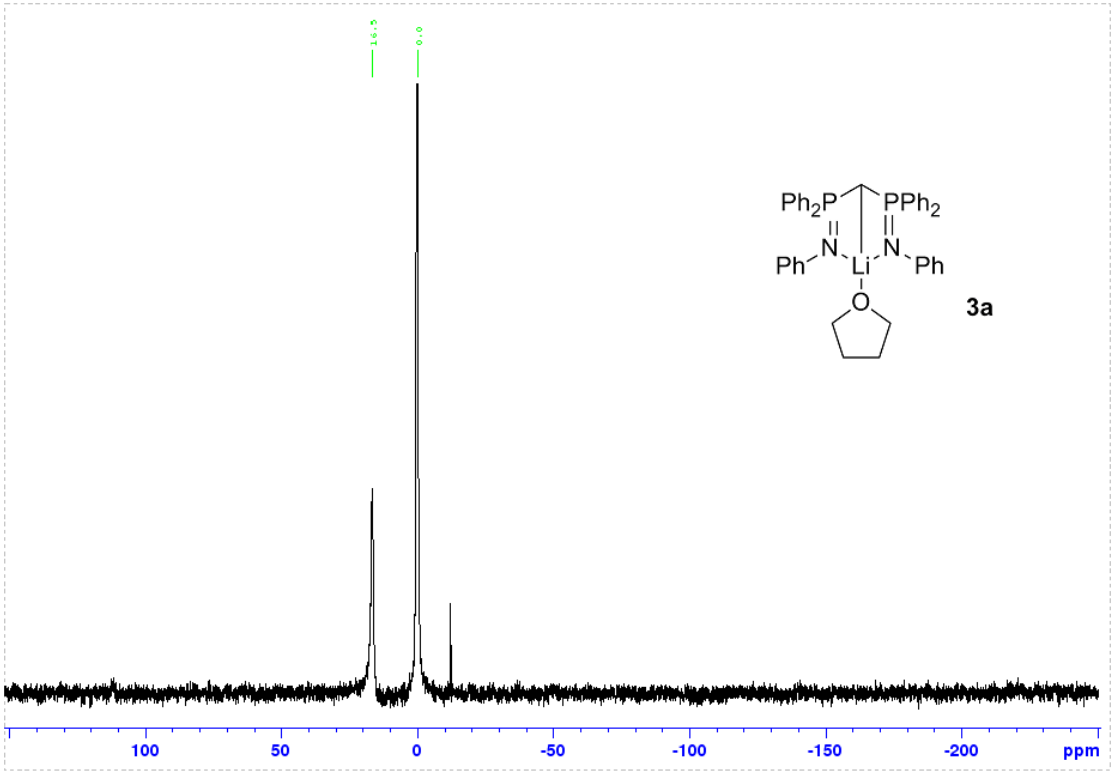
*Preparation of lithium adduct **3a***



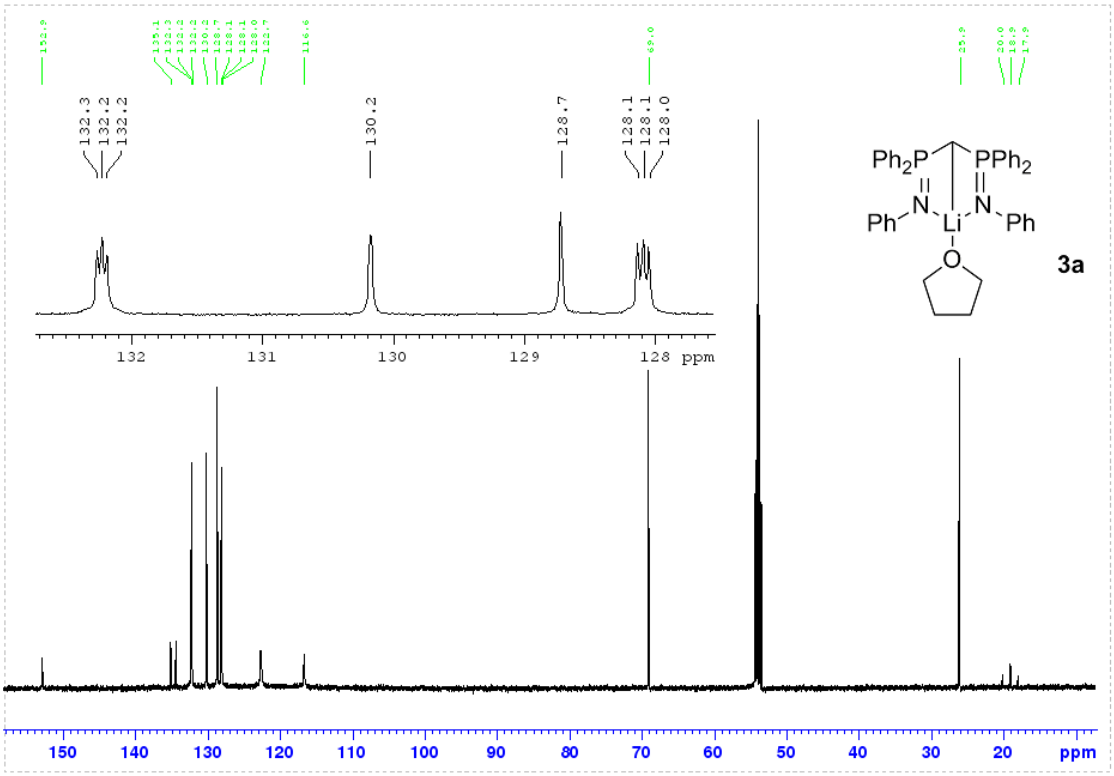
1.04 g (94 %)



^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)

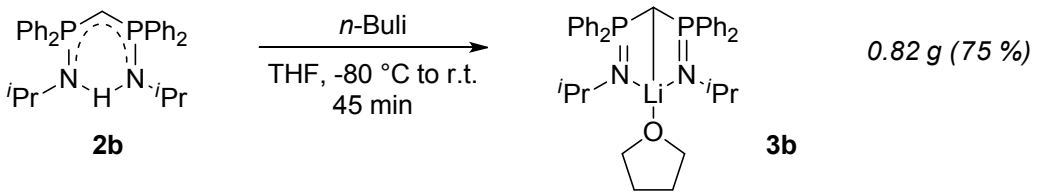


$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 300 K)

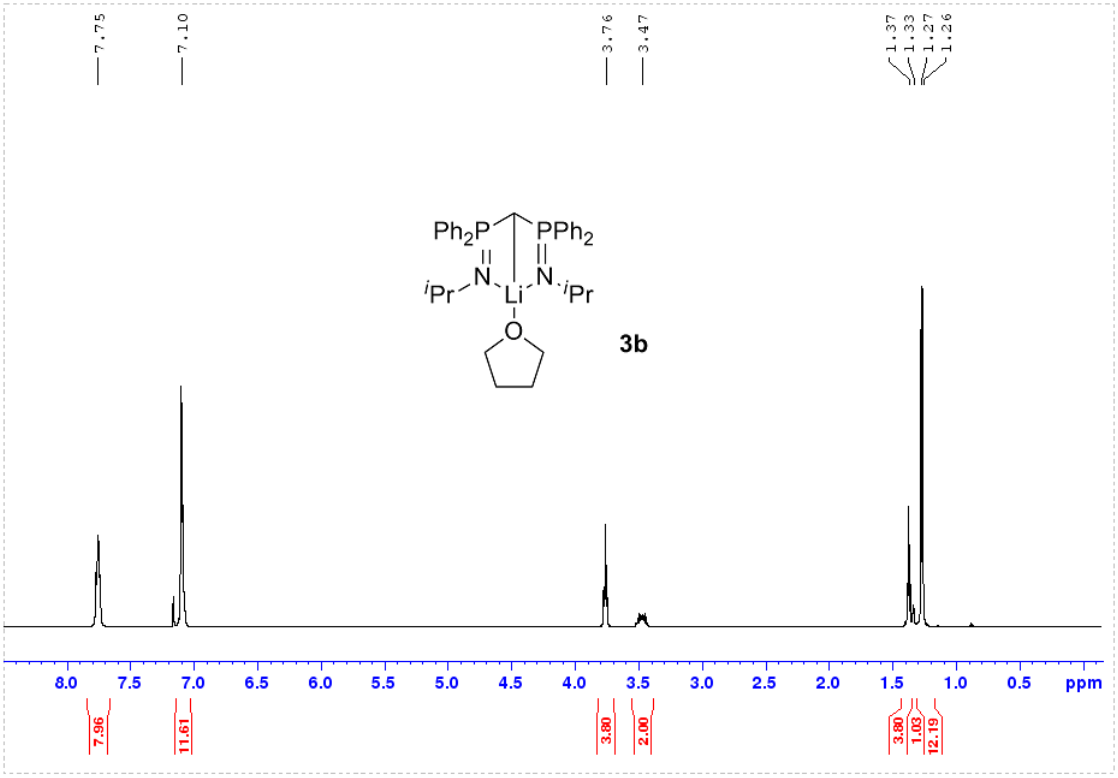


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 300 K)

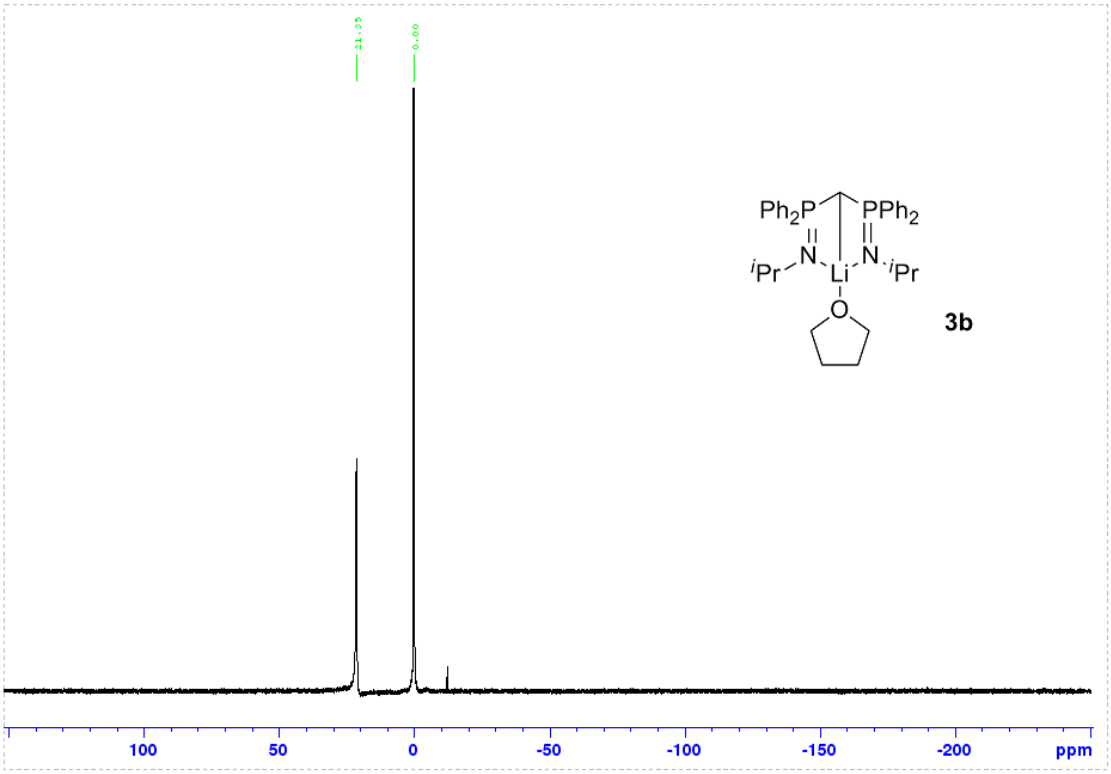
*Preparation of lithium adduct **3b***



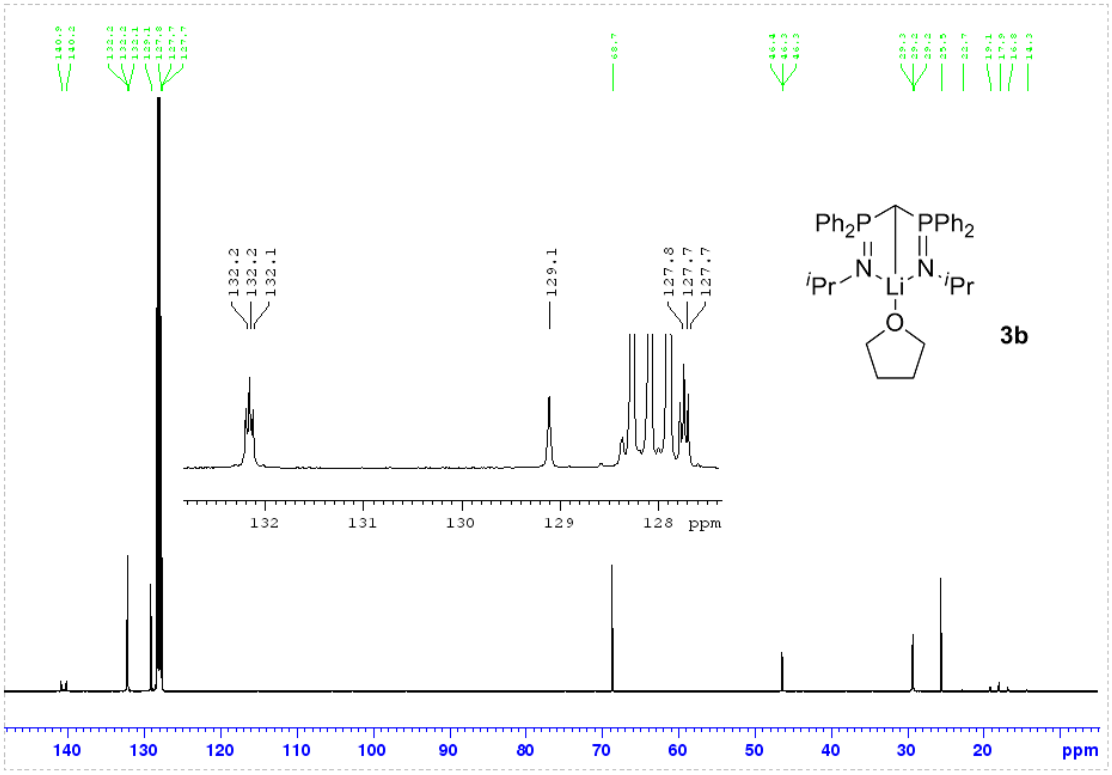
2b **3b** *0.82 g (75 %)*



^{1}H NMR (500 MHz, C_6D_6, 300 K)

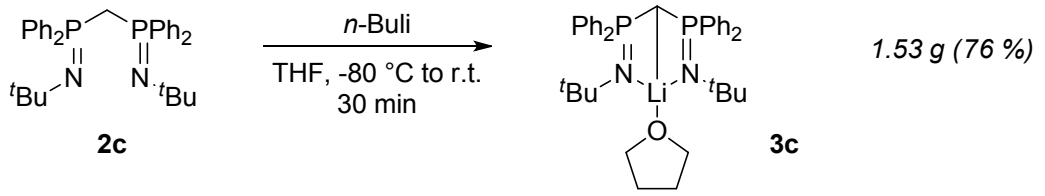


$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 300 K)

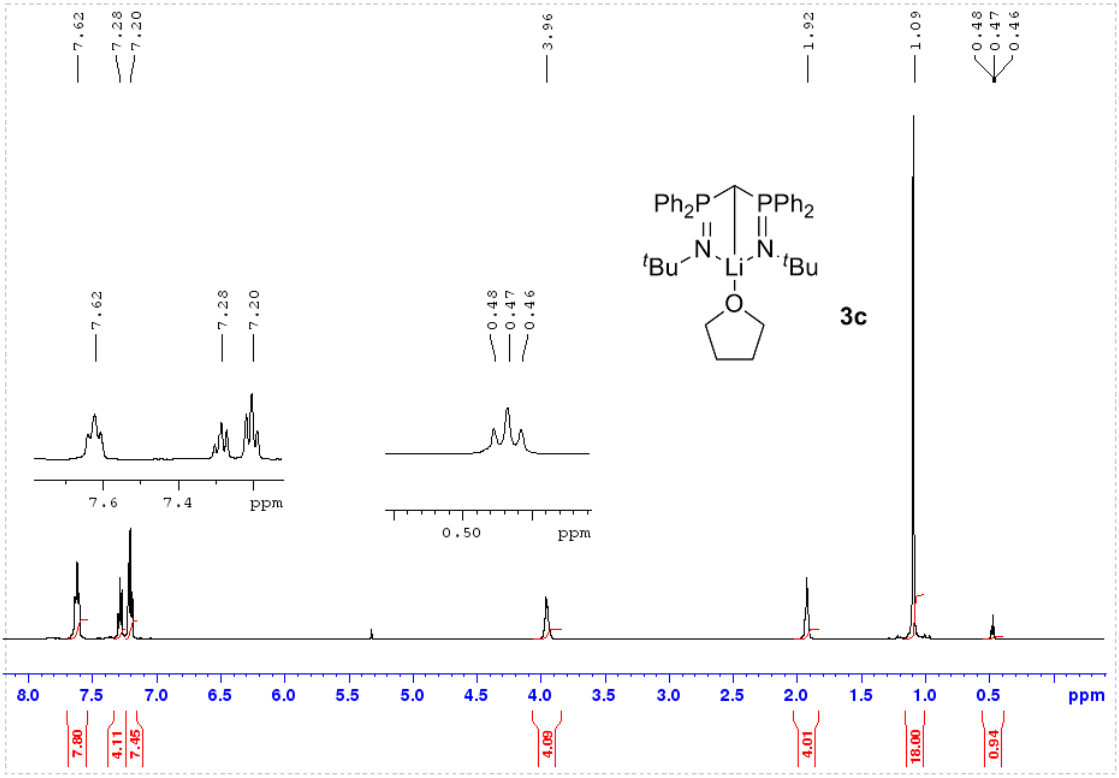


$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 300 K)

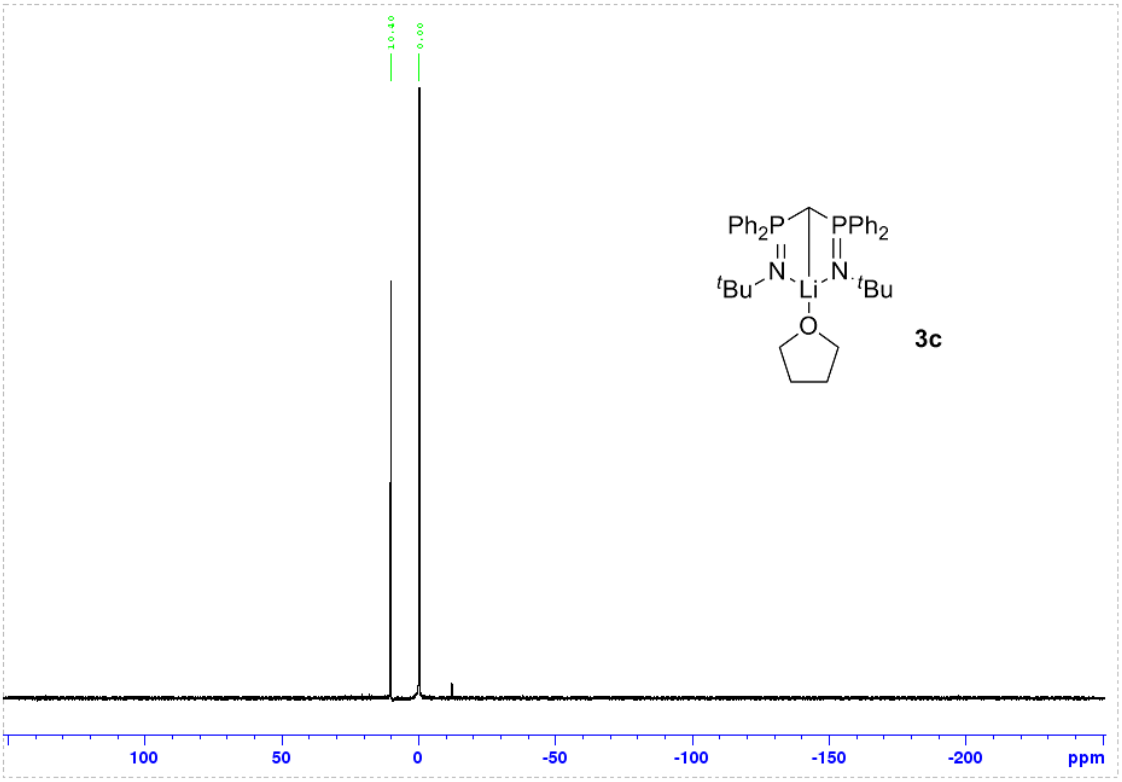
*Preparation of lithium adduct **3c***



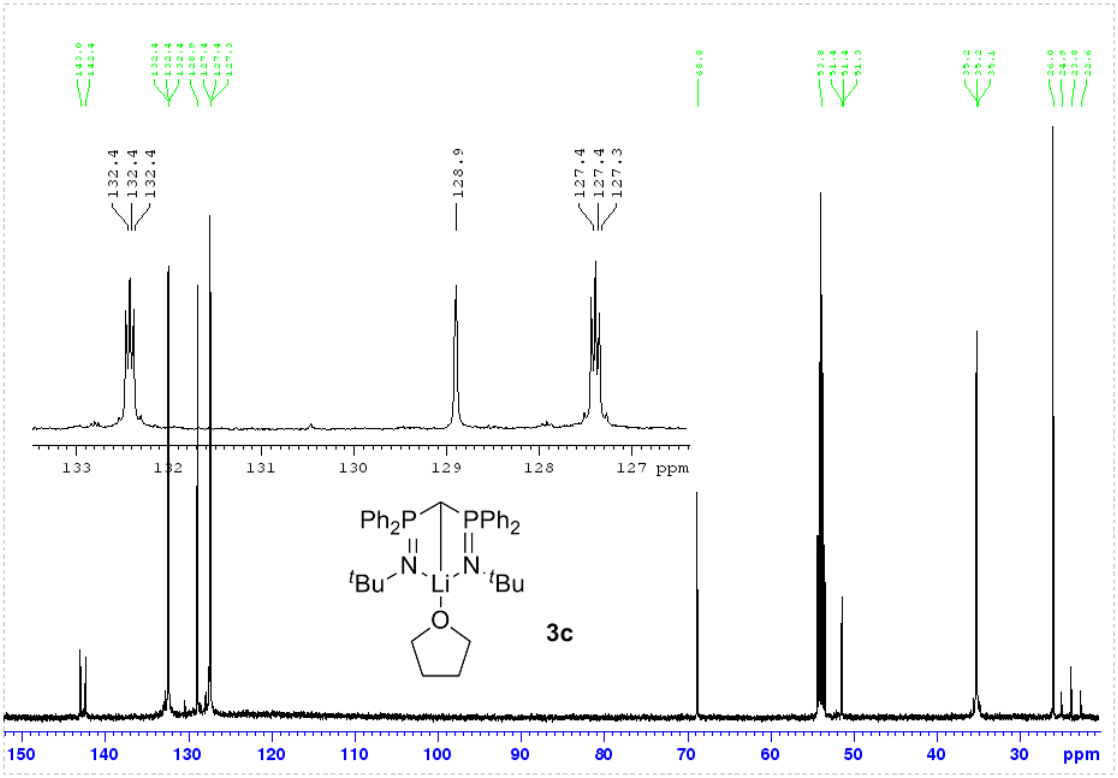
1.53 g (76 %)



^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)

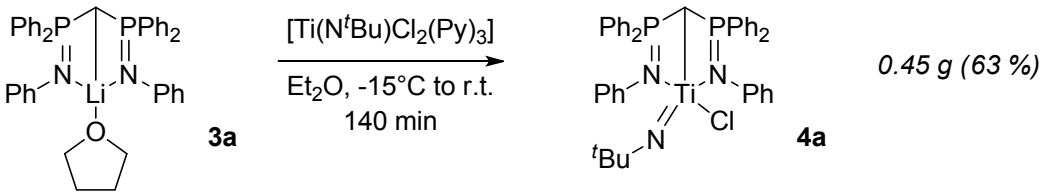


$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 300 K)

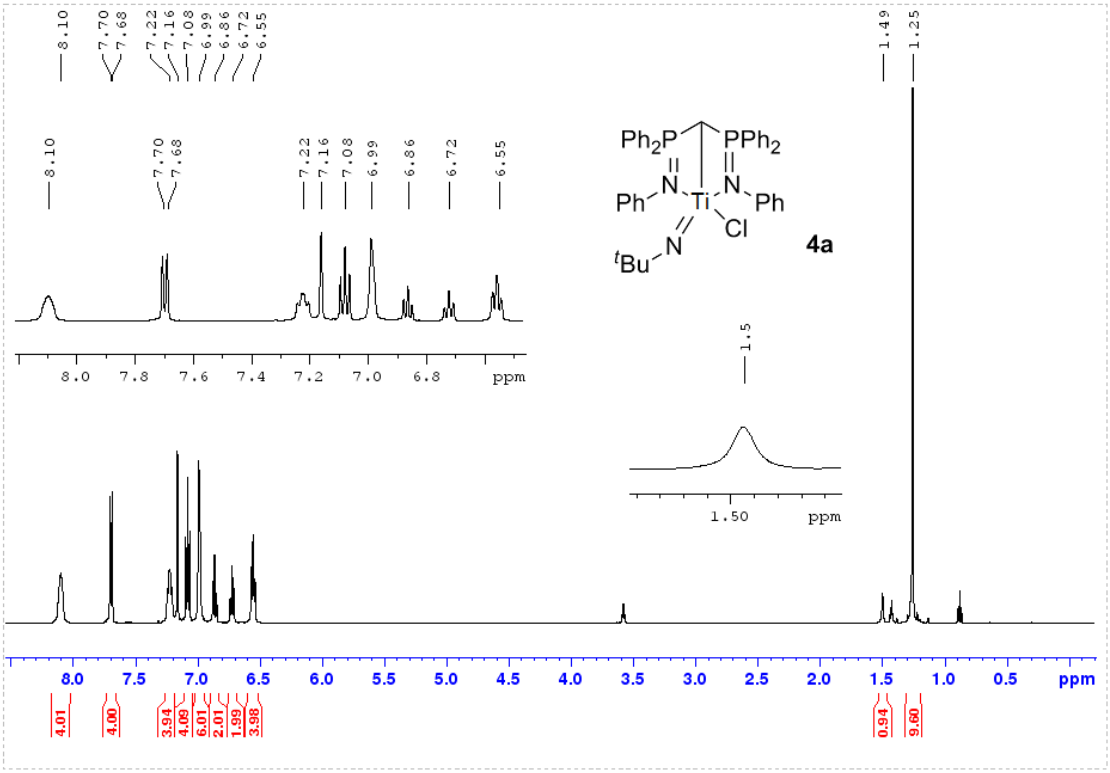


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 300 K)

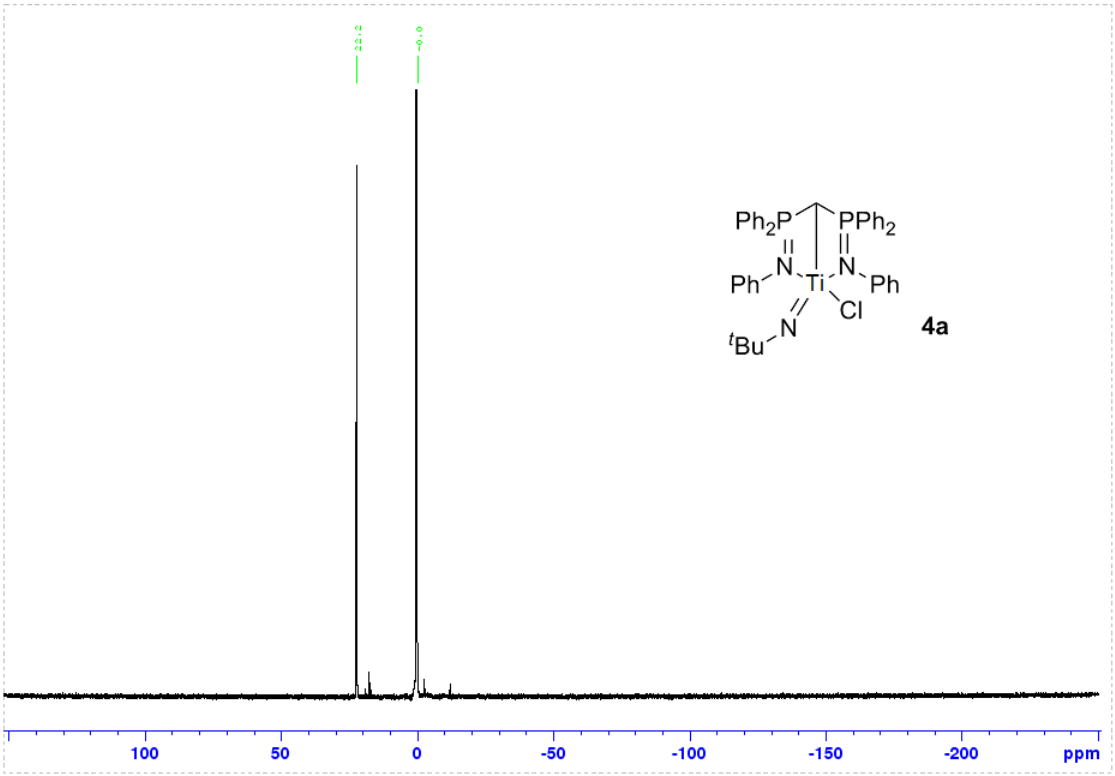
*Preparation of titanium complex **4a***



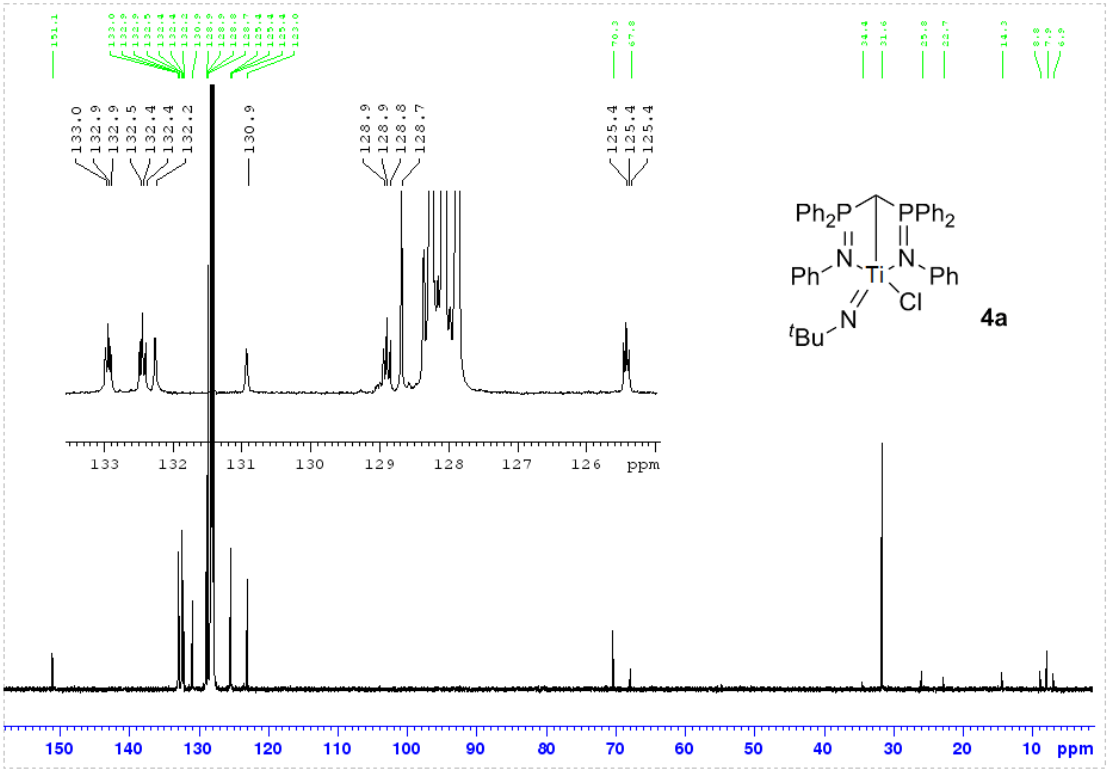
0.45 g (63 %)



^{1}H NMR (500 MHz, C_6D_6, 300 K)

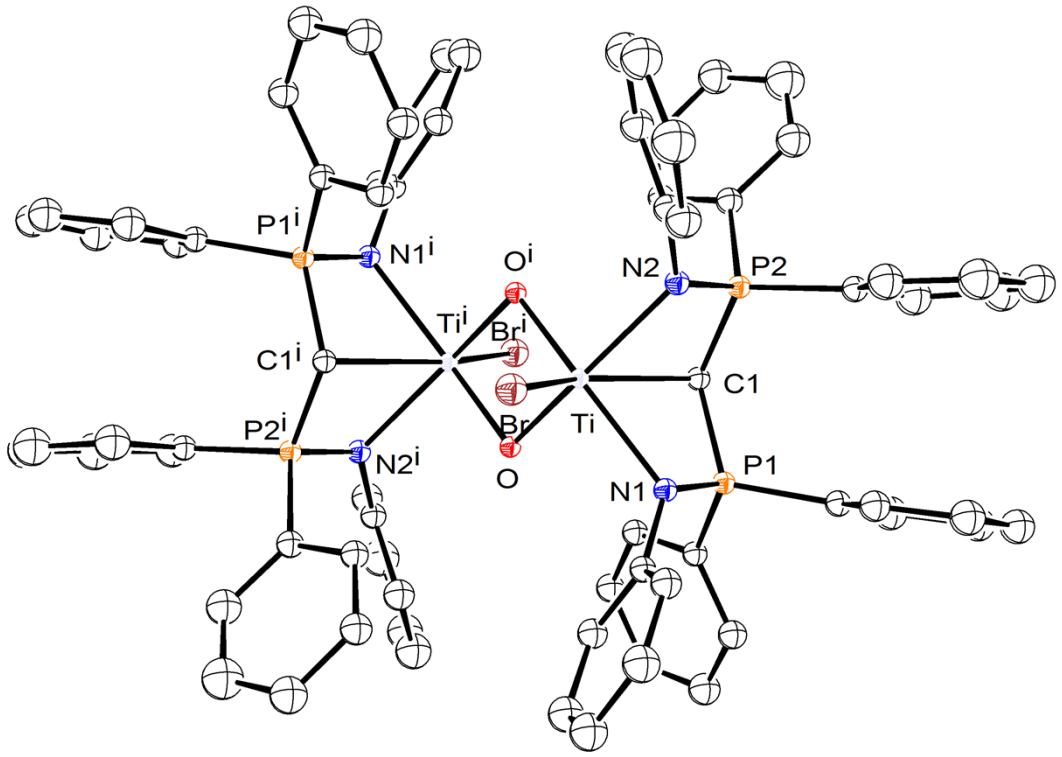


$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 300 K)

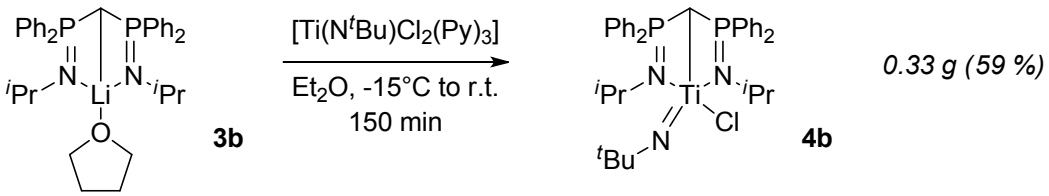


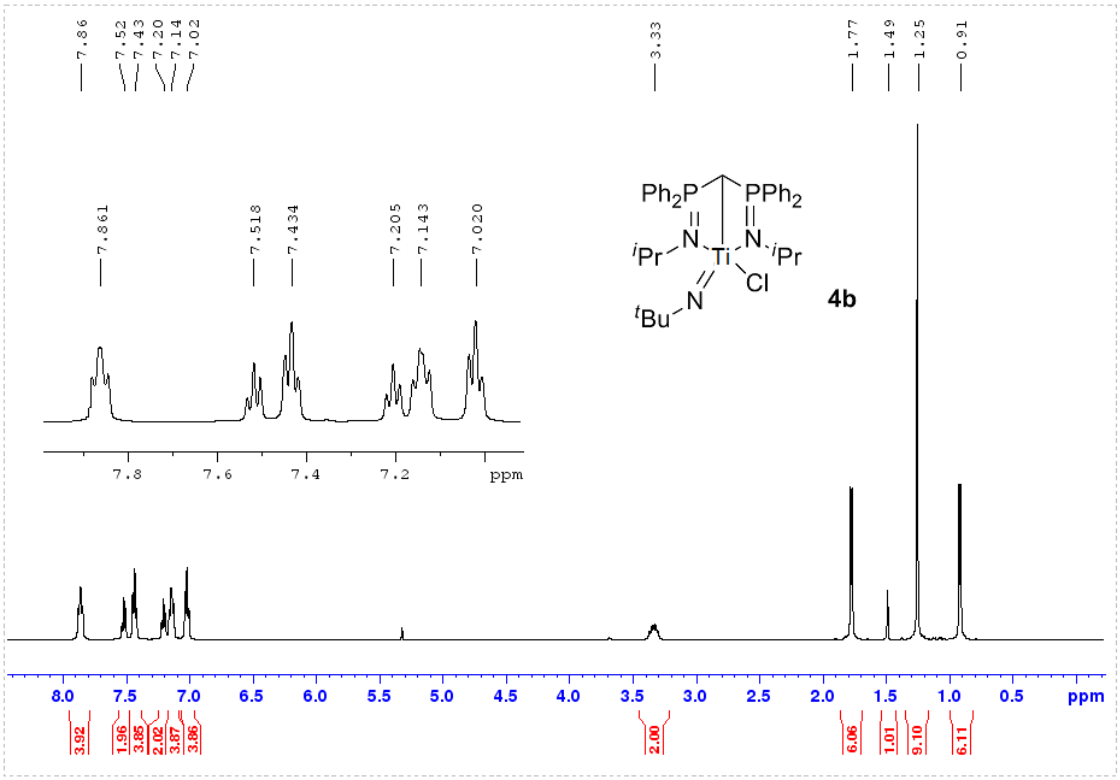
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 300 K)

Ortep depiction of [TiBr(BIPMH^{Ph})(μ-O)]$_2$ (Figure S1)

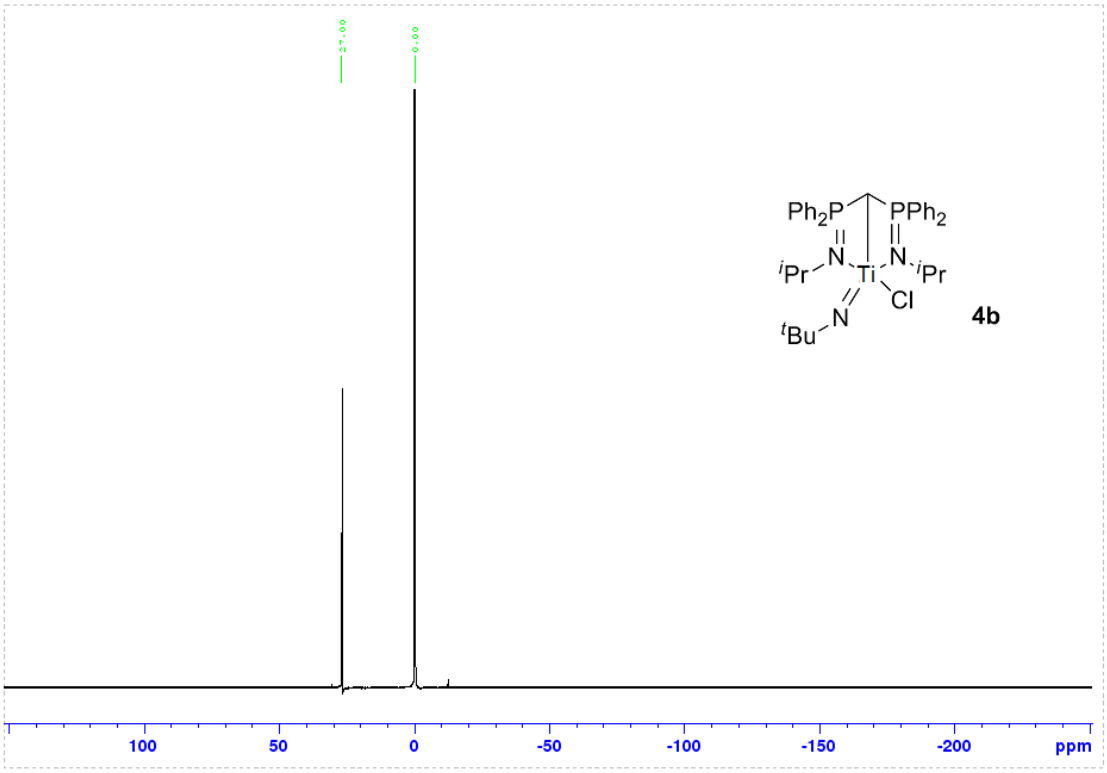


*Preparation of titanium complex **4b***

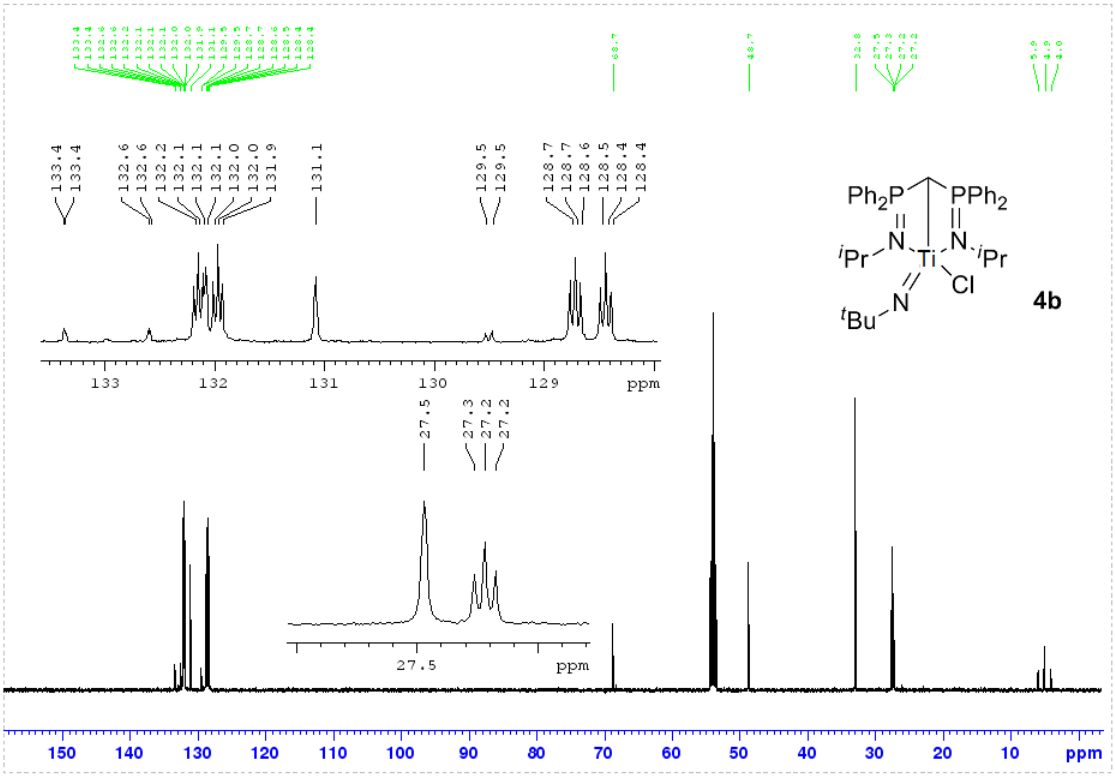




^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)

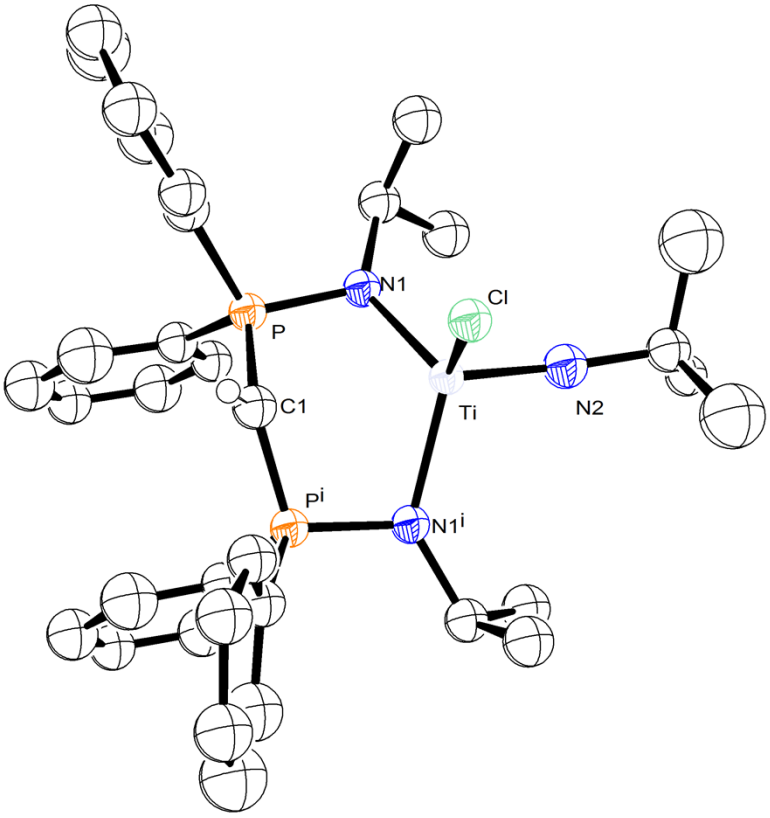


^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 300 K)

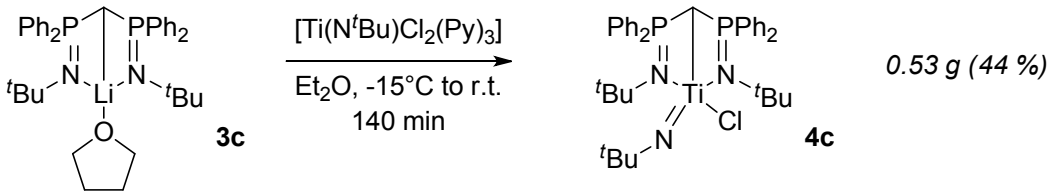


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 300 K)

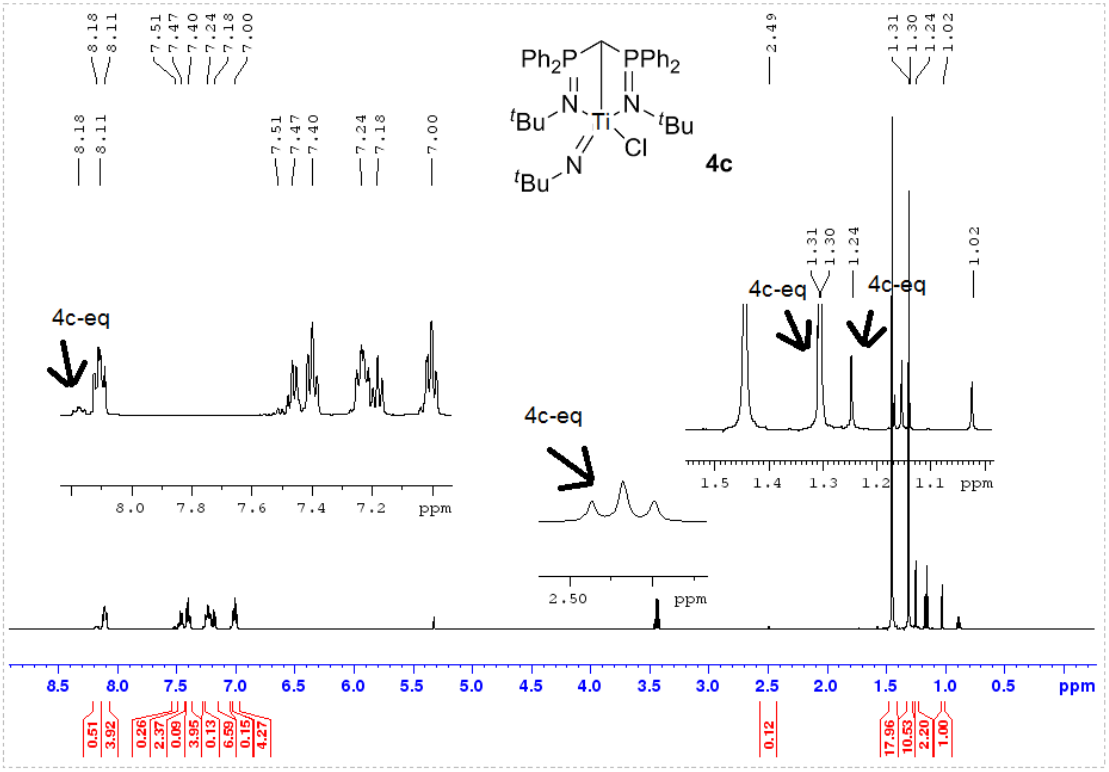
*ORTEP depiction of **4b** (Figure S2)*



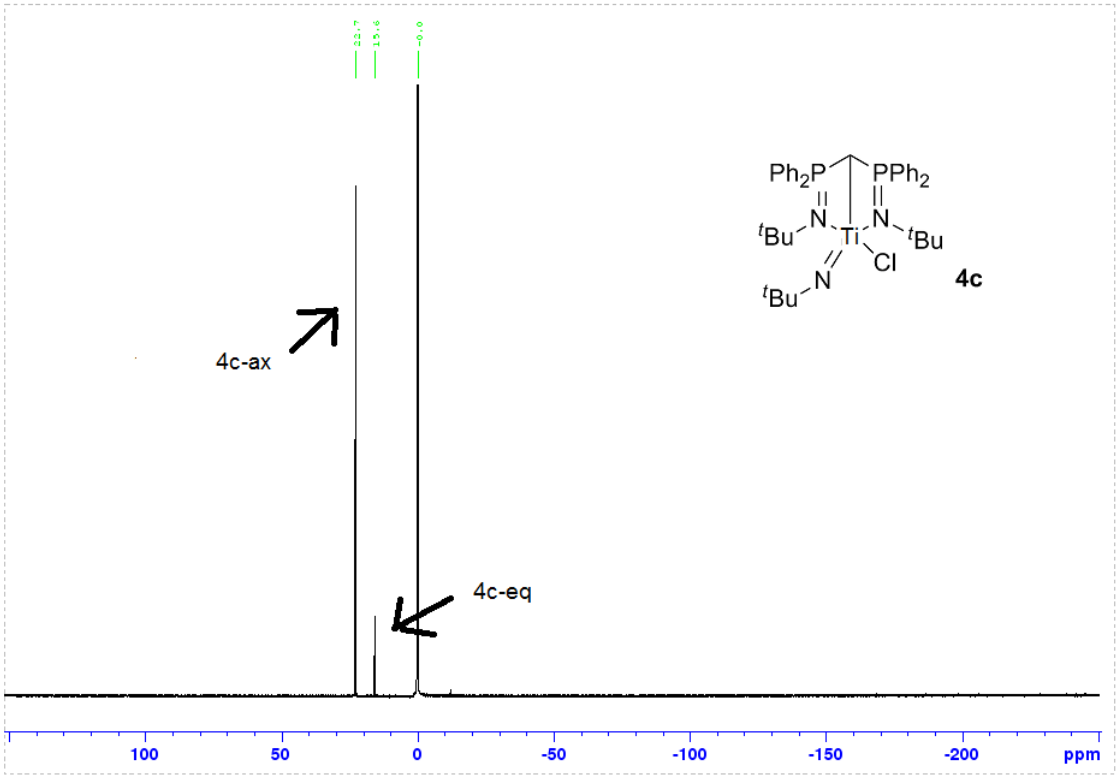
*Preparation of titanium complex **4c***



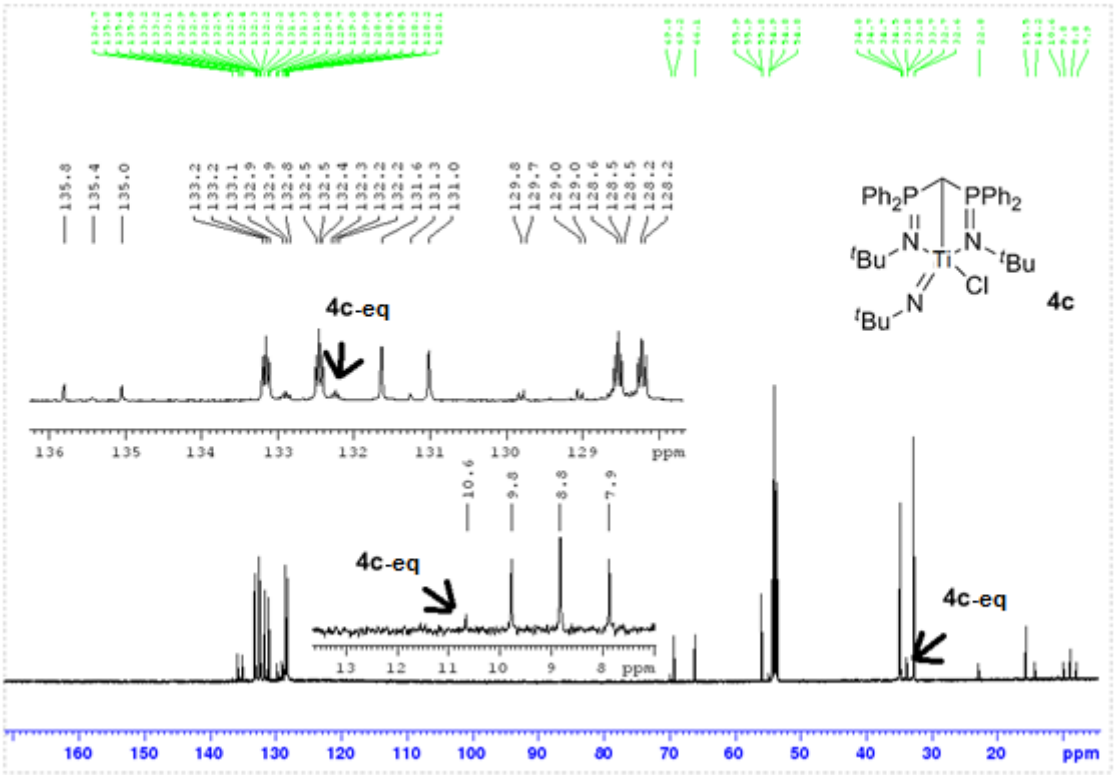
0.53 g (44 %)



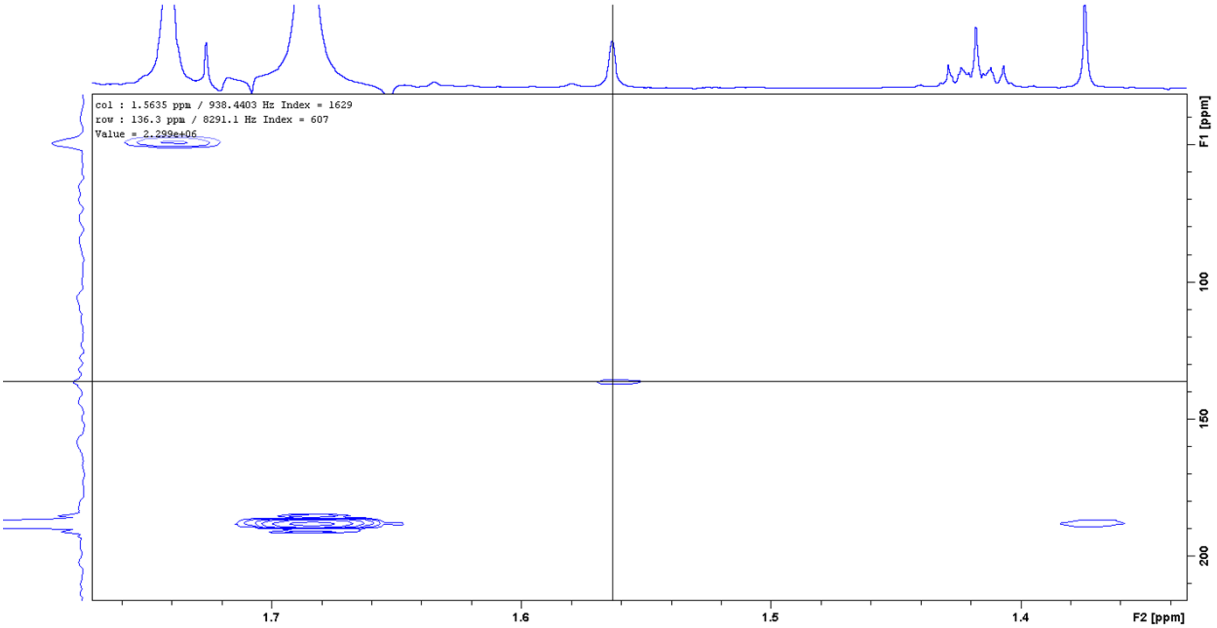
^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)



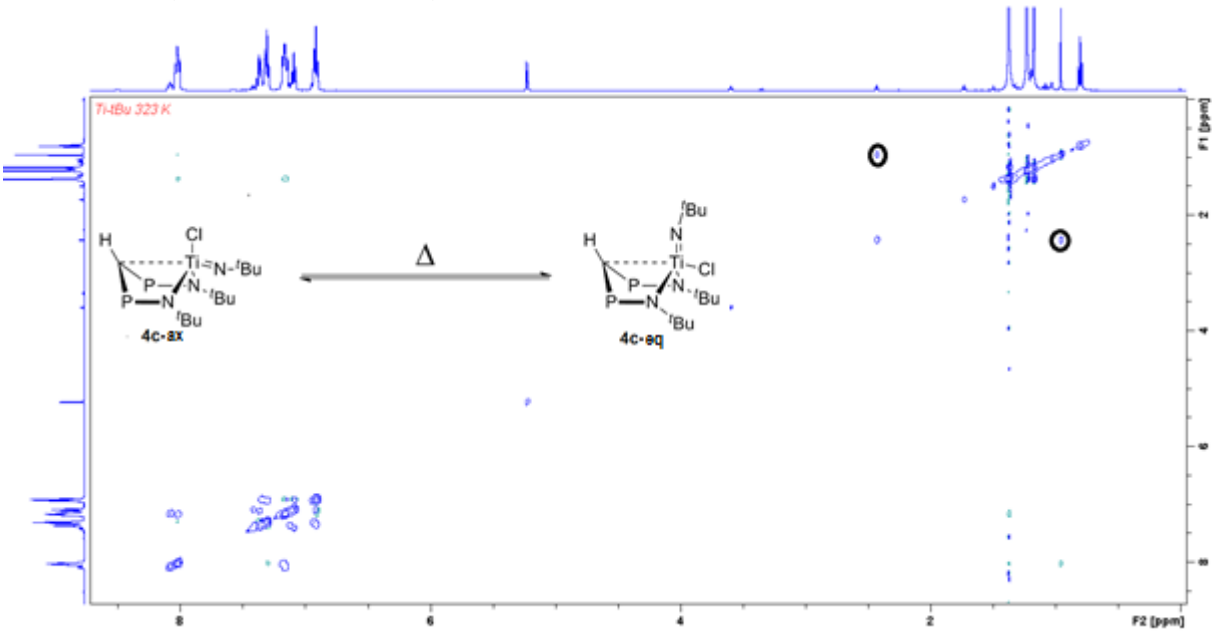
$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 300 K)



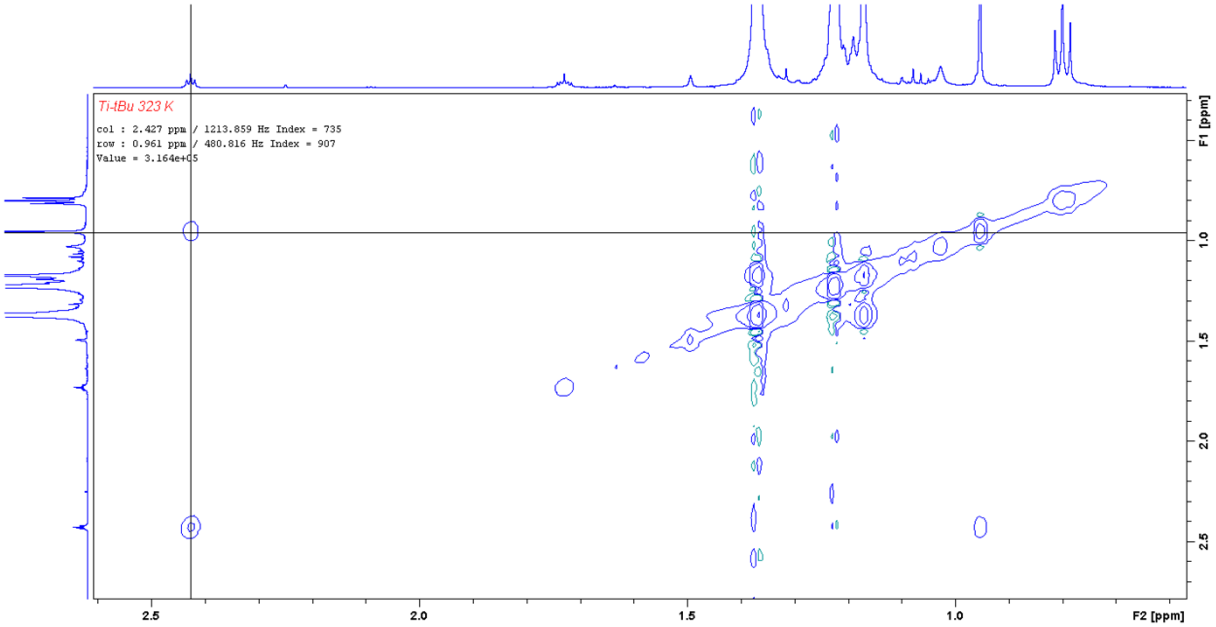
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_2Cl_2, 300 K)



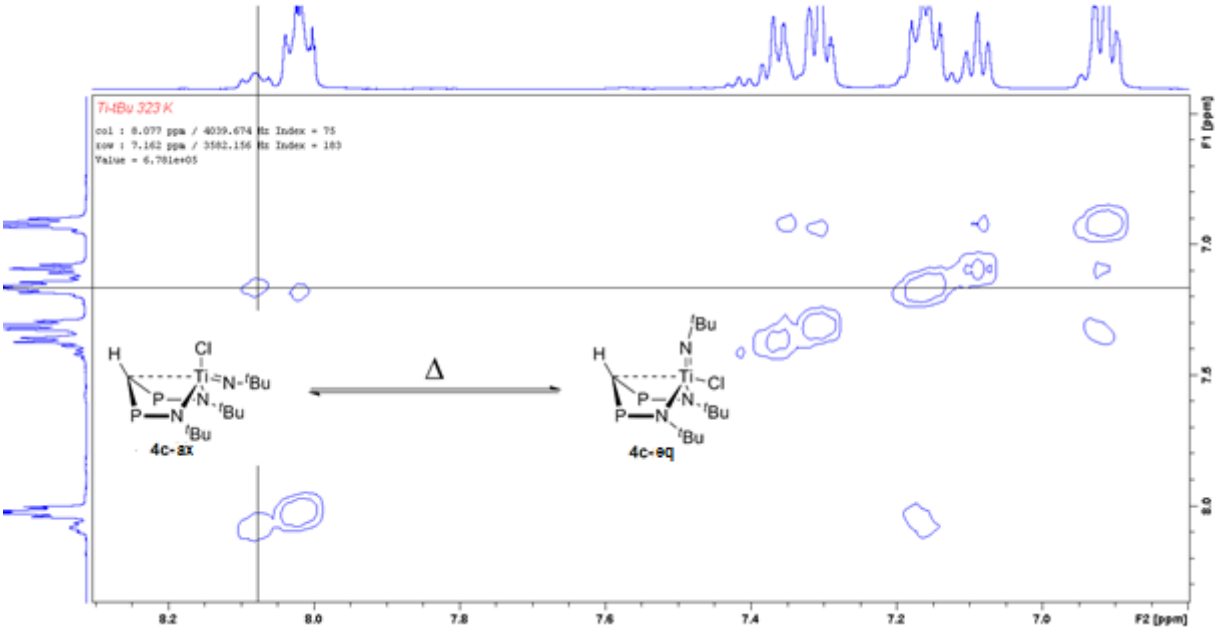
^{1}H-^{15}N HMBC (600 MHz, C_6D_6, 300 K)



EXSY NMR (500 MHz, CD_2Cl_2, 323 K)



EXSY NMR, high field region (500 MHz, CD_2Cl_2, 323 K)



EXSY NMR, low field region (500 MHz, CD_2Cl_2, 323 K)

*VT NMR study of complex **4c** (Figure S3)*

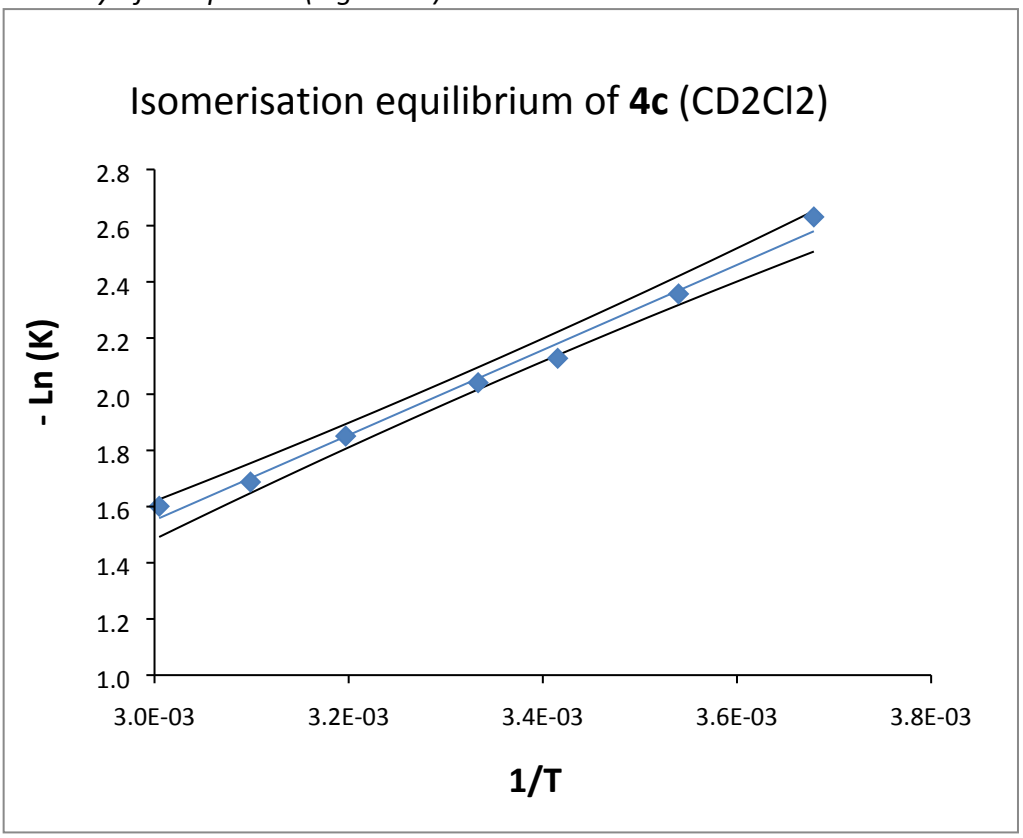


*Figure S3. Logarithmic plot of K against 1/T used in the determination of the free energy of the isomerisation equilibrium of **4c***

lnK = -ΔG°/RT, ΔH° = 12.6±1.4 kJ.mol^{-1} and ΔS° = 24.9±4.7 J.mol^{-1}.K^{-1}. The expanded uncertainties are estimated from the least-squares fit at the 95% confidence level for 5 degrees of freedom.

2. Reactivity studies

*Reaction of ligands **2** with Ti imido precursor (Figures S4-S10)*

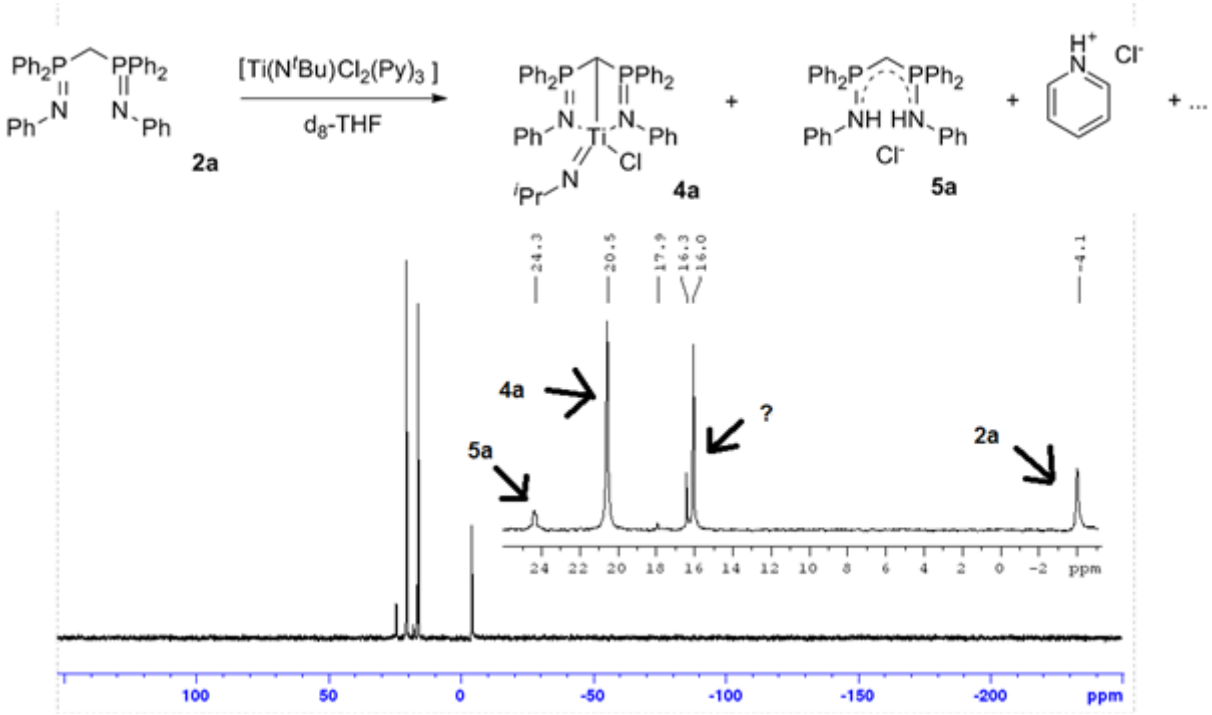


*Figure S4.$^{31}P\{^1H\}$ NMR spectrum of the reaction of **2a** with Ti imido precursor (202 MHz, d_8-THF, 300 K)*

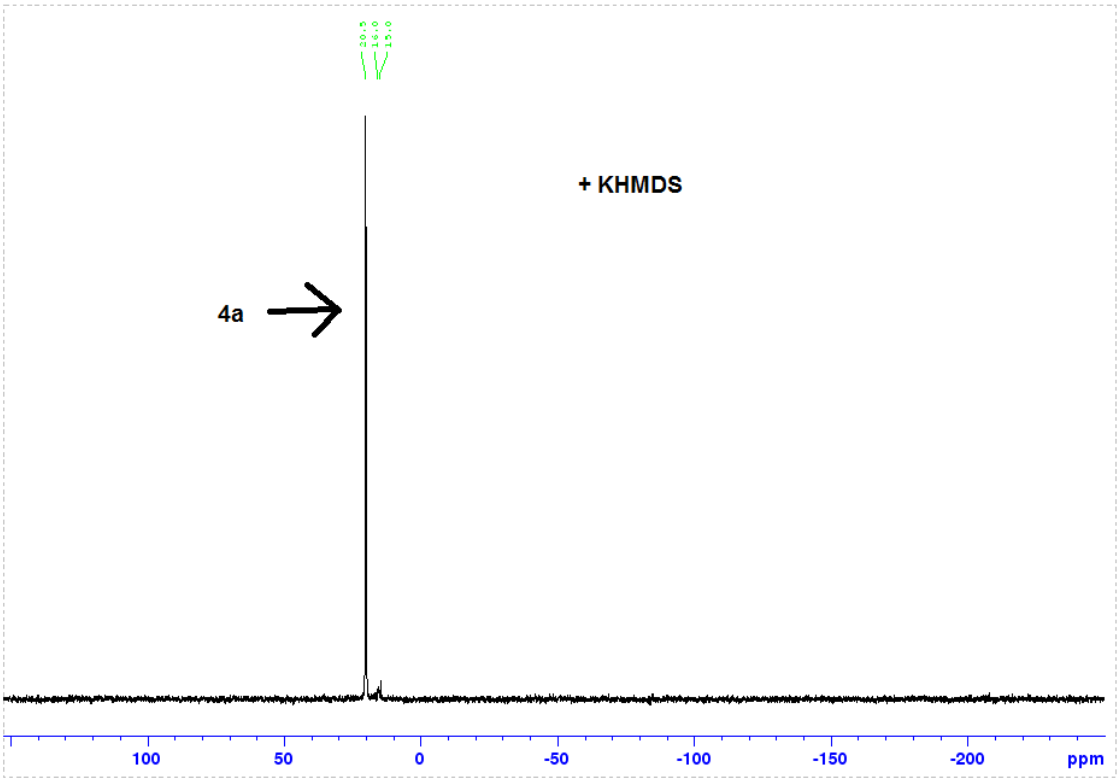


*Figure S5. $^{31}P\{^1H\}$ NMR spectrum of the reaction of **2a** with Ti imido precursor after addition of KHMDS (202 MHz, d_8-THF, 300 K)*

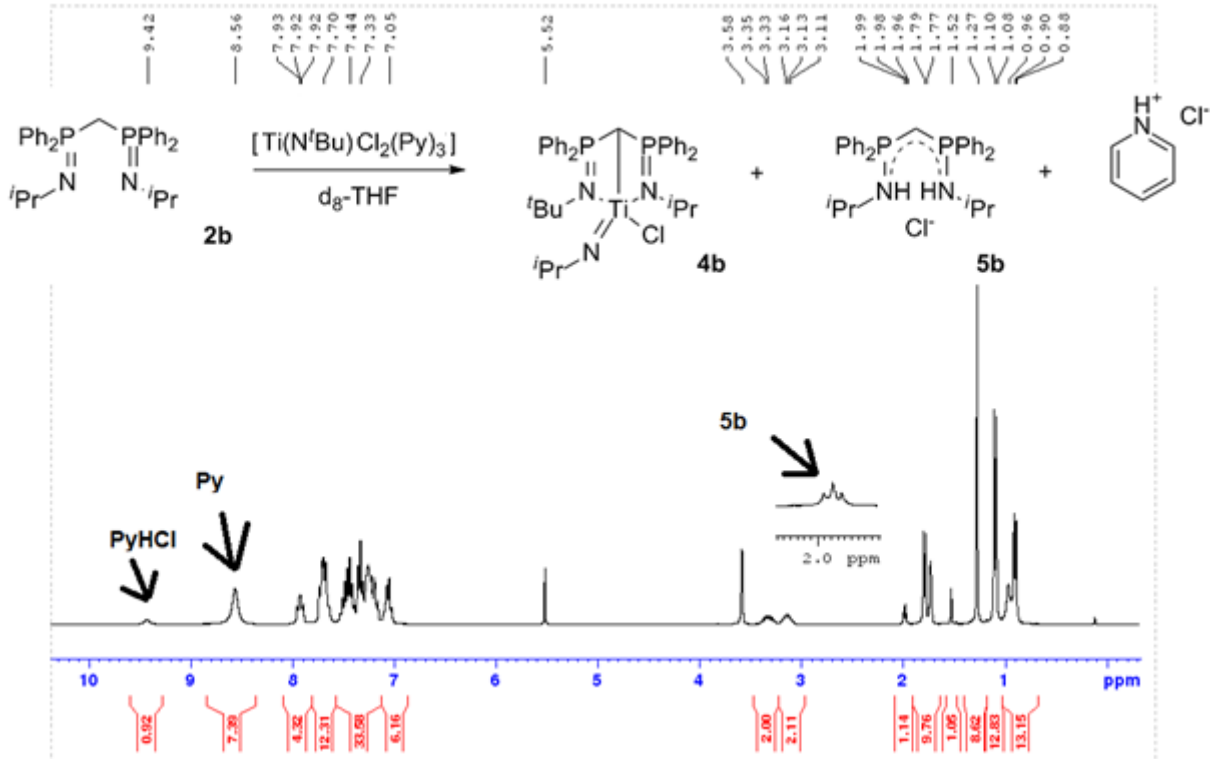


*Figure S6. ^{1}H NMR spectrum of the reaction of **2b** with Ti imido precursor (300 MHz, d$_8$-THF, 300 K)*

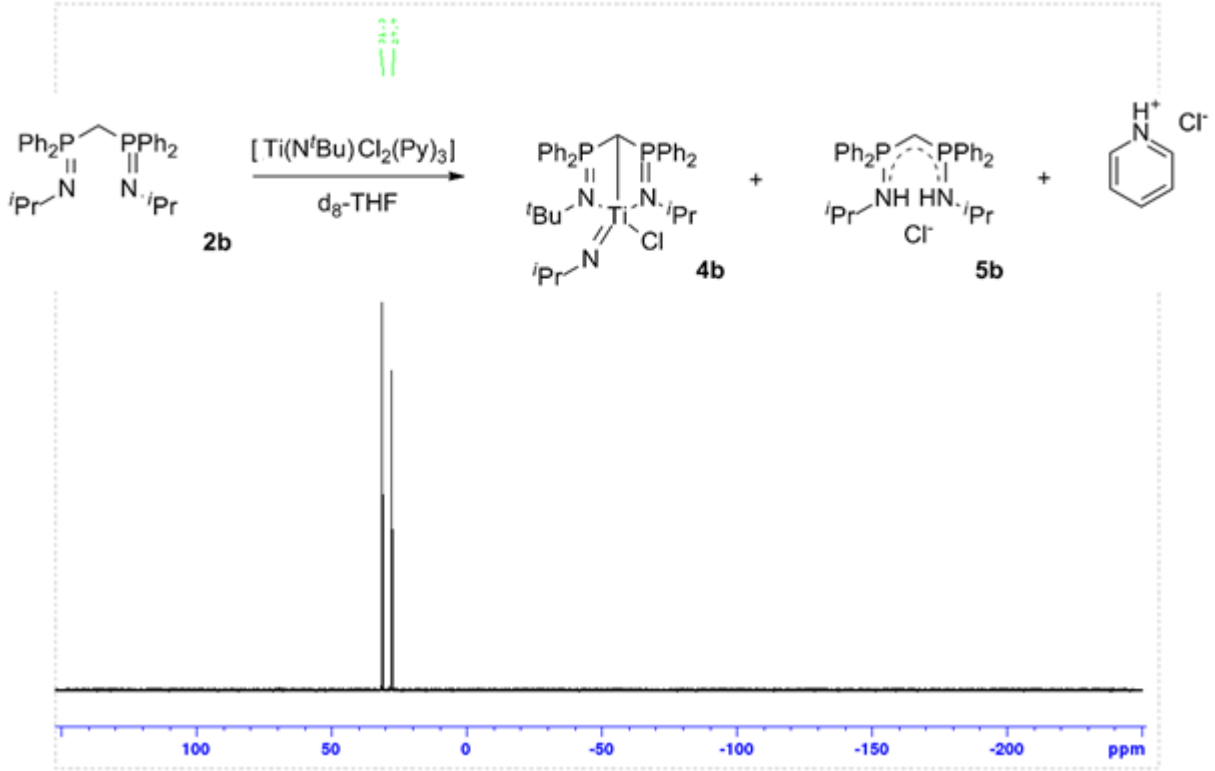


*Figure S7. ^{31}P{^{1}H} NMR spectra of the reaction of **2b** with Ti imido precursor (121 MHz, d$_8$-THF, 300 K)*

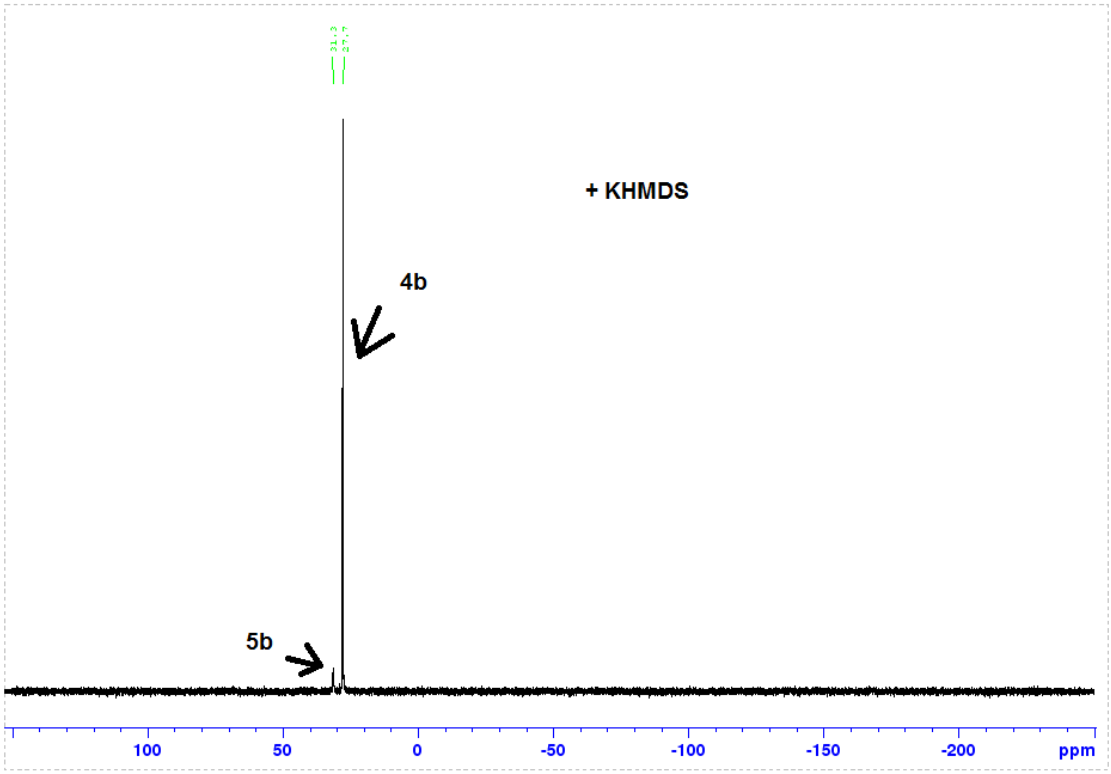


*Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **2b** with Ti imido precursor after addition of KHMDS (121 MHz, d_8-THF, 300 K)*

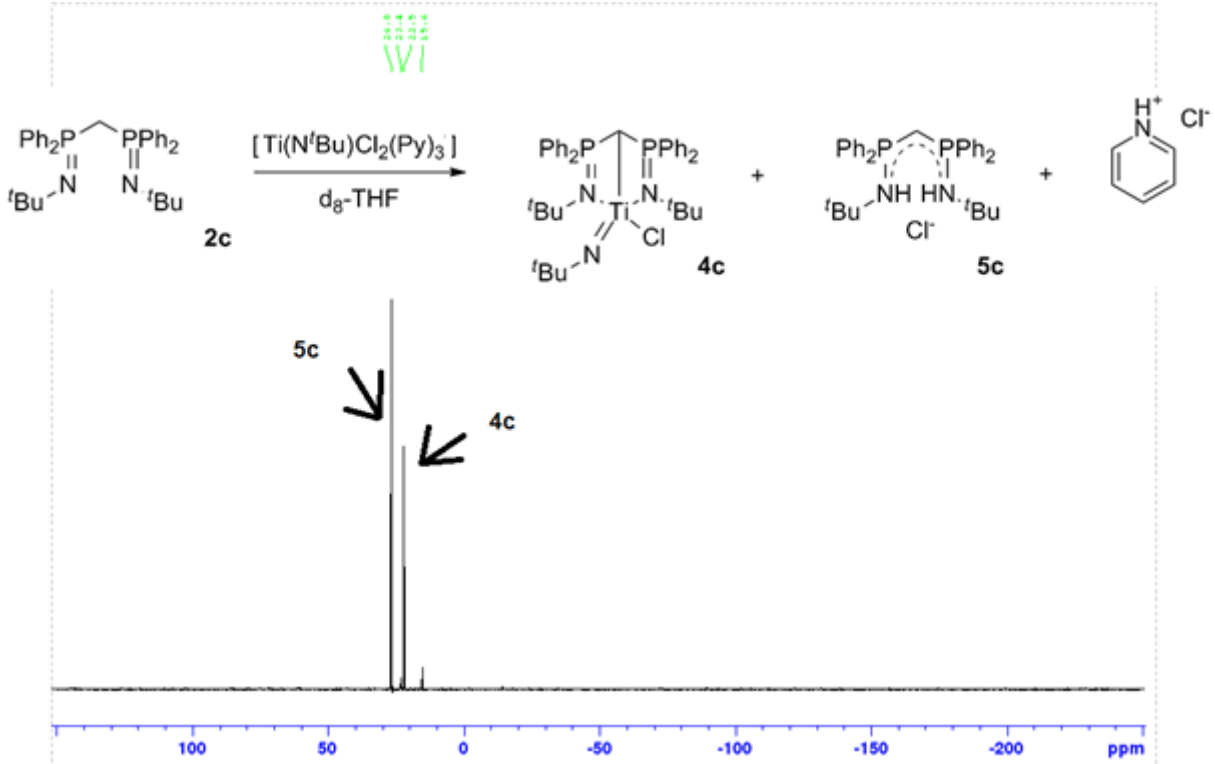


*Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **2c** with Ti imido precursor (202 MHz, d_8-THF, 300 K)*

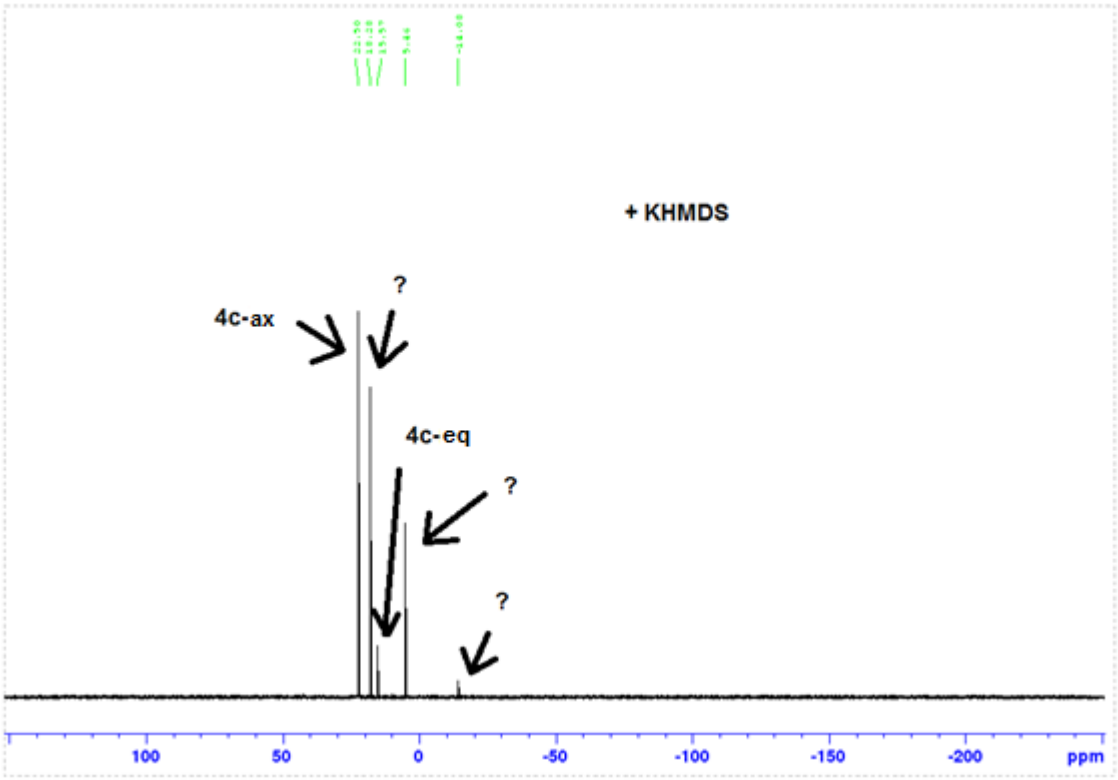


*Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **2c** with Ti imido precursor after addition of KHMDS (202 MHz, d_8-THF, 300 K)*

*Reaction of complexes **4** with hydroamination substrates (Figures S11-S22)*

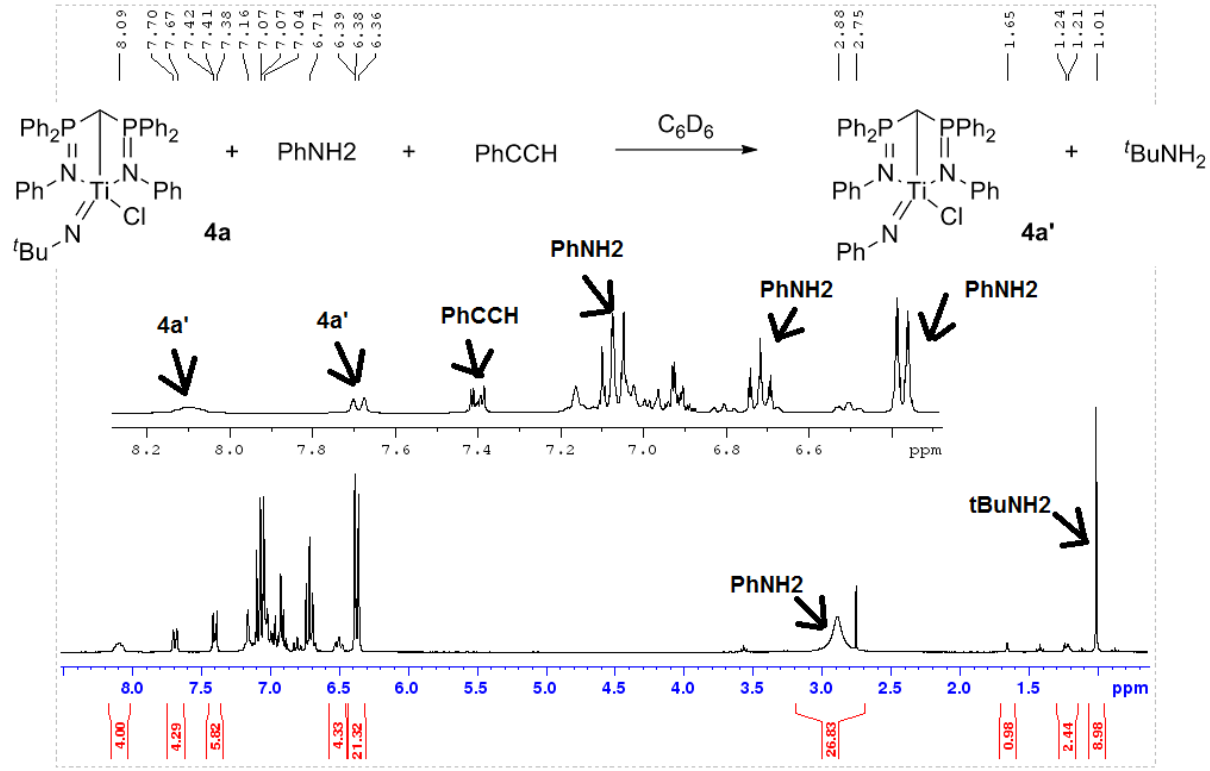


*Figure S11. ^{1}H NMR of **4a** after 4 hrs at r.t. (300 MHz, C_6D_6, 300 K)*

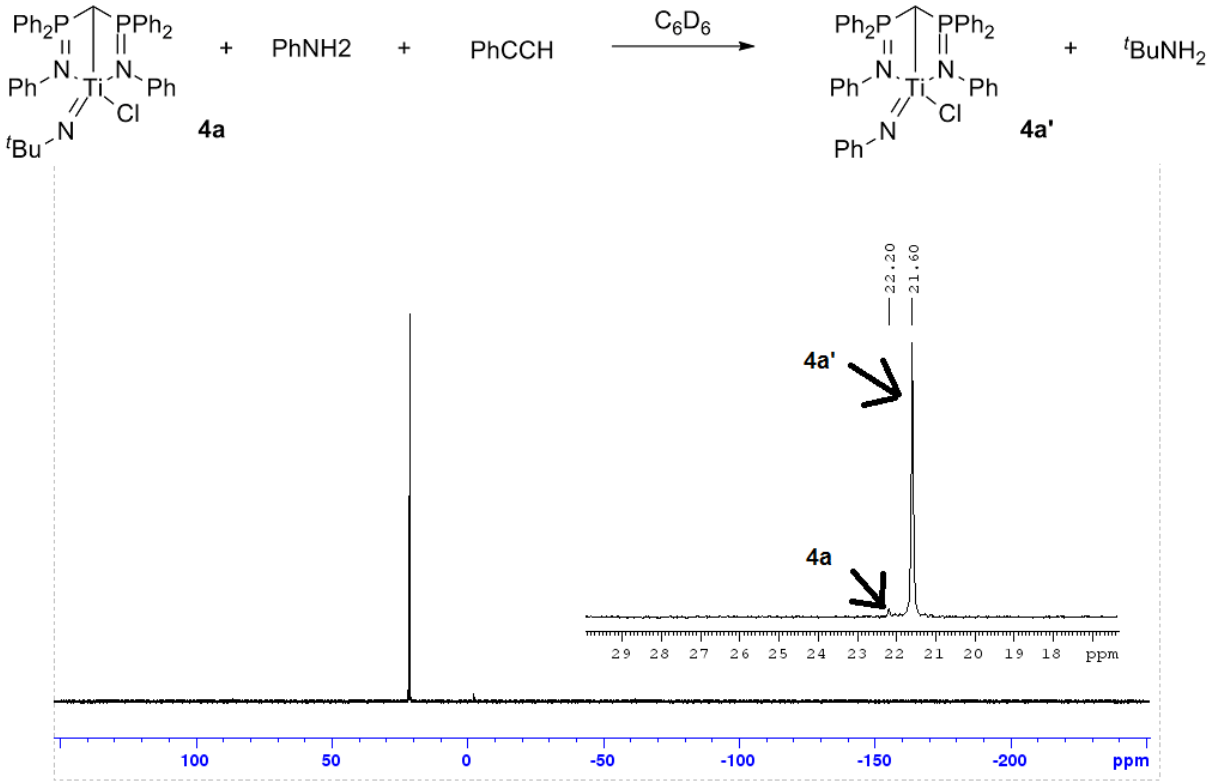


*Figure S12. ^{31}P NMR of **4a** after 4 hrs (121 MHz, C_6D_6, 300 K)*

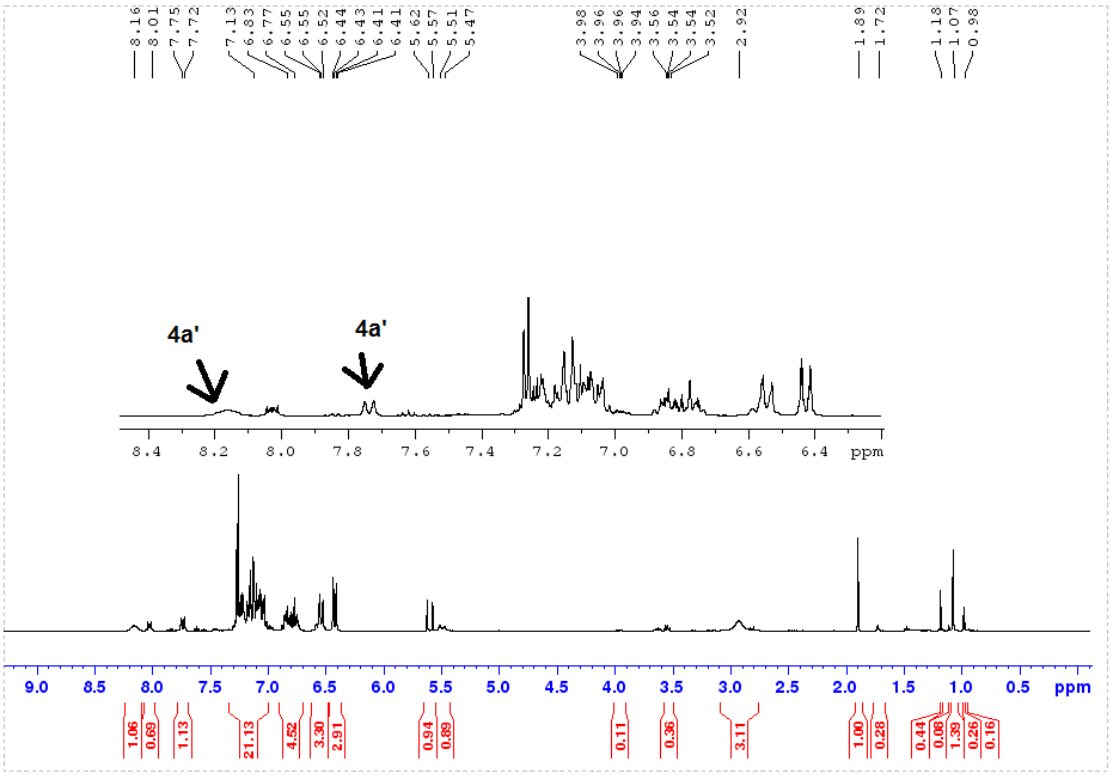


*Figure S13. ^{1}H NMR of **4a** after a further 13 hrs at 105°C (300 MHz, C_6D_6, 300 K)*

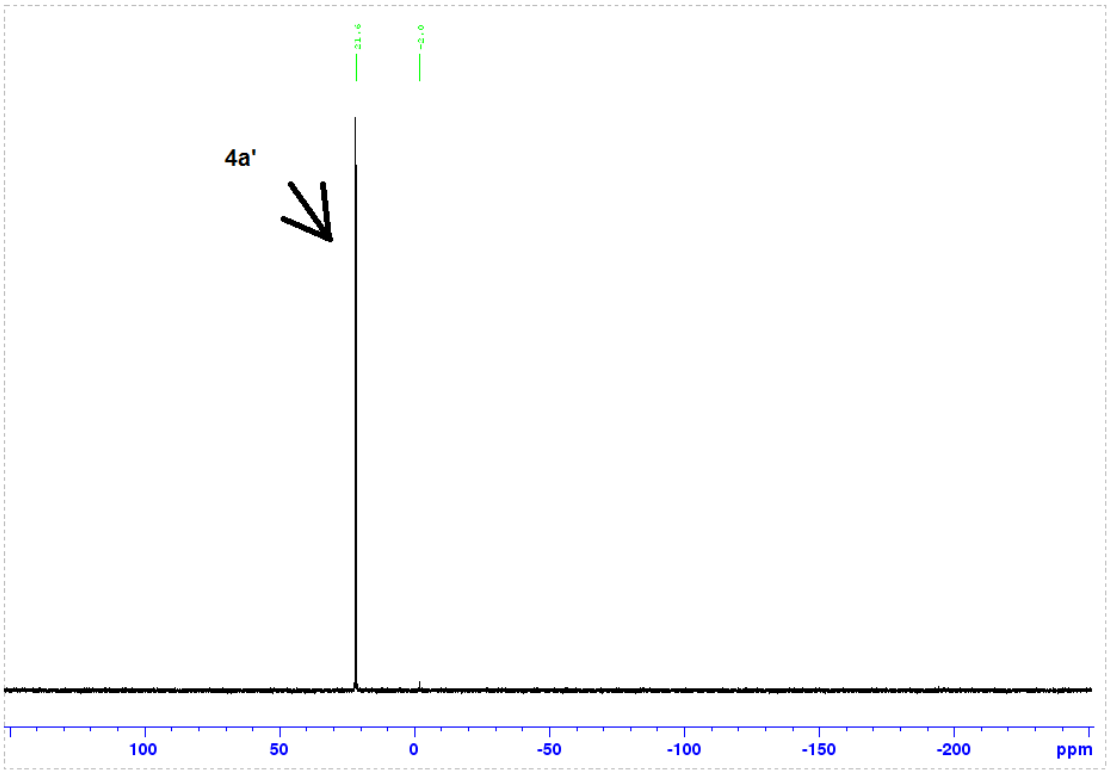


*Figure S14. $^{31}P\{^{1}H\}$ NMR of **4a** after a further 13 hrs at 105°C (121 MHz, C_6D_6, 300 K)*

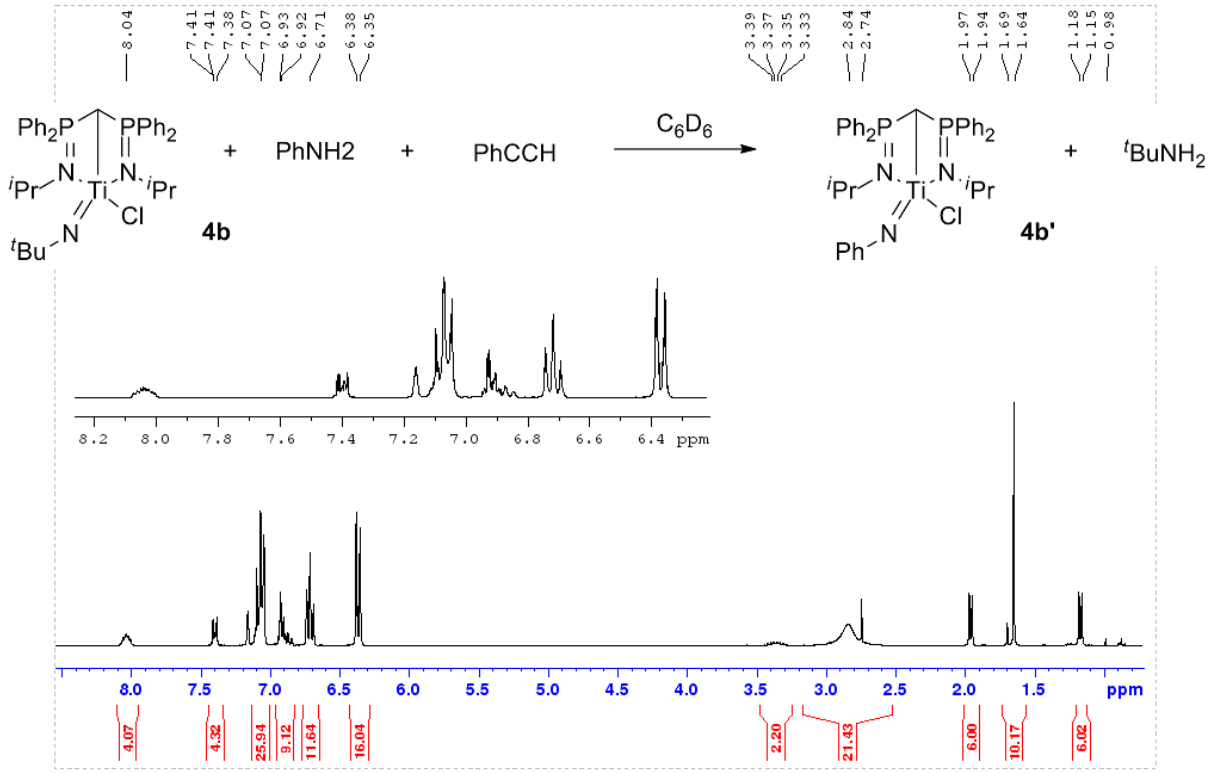


Figure S15. ^{1}H *NMR of* ***4b*** *after 13 hrs at r.t. (300 MHz,* C_6D_6*, 300 K)*

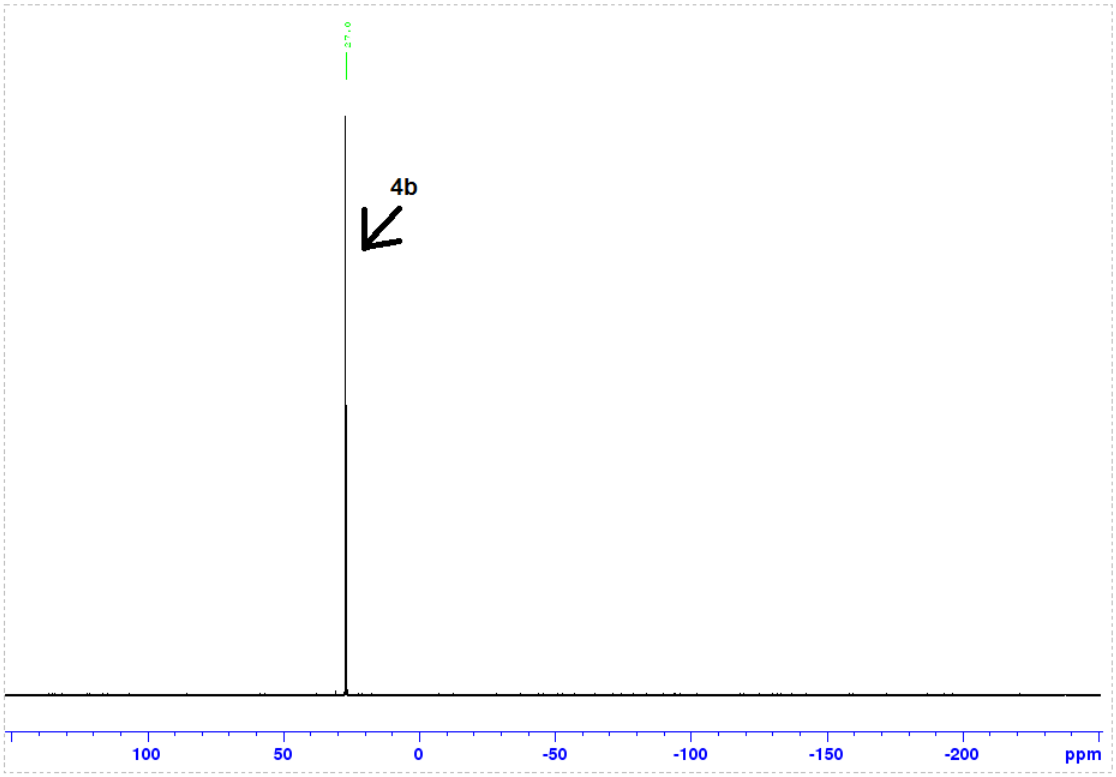


Figure S16. $^{31}P\{^{1}H\}$ *NMR of* ***4b*** *after 13 hrs (121 MHz,* C_6D_6*, 300 K)*

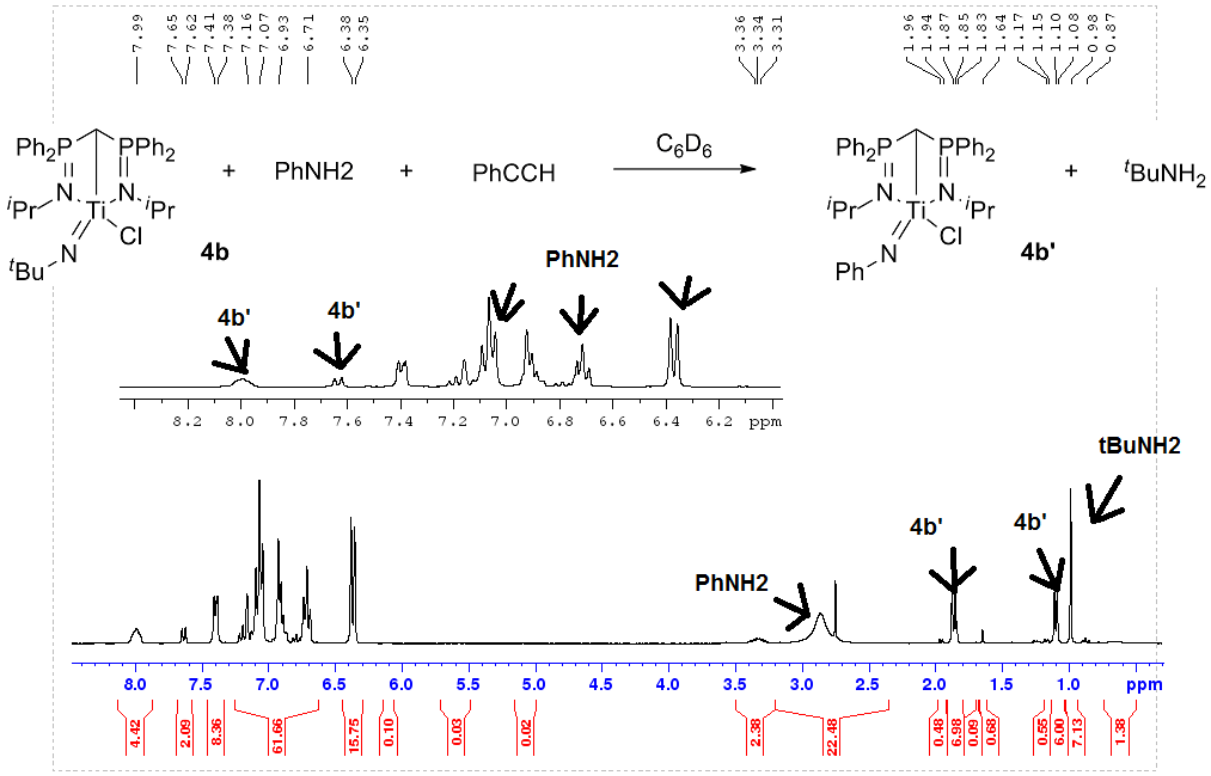


Figure S17. ^{1}H *NMR of* ***4b*** *after a further 13 hrs at 105°C (300 MHz,* C_6D_6*, 300 K)*

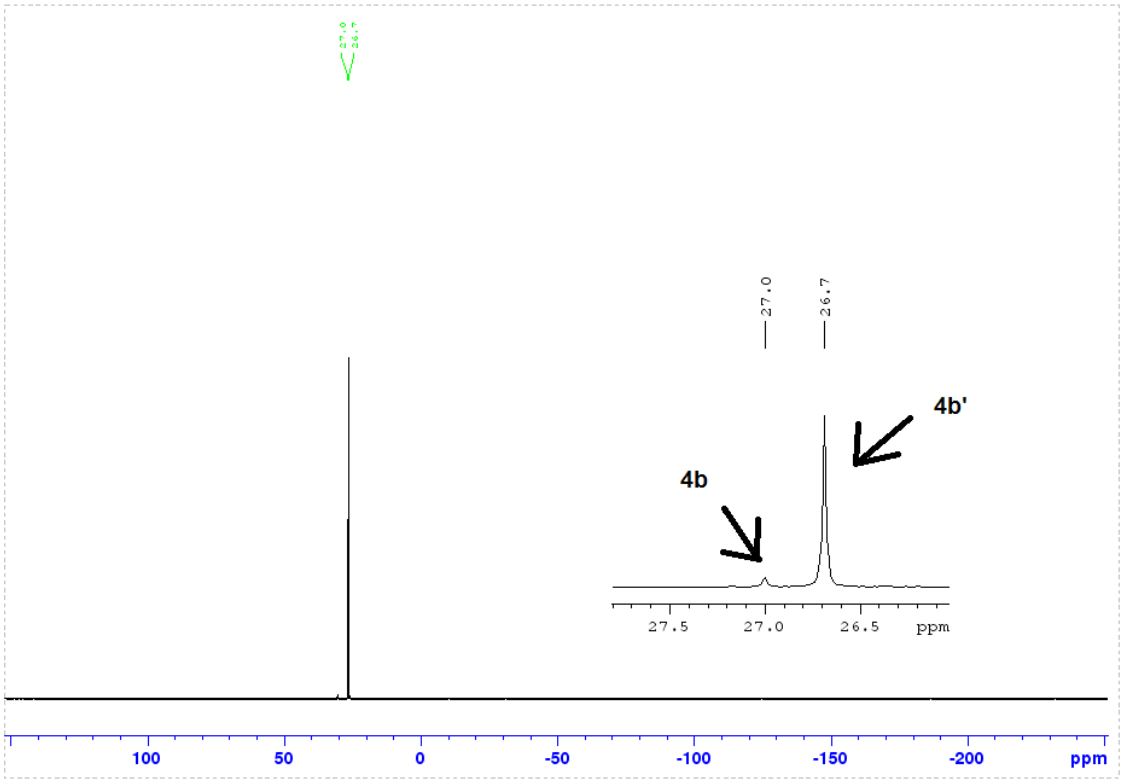


Figure S18. $^{31}P\{^{1}H\}$ *NMRof* ***4b*** *after a further 13hrs at 105°C (121 MHz,* C_6D_6*, 300 K)*

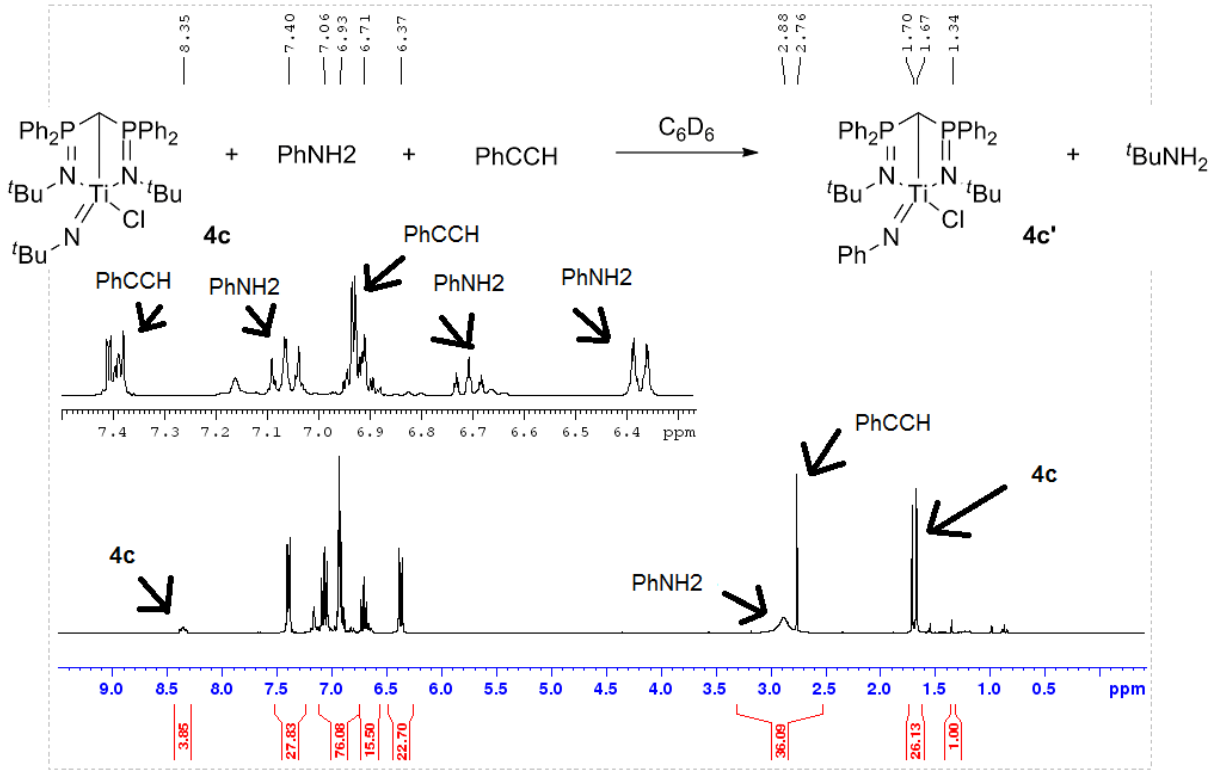


Figure S19. ^{1}H *NMR of* ***4c*** *after 10 hrs at r.t. (300 MHz,* C_6D_6*, 300 K)*

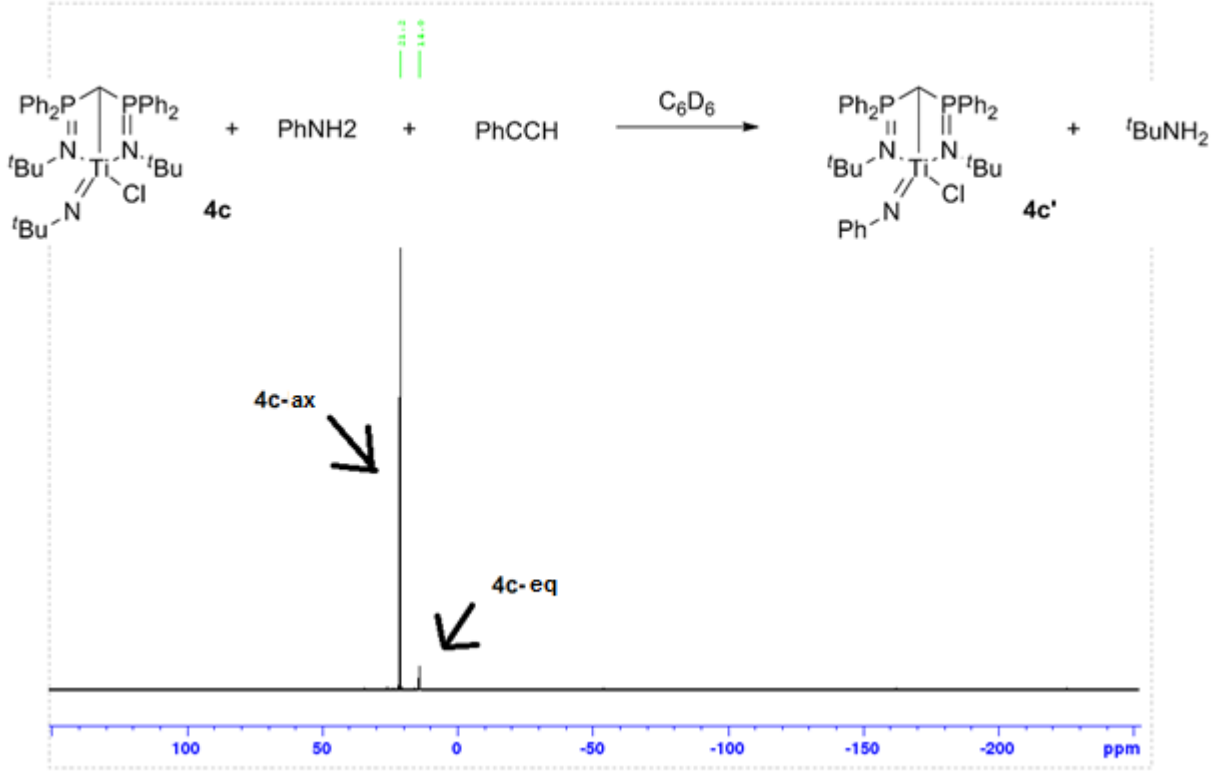


Figure S20. $^{31}P\{^{1}H\}$ *NMR of* ***4c*** *after 10 hrs (121 MHz,* C_6D_6*, 300 K)*

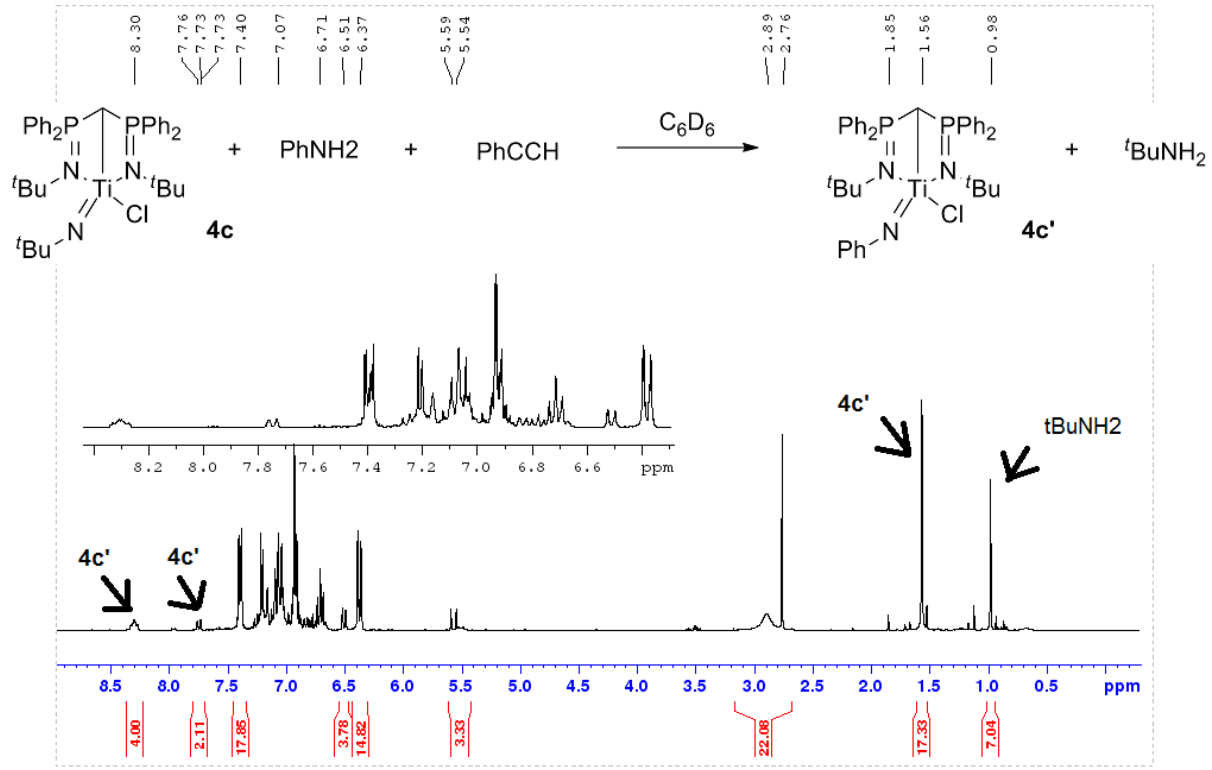


*Figure S21. ^{1}H NMR of **4c** after a further 13 hrs at 105°C (300 MHz, C_6D_6, 300 K)*

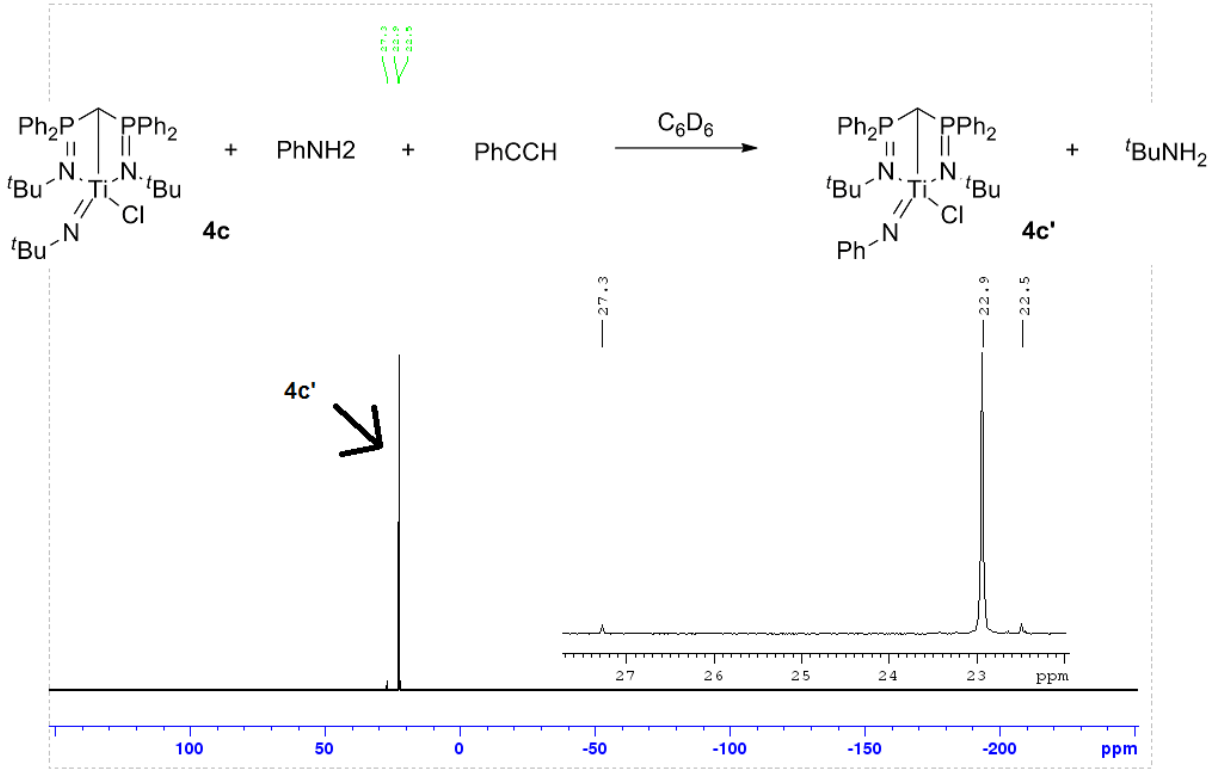
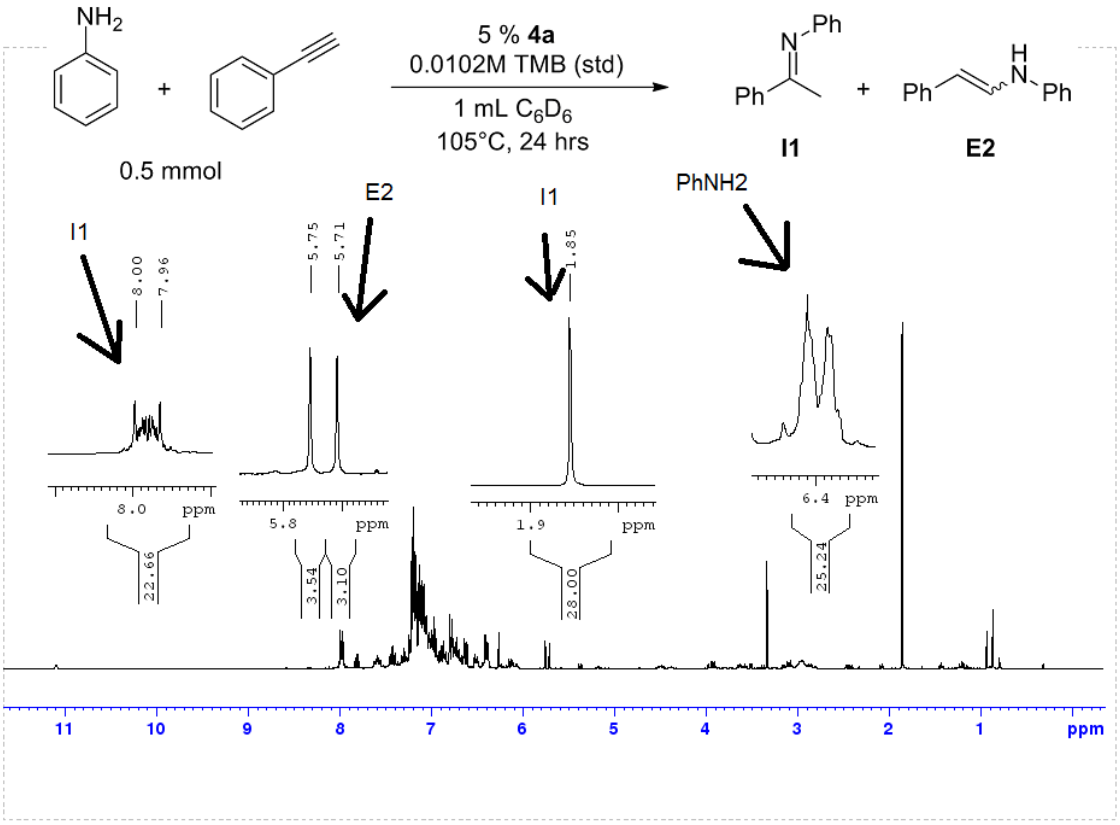


*Figure S22. $^{31}P\{^{1}H\}$ NMR of **4c** after a further 13 hrs at 105°C (121 MHz, C_6D_6, 300 K)*

Representative ^{1}H NMR spectrum for the hydroamination of alkynes



^{1}H NMR (300 MHz, C_6D_6, 300 K)

*Hydrolysis / alcoholysis of **4a-c** (Figures S23-S30)*

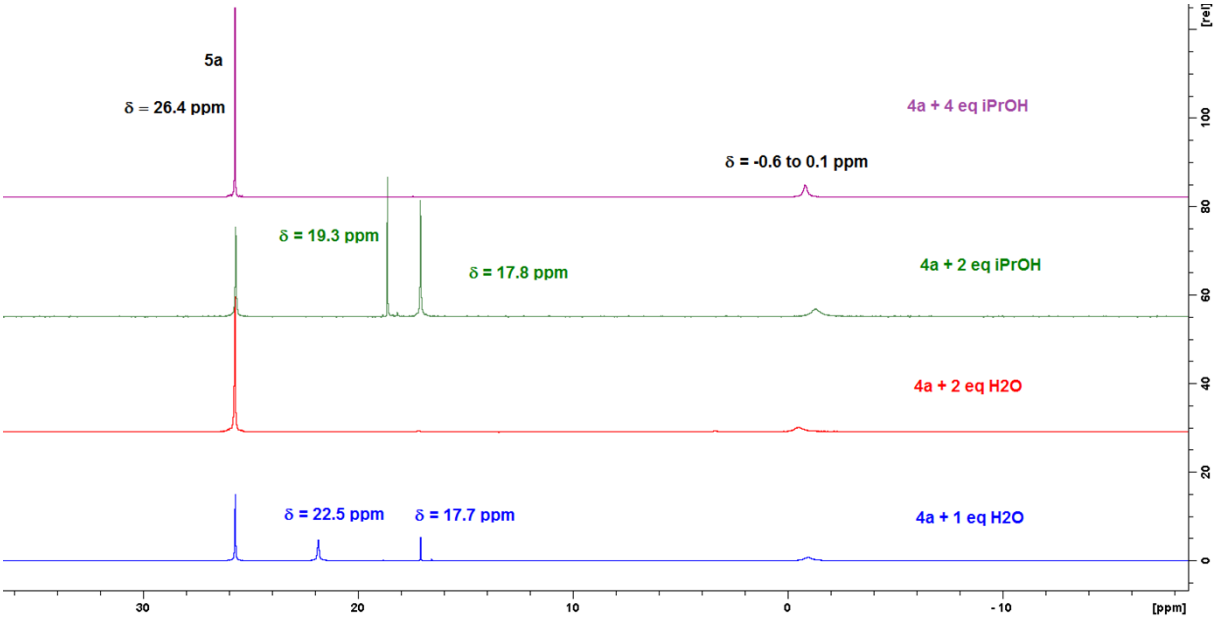


*Figure S23. $^{31}P\{^{1}H\}$ NMR of the gradual addition of $^{i}PrOH$ or H_2O to **4a** (202 MHz, CD_2Cl_2, 300 K)*

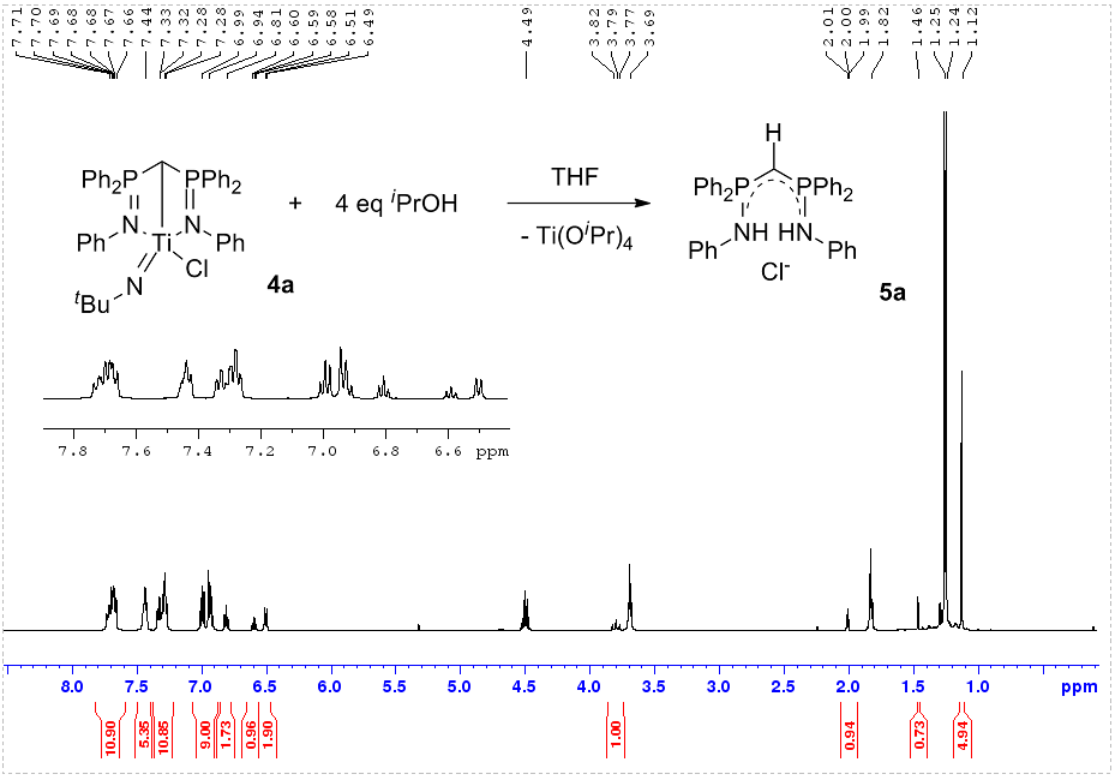


*Figure S24. ^{1}H NMR of **5a** (500 MHz, CD_2Cl_2, 300 K)*

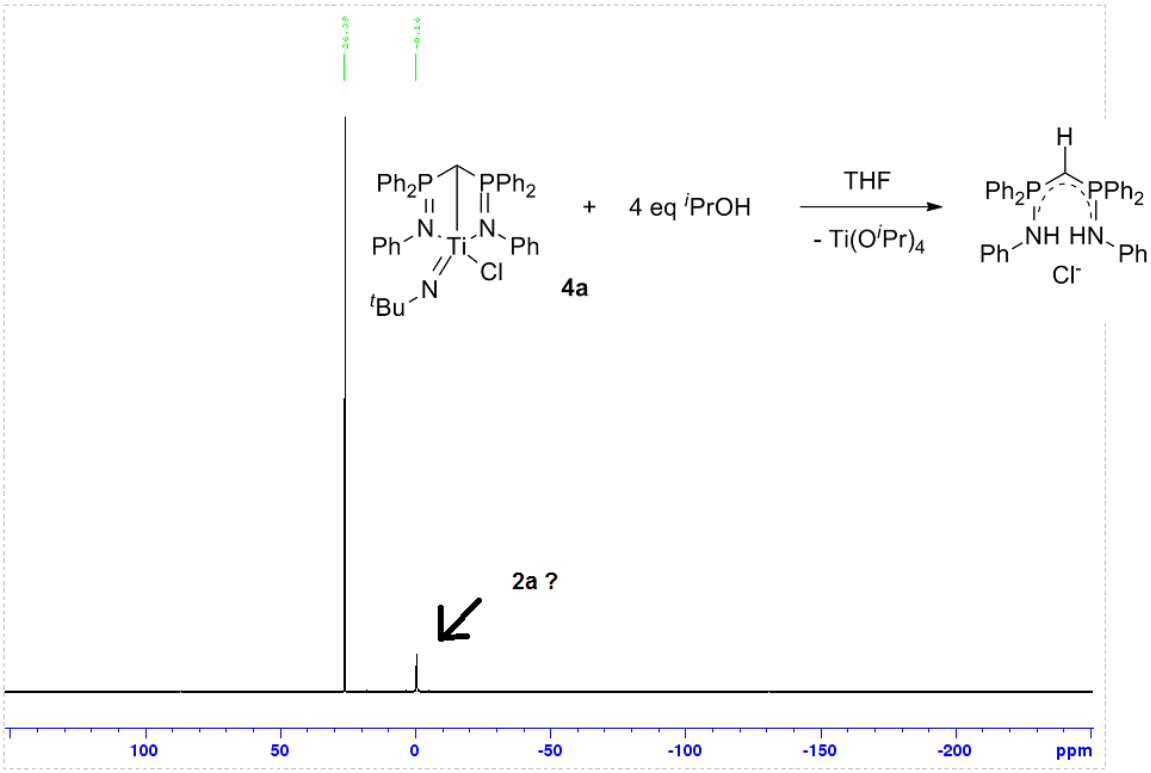


Figure S25. $^{31}P\{^{1}H\}$ NMR of **5a** (202 MHz, CD_2Cl_2, 300 K)

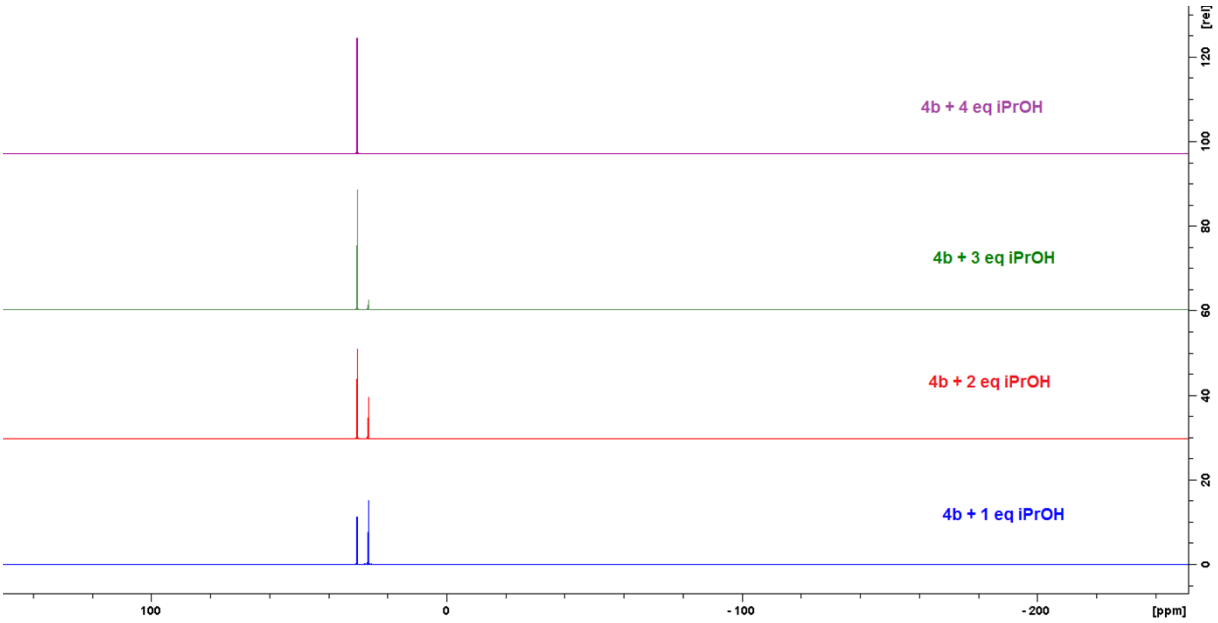


*Figure S26. $^{31}P\{^{1}H\}$ NMR of the gradual addition of $^{i}PrOH$ to **4b** (202 MHz, CD_2Cl_2, 300 K)*

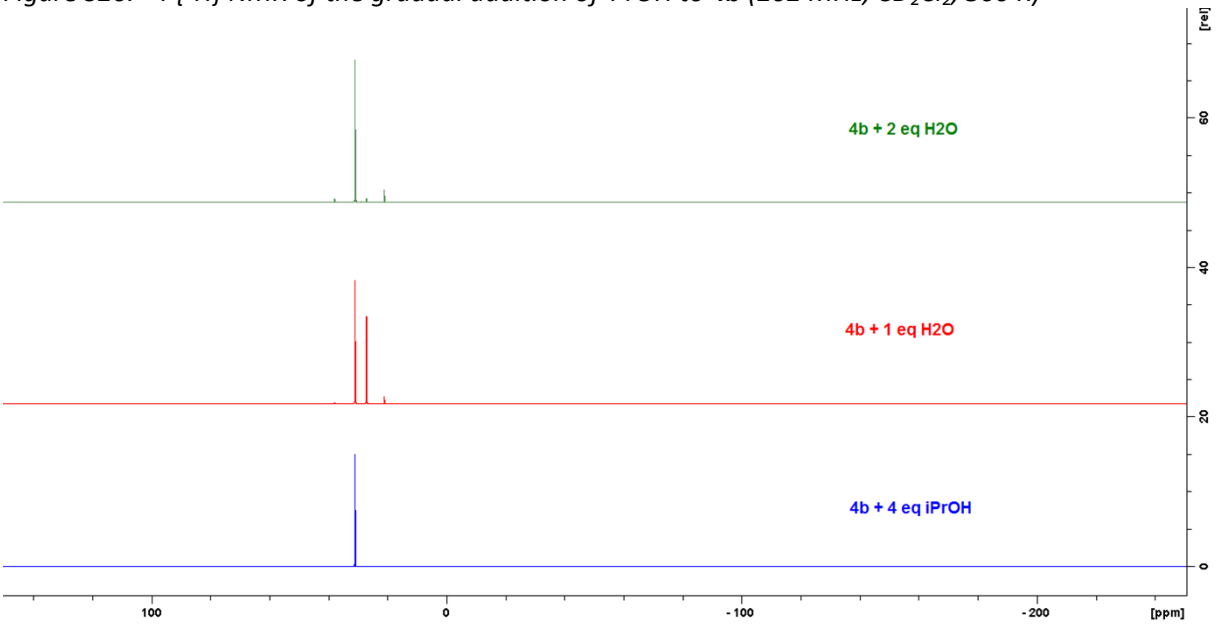


*Figure S27. $^{31}P\{^{1}H\}$ NMR of the gradual addition of $^{i}PrOH$ or H_2O to **4b** (202 MHz, CD_2Cl_2, 300 K)*

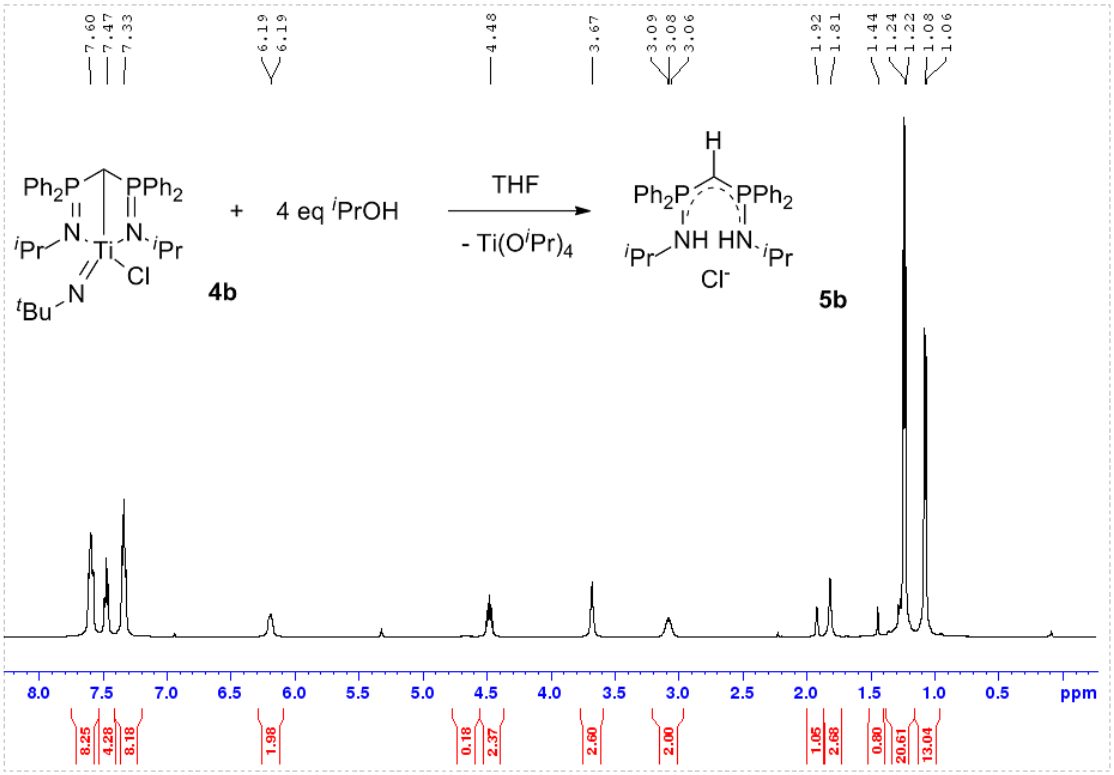


*Figure S28. ^{1}H NMR of **5b** (500 MHz, CD_2Cl_2, 300 K)*

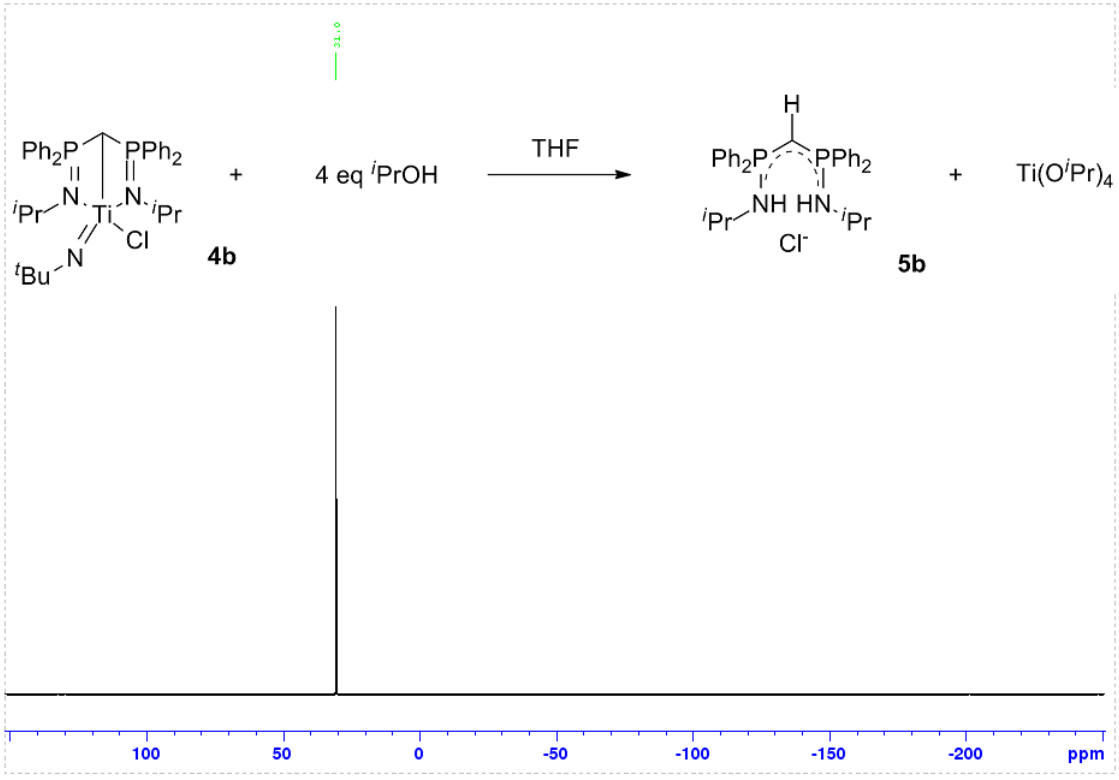


*Figure S29. $^{31}P\{^{1}H\}$ NMR of **5b** (202 MHz, CD_2Cl_2, 300 K)*

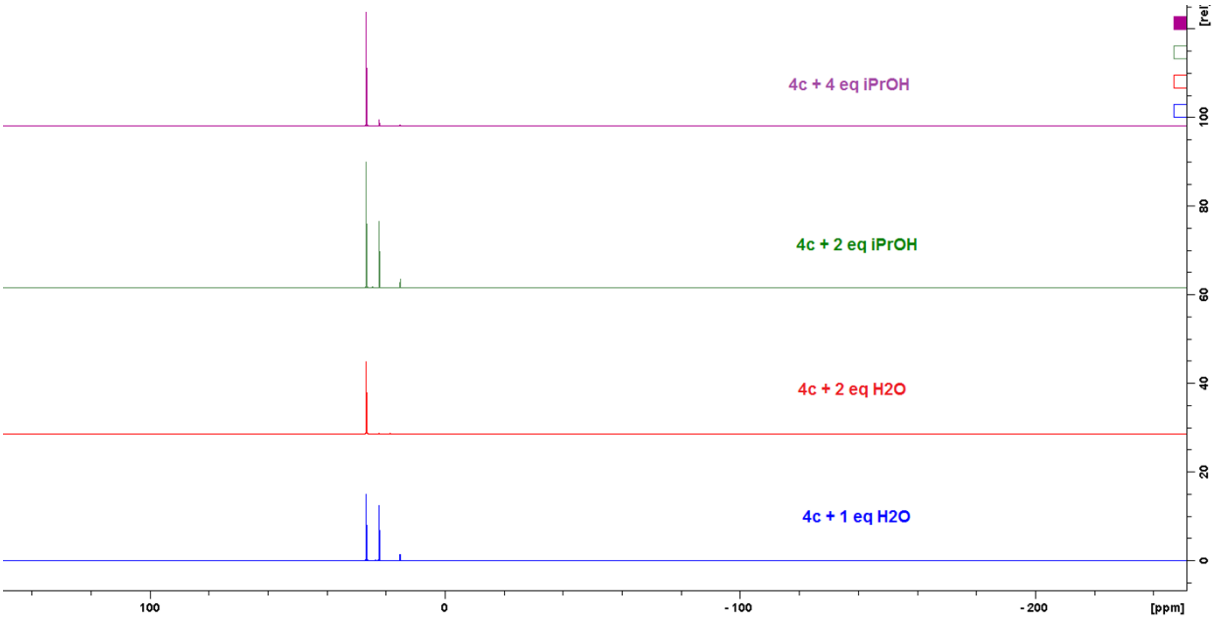
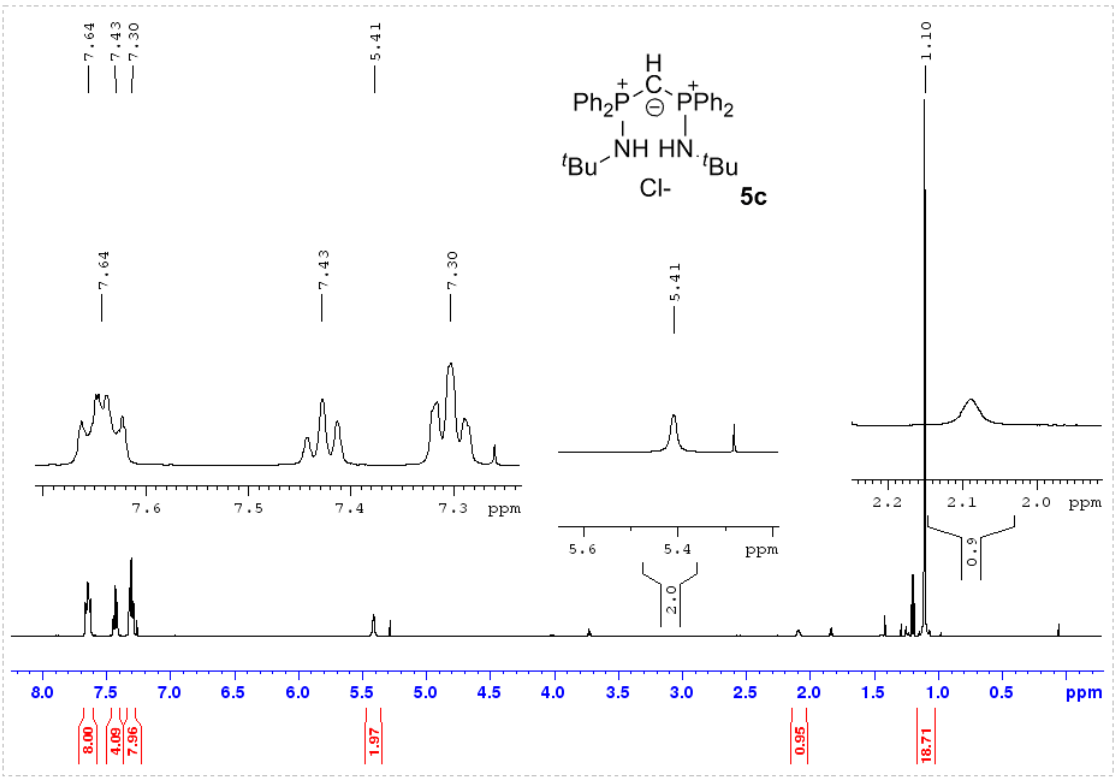
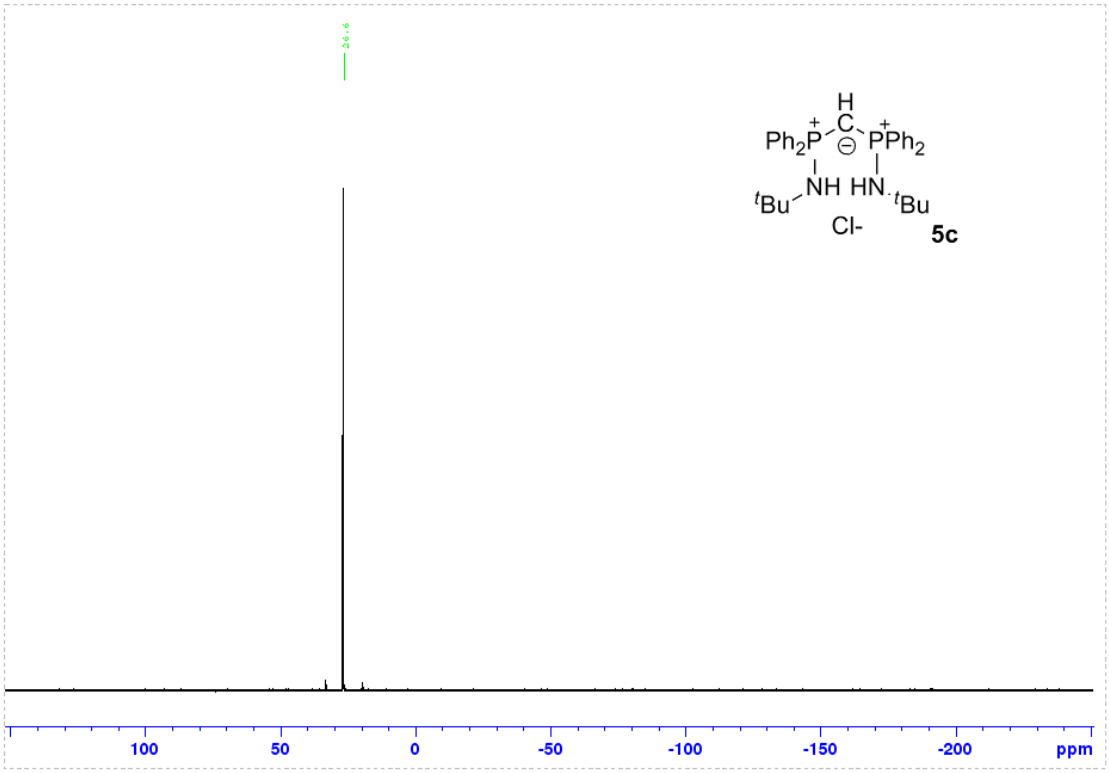


*Figure S30. $^{31}P\{^{1}H\}$ NMR of the gradual addition of $^{i}PrOH$ or H_2O to **4c** (202 MHz, CD_2Cl_2, 300 K)*

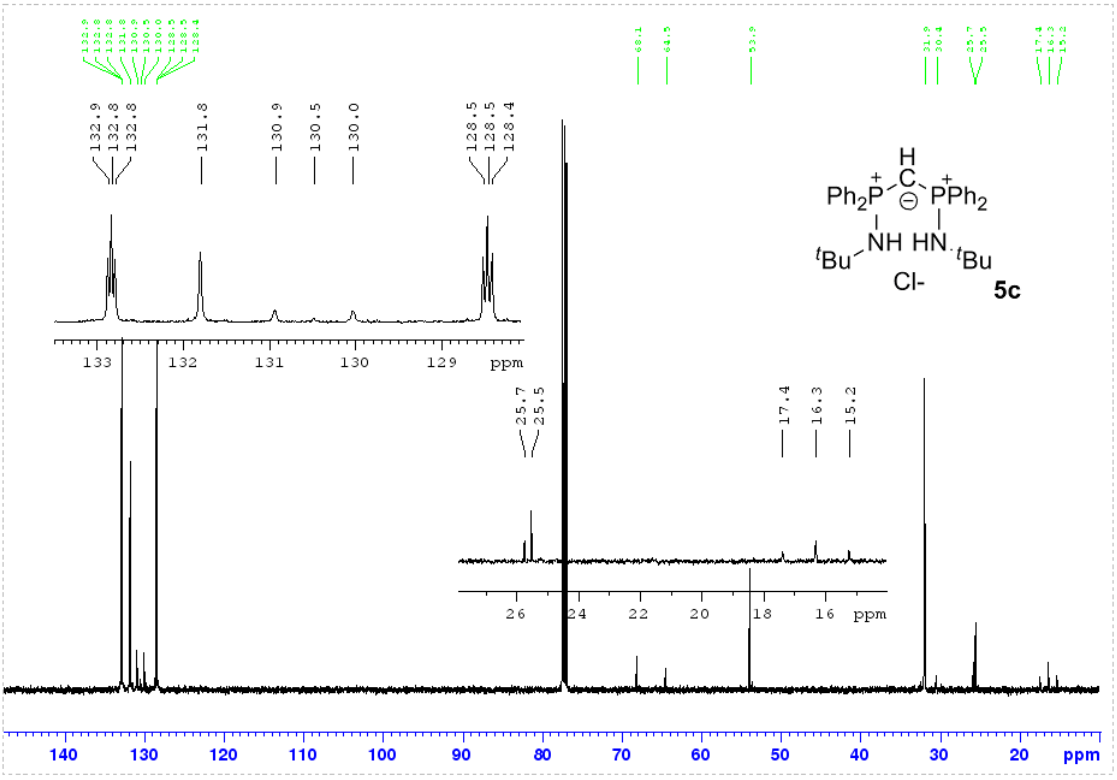
*NMR spectra of the chloride salt of monocation **5c***



^{1}H NMR (500 MHz, $CDCl_3$, 300 K)



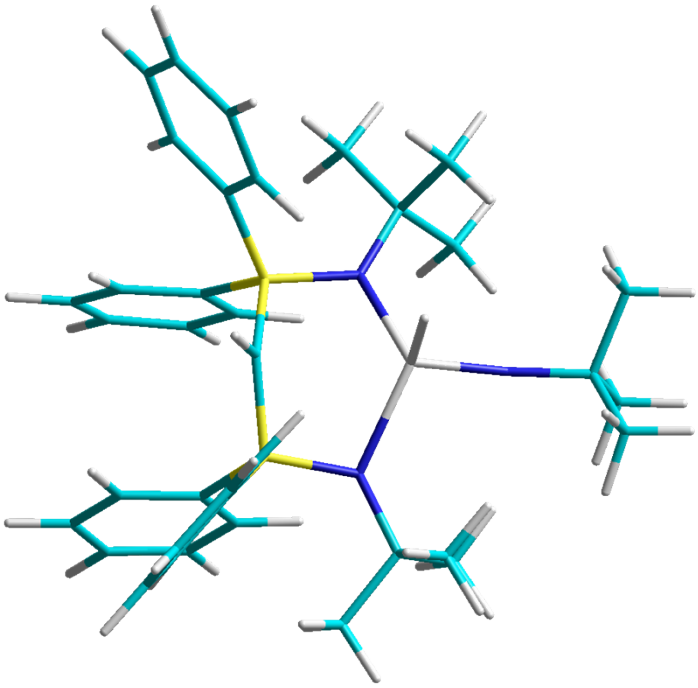
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 300 K)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 300 K)

3. Geometries of DFT molecular structures

4c-ax *(DFT):*

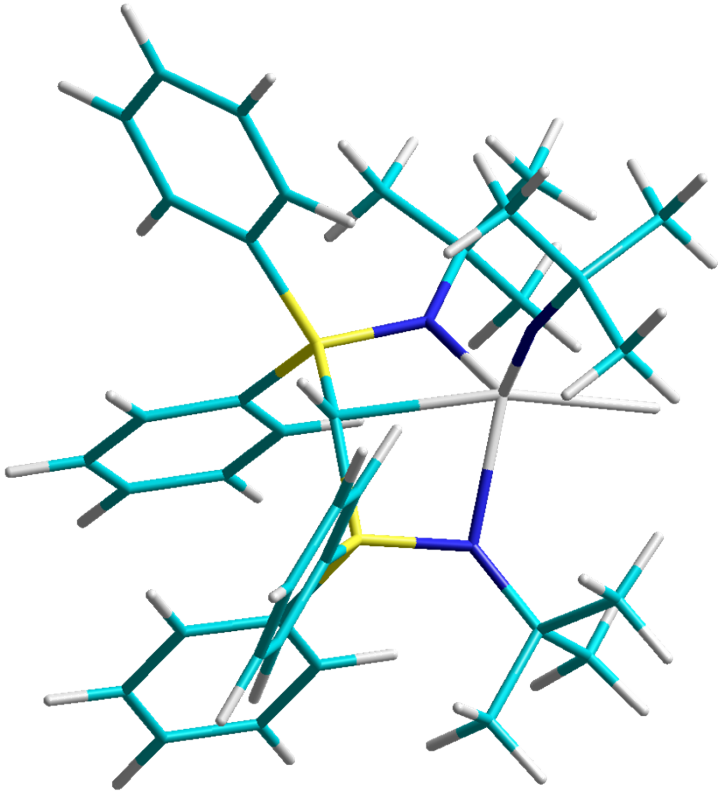


final geometry for **4c-ax (DFT):**

		angstroms	
atom	x	y	z
C1	-0.1627939321	0.0082084665	-1.5037210567
H1	0.0240451782	-0.4297693402	-2.4716702572
C2	2.0216856985	-2.6041414370	3.1932677879
C3	1.4568832335	-4.0423598924	3.2130781271
H2	0.3830084140	-4.0380159263	3.4202981607
H3	1.9498560596	-4.6386621629	3.9901613006
H4	1.6220052597	-4.5263962617	2.2458376814
C4	3.5515299368	-2.6817982701	2.9878549094
H5	4.0030459773	-1.6865852046	3.0302944445
H6	3.7796416330	-3.1252232733	2.0139453904
H7	4.0147164050	-3.2974510507	3.7683092650
C5	1.7244972167	-1.9235873542	4.5502664978
H8	2.1291207434	-0.9075700358	4.5796634704
H9	2.1787871863	-2.4928552033	5.3702186861
H10	0.6476585760	-1.8647564390	4.7351305665
C6	-2.1348561094	-2.1641481264	1.4532198163
C7	-3.6406896503	-2.0269712185	1.1371052871
H11	-3.8781703272	-2.3294819157	0.1143531264
H12	-4.0149483799	-1.0137184053	1.2994845356
H13	-4.1991331688	-2.6914594475	1.8054007219
C8	-1.7370846553	-3.6330675711	1.2018105989
H14	-1.9229224444	-3.9052500414	0.1579796520
H15	-2.3197274144	-4.3076846295	1.8407969114
H16	-0.6770982379	-3.7900045390	1.4077184881
C9	-1.9217259212	-1.8010042364	2.9325492100
H17	-0.8592728645	-1.8217594934	3.1748817282
H18	-2.4518456465	-2.5086695840	3.5804181464
H19	-2.3029880812	-0.7968738597	3.1508635460
C10	3.0054835951	1.1854431566	0.9322208713
C11	2.8045491346	1.2710578164	2.4544756487
H20	2.0717779301	2.0444054896	2.7119955506
H21	3.7481033793	1.5247598116	2.9513031088
H22	2.4427957285	0.3179625126	2.8395092347
C12	4.1498771389	0.2070418318	0.5977215196
H23	4.3217245228	0.1762110619	-0.4829031149
H24	3.9068893035	-0.8036902934	0.9294209213

H25	5.0820186017	0.5190455221	1.0841607780
C13	3.4209817369	2.5840843616	0.4246535381
H26	3.6400122289	2.5883313070	-0.6458354703
H27	4.3398424842	2.8831375542	0.9406597480
H28	2.6685327814	3.3482174894	0.6322307800
C14	-2.4422470393	-1.5690222364	-2.0535557955
C15	-3.7874645658	-1.4645162413	-2.4362829222
H29	-4.4344268596	-0.7273437293	-1.9732709722
C16	-4.3128916178	-2.3127286794	-3.4126830433
H30	-5.3564826190	-2.2164078868	-3.7004087501
C17	-3.5056858631	-3.2790077413	-4.0133746185
H31	-3.9157521151	-3.9359894121	-4.7754521551
C18	-2.1707955041	-3.4032055649	-3.6225679604
H32	-1.5369266918	-4.1611225612	-4.0743995758
C19	-1.6394363755	-2.5606431056	-2.6458658758
H33	-0.6047580456	-2.6854277692	-2.3366496491
C20	-2.8068089722	0.8961529972	-0.4508972712
C21	-3.4060495446	1.5926939307	-1.5138703493
H34	-3.2036462683	1.2982240299	-2.5394595193
C22	-4.2602761023	2.6659059975	-1.2649675358
H35	-4.7263232262	3.1866212014	-2.0973190036
C23	-4.5119182322	3.0747644474	0.0472371501
H36	-5.1799025982	3.9099518547	0.2398632073
C24	-3.8900619709	2.4143366599	1.1065115258
H37	-4.0643577587	2.7376624521	2.1292906045
C25	-3.0408484328	1.3335651081	0.8588461942
H38	-2.5522189977	0.8270900908	1.6842902454
C26	2.0991393065	1.3746250051	-2.5062153074
C27	2.4777193153	2.6023740973	-3.0688764693
H39	2.1220698660	3.5344301417	-2.6431161862
C28	3.3236288552	2.6408999048	-4.1787136863
H40	3.6047837402	3.6003747697	-4.6047251597
C29	3.8072358271	1.4569635188	-4.7360216992
H41	4.4632677190	1.4891287295	-5.6016054816
C30	3.4510255821	0.2313360838	-4.1692224290
H42	3.8324429206	-0.6960979852	-4.5873567454
C31	2.6076245314	0.1850438530	-3.0589164630
H43	2.3577889621	-0.7758340065	-2.6161053290
C32	0.2225190676	2.8631696340	-0.7594092904
C33	0.0901469250	3.3672183928	0.5403809391
H44	0.4745640257	2.7921088051	1.3759124551
C34	-0.5364747664	4.5945644033	0.7646172728
H45	-0.6283311065	4.9750803410	1.7783888906
C35	-1.0424448334	5.3280152865	-0.3077188977
H46	-1.5231146312	6.2872507865	-0.1345310293
C36	-0.9422099185	4.8195616693	-1.6050192734
H47	-1.3508663653	5.3783549778	-2.4427812786
C37	-0.3249214419	3.5904799802	-1.8292840473
H48	-0.2730054352	3.1945563317	-2.8392042401
N1	-1.2308041444	-1.2949410906	0.6142776246
N2	1.7419036870	0.6391282647	0.3150804162
N3	1.4198725581	-1.8588894127	2.1003898293
P1	-1.6517656400	-0.5029700453	-0.7718838579
P2	0.9946460733	1.2152539144	-1.0391505088
Cl1	1.7589605865	-2.8493685462	-0.9006515459
Ti1	0.8745239552	-1.2564331678	0.6001983558

4c-eq *(DFT):*

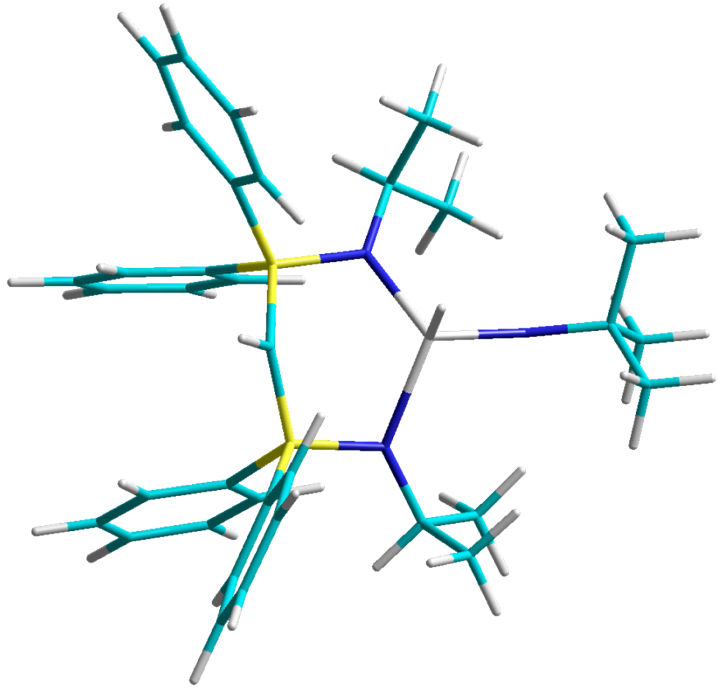


final geometry for **4c-eq (DFT):**

atom	x	y	z
		angstroms	
H1	-0.0074219450	-0.0336475650	-2.6535828200
H2	1.2259469285	-4.8898112890	-0.3620529388
H3	2.8603347216	-5.4509720253	-0.7843209752
H4	2.6216905225	-4.2836556702	0.5410469178
H5	4.0224180719	-2.1844967161	-2.2717341555
H6	4.3008165339	-2.7208031292	-0.6064828396
H7	4.4955520882	-3.8673310798	-1.9509322311
H8	1.9244736102	-3.0047288429	-3.5389607253
H9	2.4298932095	-4.6782723548	-3.2301566776
H10	0.8122623674	-4.1369466260	-2.7403337210
H11	-3.6693217332	-2.4869943222	-0.2960943198
H12	-3.9878413967	-1.0998117142	0.7682842448
H13	-4.0914275581	-2.7419052119	1.3984945040
H14	-1.5241675833	-3.8117631339	-0.0830235739
H15	-2.0767290681	-4.2153346806	1.5569188903
H16	-0.4487746416	-3.5582515918	1.3067850146
H17	-0.9235631346	-1.5683838499	2.9354983320
H18	-2.4469314528	-2.4252535232	3.2433290051
H19	-2.4760810928	-0.7170845384	2.8005346496
H20	2.0641404034	2.4313344902	2.4038638948
H21	3.6790817219	1.8340626682	2.8002310916
H22	2.3195536996	0.6980758603	2.6919357482
H23	4.3935268104	0.1436624951	-0.4488343923
H24	3.8530097369	-0.6329713971	1.0537714453
H25	5.0856959924	0.6400746959	1.1103813427
H26	3.9348403897	2.5981085873	-0.8582863101
H27	4.4846420960	3.0243666746	0.7626338833
H28	2.8779031100	3.5186524037	0.2354144209
H29	-4.4474123769	-0.1769367315	-2.1713710615
H30	-5.4377892564	-1.5080418176	-3.9896114760
H31	-4.0762355489	-3.2098499316	-5.1862844163
H32	-1.7035250074	-3.5755883686	-4.5254421364
H33	-0.7072410133	-2.2567703307	-2.6916885613
H34	-3.0761365494	1.8532695462	-2.5420891073
H35	-4.5314575525	3.7470881908	-1.9281422615
H36	-5.0316310645	4.2195302237	0.4620382798
H37	-4.0270623373	2.7943742422	2.2365167975

H38	-2.5656973840	0.8923353357	1.6187747075
H39	2.2566279091	3.8728275688	-2.7666342724
H40	3.7050575750	3.9442994108	-4.7531936718
H41	4.4058222482	1.8379396707	-5.8744359913
H42	3.6525992239	-0.3516448989	-4.9605751903
H43	2.2162799835	-0.4337971034	-2.9528931229
H44	0.5251728132	3.0846937944	1.2128063303
H45	-0.5397539316	5.2787642580	1.6427622756
H46	-1.3842775900	6.6471174274	-0.2551429645
H47	-1.1965015857	5.7792744250	-2.5789090629
H48	-0.1515106012	3.5882128571	-3.0054601580
C1	-0.1022659792	0.2833841112	-1.6245451443
C2	2.4105829601	-3.4092528720	-1.4436325797
C3	2.2738967811	-4.5857769584	-0.4508788816
C4	3.9009980614	-3.0238555121	-1.5784798326
C5	1.8611481983	-3.8329666247	-2.8238207131
C6	-2.0476375692	-2.0774664282	1.1316347333
C7	-3.5327839586	-2.0942155105	0.7145195400
C8	-1.4857763914	-3.5045599849	0.9669937164
C9	-1.9622211201	-1.6668476420	2.6172057644
C10	3.0681108845	1.3856361550	0.7581687486
C11	2.7577915983	1.5965730311	2.2551178272
C12	4.1669101539	0.3138464647	0.6083103527
C13	3.6121135492	2.7092235641	0.1803567469
C14	-2.4927346653	-1.0915155268	-2.3248287343
C15	-3.8332407581	-0.9052495766	-2.6900343710
C16	-4.3972860080	-1.6641551947	-3.7177019529
C17	-3.6344508219	-2.6207429656	-4.3875110405
C18	-2.3028807005	-2.8244451344	-4.0182903627
C19	-1.7352293662	-2.0714936319	-2.9912326555
C20	-2.7502435977	1.2127802638	-0.5002159123
C21	-3.2927401497	2.0441810333	-1.4949200718
C22	-4.1118168575	3.1172642647	-1.1484408194
C23	-4.3894125402	3.3849429234	0.1945815147
C24	-3.8290985225	2.5838820903	1.1890492749
C25	-3.0105039489	1.5061909099	0.8441699736
C26	2.0900623862	1.7152803388	-2.7405458942
C27	2.5401837200	2.9428730807	-3.2477487837
C28	3.3674438118	2.9843227298	-4.3719281796
C29	3.7629136548	1.8030256123	-4.9993396678
C30	3.3374854935	0.5749630326	-4.4884465413
C31	2.5131183928	0.5273950964	-3.3645104827
C32	0.3001386733	3.1984335117	-0.9240348925
C33	0.1609726657	3.6808402581	0.3835668907
C34	-0.4442209735	4.9162767428	0.6229690135
C35	-0.9218168862	5.6815786473	-0.4406303235
C36	-0.8134115999	5.1957110065	-1.7459557585
C37	-0.2166303490	3.9591522237	-1.9868387152
N1	-1.2062958133	-1.1475941972	0.3035628211
N2	1.8301884268	0.8929002116	0.0629445239
N3	1.6604725771	-2.2808573550	-0.9389954845
P1	-1.6544386384	-0.1958346758	-0.9437770076
P2	1.0558894214	1.5442418270	-1.2171945050
Cl1	1.5719613148	-1.7671885200	2.2019365548
Ti1	0.9321348946	-1.0805589471	0.0241265555

4b-ax *(DFT):*

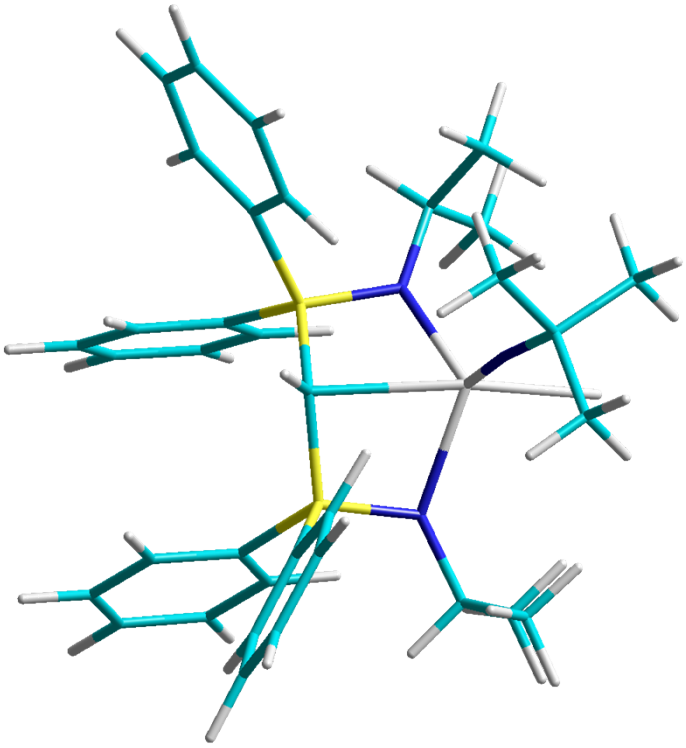


final geometry for **4b-ax (DFT):**

atom	x	y	z
		angstroms	
C1	-0.5936157514	0.5908205285	-1.9173183581
H1	-0.4881328877	0.2687236042	-2.9414800436
C2	1.6976186704	-2.1720165316	2.7254966634
C3	1.0966960775	-3.5953945019	2.6782822632
H2	0.0278033486	-3.5703721831	2.9140164422
H3	1.5910369504	-4.2526410223	3.4041745121
H4	1.2190836305	-4.0226057073	1.6784575138
C4	3.2115252744	-2.2533338970	2.4247520161
H5	3.6687442108	-1.2600454445	2.4802857997
H6	3.3740816504	-2.6513784442	1.4186741965
H7	3.7199398843	-2.9040359388	3.1469349138
C5	1.4811784955	-1.5677170557	4.1310913693
H8	1.9074067031	-0.5616867276	4.1947385772
H9	1.9605435490	-2.1892564312	4.8967853524
H10	0.4146185000	-1.4984681309	4.3668565326
C6	-2.5812450313	-1.3000952120	1.1767448174
H11	-3.5792399553	-0.9105708916	0.9227656872
C7	-2.6066926913	-2.8187841008	0.9474566216
H12	-2.8407606449	-3.0554925255	-0.0941953722
H13	-3.3617945592	-3.2935590659	1.5855790731
H14	-1.6303735492	-3.2528783997	1.1829390371
C8	-2.3151142800	-0.9701529984	2.6493603279
H15	-1.3156480592	-1.3092577400	2.9302622103
H16	-3.0549179559	-1.4631437176	3.2903755853
H17	-2.3624595051	0.1071695516	2.8405513370
C9	2.3256505707	1.9393475620	0.6807647771
C10	2.1218337999	1.9746158869	2.1988741499
H18	1.1858708604	2.4729287426	2.4727151687
H19	2.9472293149	2.5094773632	2.6825680127
H20	2.0782655104	0.9557088284	2.5895727892
C11	3.6874610781	1.3263094399	0.3212730451
H21	3.8522516917	1.3402898302	-0.7596745882
H22	3.7338010434	0.2862825778	0.6580013904
H23	4.5014156598	1.8838408084	0.8001716616
H24	2.3246664813	2.9793316936	0.3193980224
C12	-2.8868795878	-1.0644907967	-2.2856423690
C13	-4.2801223469	-1.0802452388	-2.4485658040
H25	-4.9034366438	-0.3756904722	-1.9079390591
C14	-4.8786171801	-1.9969111591	-3.3149548623
H26	-5.9586006103	-1.9946881358	-3.4355562808
C15	-4.0953991668	-2.9082431224	-4.0230245725

H27	-4.5626722802	-3.6172623182	-4.7008327946
C16	-2.7091498088	-2.9118057257	-3.8500567122
H28	-2.0935393015	-3.6281278147	-4.3867855727
C17	-2.1042064277	-2.0034699148	-2.9819967763
H29	-1.0291492780	-2.0399310522	-2.8279650605
C18	-3.2432335537	1.4276498619	-0.7917818509
C19	-3.8653456261	2.0824305501	-1.8685361628
H30	-3.6734059835	1.7552519663	-2.8866734530
C20	-4.7273500542	3.1527736047	-1.6419868823
H31	-5.2055374819	3.6475784708	-2.4830923027
C21	-4.9728295478	3.5911286381	-0.3379911822
H32	-5.6465068181	4.4256288562	-0.1625342995
C22	-4.3438415205	2.9614270435	0.7347474458
H33	-4.5211782485	3.3052693522	1.7501961853
C23	-3.4796220536	1.8877412369	0.5094248807
H34	-2.9787959613	1.4135014762	1.3450357610
C24	1.7637903890	1.9624009682	-2.7517624998
C25	2.3226765355	3.2013777000	-3.0994245787
H35	2.0070890936	4.1072810875	-2.5925574552
C26	3.2857226091	3.2817615557	-4.1064970975
H36	3.7081710667	4.2476411686	-4.3699956204
C27	3.7021831839	2.1289865846	-4.7716694420
H37	4.4487112950	2.1942602540	-5.5586549661
C28	3.1646438761	0.8895702969	-4.4174507350
H38	3.4956579887	-0.0140293721	-4.9215650994
C29	2.2070314940	0.8000352737	-3.4083516420
H39	1.8248689848	-0.1733468070	-3.1135519257
C30	-0.1588406502	3.4535426030	-1.1267968627
C31	-0.3276534970	3.9759192856	0.1613563320
H40	0.0020673524	3.4024175676	1.0196470530
C32	-0.9285260253	5.2230007860	0.3462770703
H41	-1.0493813348	5.6179749936	1.3513157015
C33	-1.3735340750	5.9559544712	-0.7527217797
H42	-1.8384123352	6.9276565189	-0.6088302349
C34	-1.2281768803	5.4342518795	-2.0410026513
H43	-1.5829917054	5.9964105140	-2.9007057438
C35	-0.6302170065	4.1900788675	-2.2271995589
H44	-0.5295006155	3.7891322477	-3.2319858855
N1	-1.5729023579	-0.6503902367	0.2946136049
N2	1.2213931379	1.1969702454	0.0129136406
N3	1.0561132155	-1.3516200744	1.7170597547
P1	-2.0403513440	0.0721127549	-1.1158210590
P2	0.5535731445	1.7751072329	-1.3836082742
Cl1	1.3543214723	-2.2808350327	-1.3213528800
Ti1	0.4968536380	-0.7306293641	0.2367098517

4b-eq *(DFT):*

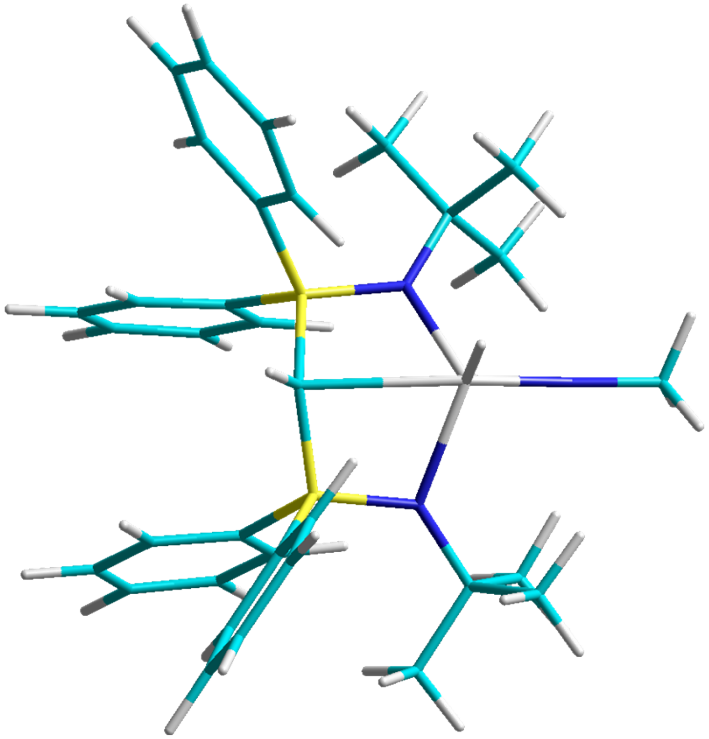


final geometry:for **4b-eq (DFT):**

atom	x	y	z
	angstroms		
H1	-0.3654970428	0.4507078031	-3.1058341888
H2	0.9288752632	-4.3885030703	-0.6188604085
H3	2.5559246877	-4.9538434809	-1.0628632894
H4	2.3406877705	-3.7570861595	0.2406108737
H5	3.6712116289	-1.7175034082	-2.6511354161
H6	3.9986412980	-2.2293078580	-0.9872447668
H7	4.1535522381	-3.3961535033	-2.3195569530
H8	1.5556527297	-2.5717840470	-3.8512227406
H9	2.0372450096	-4.2462157423	-3.5110351413
H10	0.4421309217	-3.6595836307	-2.9950873901
H11	-2.2784980539	-3.1693393191	-0.8544663986
H12	-2.9299111597	-3.6821364041	0.7173590990
H13	-1.2041961307	-3.2923496382	0.5514142037
H14	-1.4532027939	-1.5471742870	2.4960239666
H15	-3.1604548684	-2.0392674816	2.5980152721
H16	-2.7356195086	-0.3336893280	2.3977330786
H17	1.6740281481	2.8037654402	2.0569558547
H18	3.4307885826	2.6229537451	2.1836217085
H19	2.3730685950	1.1936364592	2.2631224818
H20	3.9869037532	1.0695479339	-1.1808970528
H21	3.7970345198	0.1633813799	0.3313898157
H22	4.7868902852	1.6384452732	0.3001182025
H23	-4.8758820351	0.1014860096	-2.2236125401
H24	-6.0120695521	-1.3130956821	-3.8910995920
H25	-4.7024799160	-2.8838616965	-5.3043793814
H26	-2.2378604722	-3.0526683437	-5.0022973603
H27	-1.0980740555	-1.6758315385	-3.3009357833
H28	-3.5149767018	2.2848611485	-2.9284317397
H29	-4.9651835270	4.1719936586	-2.2720844867
H30	-5.3902891594	4.6455048140	0.1319805980
H31	-4.3292590848	3.2269135016	1.8768351663
H32	-2.8618877585	1.3386601042	1.2168207067
H33	2.0697699496	4.3469656835	-2.9187270519
H34	3.7083577574	4.4817548360	-4.7539887148
H35	4.3963709744	2.4283094306	-5.9726952171
H36	3.4545597349	0.2239179431	-5.3085956384
H37	1.8510613647	0.0722758527	-3.4334488568
H38	0.2647702658	3.6098985492	0.7835584322
H39	-0.7378782609	5.8416256497	1.1899539866
H40	-1.6156524318	7.1750120489	-0.7150377914

H41	-1.5018766310	6.2587448224	-3.0235463789
H42	-0.4997365509	4.0385306939	-3.4285599183
C43	-0.4682166112	0.7697176941	-2.0782216213
C44	2.0840657645	-2.9289042996	-1.7585876949
C45	1.9736857819	-4.0830248801	-0.7367395134
C46	3.5702381794	-2.5468028333	-1.9427381777
C47	1.4943605716	-3.3802031942	-3.1132487618
C48	-2.4986157066	-1.5498513289	0.5906910156
H49	-3.5207478706	-1.3168413420	0.2513864608
C50	-2.2120713412	-3.0143433408	0.2263786324
C51	-2.4573075358	-1.3527061795	2.1120268807
C52	2.6388299250	1.9977112591	0.2622960370
C53	2.5190351323	2.1641090180	1.7832304170
C54	3.8797242338	1.1674042418	-0.0968880935
H55	2.7728074527	3.0015872701	-0.1723397758
C56	-2.8988312921	-0.6556266131	-2.6669422708
C57	-4.2896435309	-0.5817938582	-2.8292105429
C58	-4.9338382931	-1.3822939272	-3.7754332044
C59	-4.1996347512	-2.2647666604	-4.5667533010
C60	-2.8154790406	-2.3573897141	-4.3994297404
C61	-2.1684068427	-1.5675871206	-3.4506134681
C62	-3.1080815574	1.6651113598	-0.8949353731
C63	-3.6954722858	2.4828625484	-1.8753434220
C64	-4.5133739332	3.5482405144	-1.5055993412
C65	-4.7501601290	3.8154425264	-0.1540243589
C66	-4.1566010622	3.0187779896	0.8244772695
C67	-3.3359616777	1.9496797908	0.4569579859
C68	1.8086705891	2.2045039285	-3.0717276077
C69	2.3614562239	3.4403306992	-3.4384245680
C70	3.2893606693	3.5176814756	-4.4788423621
C71	3.6766837867	2.3652686637	-5.1610586721
C72	3.1451869535	1.1277365108	-4.7908462616
C73	2.2252190783	1.0427889779	-3.7472233025
C74	-0.0262020664	3.6815709186	-1.3468483624
C75	-0.1106921643	4.1959878709	-0.0476140021
C76	-0.6813585600	5.4503815304	0.1779408811
C77	-1.1758354653	6.1969295951	-0.8906334864
C78	-1.1109165240	5.6832763816	-2.1886986052
C79	-0.5443226909	4.4314328725	-2.4164172649
N80	-1.5432269898	-0.6487147934	-0.1081819621
N81	1.4125258663	1.3845386148	-0.3157298735
N82	1.3464540859	-1.7914114072	-1.2606381777
P83	-1.9954499522	0.2837507895	-1.3683274202
P84	0.6804035925	2.0122620130	-1.6316542349
Cl85	1.1731013238	-1.2151827896	1.8642666715
Ti86	0.5827837950	-0.5926916463	-0.3244780440

4d-ax *(DFT):*

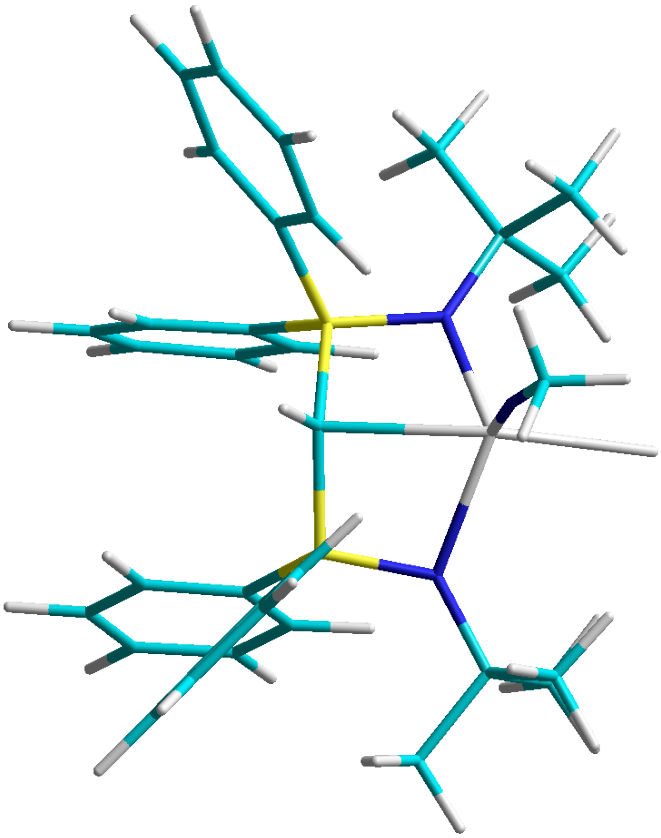


final geometry: for **4d-ax (DFT):**

		angstroms	
atom	x	y	z
C1	-0.1489225962	0.0109349774	-1.5140062119
H1	0.0480709997	-0.4089386511	-2.4882016535
C2	1.9846624860	-2.5882680969	3.2722634643
C3	1.3722380533	-4.0035585506	3.3804718320
H2	0.2942021236	-3.9486300526	3.5577521544
H3	1.8240605938	-4.5634312519	4.2086399762
H4	1.5408372220	-4.5610077178	2.4537303549
C4	3.5143195524	-2.7311061804	3.0982443799
H5	3.9946102300	-1.7489746904	3.0636715779
H6	3.7405104231	-3.2570744946	2.1653755799
H7	3.9535915307	-3.2956155985	3.9300946763
C5	1.6968194513	-1.8202165823	4.5854017192
H8	2.1385598862	-0.8195547990	4.5603255248
H9	2.1150172516	-2.3535227756	5.4482339770
H10	0.6198124727	-1.7092372718	4.7446313558
C6	-2.1729035414	-2.1227900358	1.4447203440
C7	-3.6735934425	-1.9864943518	1.1047910268
H11	-3.8982716443	-2.3174613673	0.0874774793
H12	-4.0419653806	-0.9656601420	1.2302905941
H13	-4.2477706563	-2.6259664972	1.7841502633
C8	-1.7806570601	-3.6025418782	1.2520216502
H14	-1.9504351737	-3.9098686129	0.2146054741
H15	-2.3788299313	-4.2515600875	1.9033408562
H16	-0.7253978374	-3.7542247428	1.4864355151
C9	-1.9703242106	-1.7119906762	2.9136524975
H17	-0.9090766738	-1.7363917902	3.1640469993
H18	-2.5143649766	-2.3903119697	3.5814067901
H19	-2.3417938146	-0.6964825820	3.0928604773
C10	3.1189494943	1.1237952375	0.8426025732
C11	2.9667551038	1.2305566191	2.3698801570
H20	2.2834136773	2.0410501642	2.6470986423
H21	3.9363584823	1.4394032528	2.8371062369
H22	2.5698569644	0.2969811682	2.7690809293
C12	4.2265998116	0.1047824691	0.5024240502
H23	4.3579377214	0.0322792212	-0.5822564330
H24	3.9681003304	-0.8856736460	0.8829388513
H25	5.1835000902	0.4086676723	0.9442310327

C13	3.5596482760	2.5016725995	0.3008908177
H26	3.7737014910	2.4752507016	-0.7703409414
H27	4.4836883151	2.8014156784	0.8075989455
H28	2.8182011442	3.2821610349	0.4903768320
C14	-2.4112258945	-1.5930990680	-2.0955843498
C15	-3.7583242752	-1.5222020006	-2.4805296455
H29	-4.4211244345	-0.7948280432	-2.0244411996
C16	-4.2666717258	-2.3892369596	-3.4499290485
H30	-5.3122438050	-2.3164984875	-3.7374746628
C17	-3.4409441566	-3.3437864049	-4.0432832323
H31	-3.8375928724	-4.0154077953	-4.7995155628
C18	-2.1041030733	-3.4373653452	-3.6508578933
H32	-1.4552365339	-4.1862397546	-4.0964825263
C19	-1.5931303526	-2.5755868399	-2.6804909683
H33	-0.5582517493	-2.6758351068	-2.3687789648
C20	-2.8167525075	0.8857553818	-0.5406932381
C21	-3.4131529007	1.5400709250	-1.6322455006
H34	-3.2042327320	1.2085664415	-2.6452289809
C22	-4.2713256758	2.6188744622	-1.4282800337
H35	-4.7364076810	3.1058881030	-2.2814221606
C23	-4.5260814018	3.0774477108	-0.1338036172
H36	-5.1952343519	3.9189820143	0.0239978072
C24	-3.9074915383	2.4612202114	0.9526042911
H37	-4.0855096470	2.8252264179	1.9607931607
C25	-3.0576539695	1.3719699314	0.7507299862
H38	-2.5730640262	0.8968533112	1.5969266802
C26	2.0466453640	1.4612417020	-2.5290910896
C27	2.3236787105	2.7109474624	-3.1005619694
H39	1.9297972269	3.6178032396	-2.6544374441
C28	3.1206131261	2.8039821009	-4.2434548522
H40	3.3255119638	3.7796290445	-4.6761611905
C29	3.6544835388	1.6542675780	-4.8246854013
H41	4.2721477809	1.7298424825	-5.7155172811
C30	3.3999905038	0.4071415557	-4.2511657735
H42	3.8220582628	-0.4927056918	-4.6899273123
C31	2.6077137812	0.3092929817	-3.1083194552
H43	2.4327216020	-0.6635487933	-2.6585156313
C32	0.2182710977	2.8302241418	-0.6356187906
C33	0.1908312540	3.2935785164	0.6859805981
H44	0.6446445681	2.6947756352	1.4673475700
C34	-0.4207712169	4.5086225296	0.9992476240
H45	-0.4289621283	4.8574283394	2.0282539026
C35	-1.0179703821	5.2700022431	-0.0043049495
H46	-1.4874713392	6.2198941174	0.2370979944
C36	-1.0246210602	4.8017623775	-1.3201794264
H47	-1.5067639400	5.3813780775	-2.1028499517
C37	-0.4208761667	3.5851220435	-1.6334482704
H48	-0.4515427424	3.2193612563	-2.6558254244
N1	-1.2523651657	-1.2915556658	0.5903948815
N2	1.8299193188	0.6009363570	0.2623388520
N3	1.4238065168	-1.8904068971	2.1326548426
P1	-1.6448194726	-0.5127858795	-0.8031471568
P2	1.0078390539	1.2118835019	-1.0236526423
C38	1.7182024426	-2.7829962947	-0.6598073338
Ti1	0.8846467868	-1.2655626820	0.6263134905
H49	1.5817392349	-2.5821570105	-1.7330366222
H50	1.2586798405	-3.7572615501	-0.4400315520
H51	2.7950708355	-2.8938721333	-0.4749039242

4d-eq *(DFT):*



final geometry: for **4d-eq (DFT):**

		angstroms	
atom	x	y	z
H1	0.1780467677	-0.4833954388	-1.8076434270
H2	-3.5952925122	-2.8035213189	0.5851550352
H3	-3.8628432635	-1.4199317133	1.6682814078
H4	-4.0035888719	-3.0660913132	2.2808249257
H5	-1.5026660633	-4.2171809621	0.7918988734
H6	-2.0360527160	-4.5856928452	2.4458610684
H7	-0.3923431323	-3.9856285821	2.1582485899
H8	-0.7847792059	-1.9865362981	3.7894805785
H9	-2.3565870909	-2.7430154490	4.1174147822
H10	-2.2807631394	-1.0426316980	3.6414427363
H11	2.3980474284	1.8473750885	3.2710620715
H12	4.0096677099	1.1905773479	3.5766244656
H13	2.6105102116	0.1006700436	3.5040895351
H14	4.5194484619	-0.4360673031	0.2566523957
H15	4.0112414839	-1.2403927457	1.7558333617
H16	5.2930932075	-0.0156634263	1.7997870050
H17	4.1307487146	2.0450847680	-0.0652899402
H18	4.7564379148	2.4115710130	1.5430253155
H19	3.1453323293	2.9645822112	1.0926343121
H20	-4.2713330185	-0.8123256518	-1.4344916396
H21	-5.1579271996	-2.2532678041	-3.2214848321
H22	-3.6937915790	-3.9359289958	-4.3206909271
H23	-1.3262960817	-4.1727849677	-3.5901585680
H24	-0.4313508290	-2.7411399235	-1.7835074804
H25	-3.0216878928	1.2256011737	-1.8636285398
H26	-4.5119816490	3.1240691477	-1.3616298832
H27	-4.9795006873	3.7603908054	0.9970683135
H28	-3.9140972223	2.4891584498	2.8506982579
H29	-2.4307323438	0.5710824519	2.3469505051
H30	2.2362162059	3.4473781377	-1.9725833214
H31	3.6720492476	3.5487513360	-3.9702654196
H32	4.5274749924	1.4586930651	-5.0093498459
H33	3.9395842125	-0.7439650978	-4.0107398336
H34	2.5095858447	-0.8554961601	-1.9959380534

H35	0.8691175848	2.5963972468	2.1374841331
H36	-0.1835582746	4.7760577936	2.6656233873
H37	-1.2126845582	6.1327037203	0.8526671069
H38	-1.2139827105	5.2735795096	-1.4810716262
H39	-0.1744561401	3.0992564849	-2.0049505595
C1	0.0469043097	-0.1638234545	-0.7832433067
C2	2.3764373734	-3.8320622476	-0.7893433625
C3	-1.9450932512	-2.4541034936	1.9978910031
C4	-3.4355137927	-2.4249726757	1.5983107345
C5	-1.4334098897	-3.9006141927	1.8377800986
C6	-1.8289626933	-2.0269495985	3.4762294520
C7	3.2923029598	0.8153157392	1.5550425065
C8	3.0573055925	0.9959031772	3.0694372214
C9	4.3427909232	-0.2913874611	1.3273752969
C10	3.8532641813	2.1364827171	0.9879833874
C11	-2.2734398348	-1.6392235175	-1.5110187849
C12	-3.6124478867	-1.5295866187	-1.9121004309
C13	-4.1182181906	-2.3516598634	-2.9213310638
C14	-3.2980374601	-3.2975023984	-3.5358697661
C15	-1.9685427370	-3.4282146078	-3.1277867420
C16	-1.4578989234	-2.6120420456	-2.1189050841
C17	-2.6531731368	0.7362163200	0.2131018165
C18	-3.2275531297	1.4843584284	-0.8289515156
C19	-4.0648773624	2.5621816644	-0.5459850008
C20	-4.3246045551	2.9214836794	0.7787350021
C21	-3.7304117950	2.2061958234	1.8179611798
C22	-2.8976976986	1.1211416892	1.5376050103
C23	2.2342305590	1.2868128133	-1.8645816510
C24	2.5871268127	2.5239440711	-2.4206774456
C25	3.4070288975	2.5824540963	-3.5498529560
C26	3.8893712422	1.4101936868	-4.1313792387
C27	3.5573603651	0.1738111828	-3.5722791129
C28	2.7410804111	0.1084487804	-2.4436201650
C29	0.4603049435	2.7145565497	0.0285329693
C30	0.4288813722	3.1911312177	1.3451791245
C31	-0.1712459699	4.4168189277	1.6402987433
C32	-0.7516510163	5.1757252275	0.6244710987
C33	-0.7490642576	4.6950595917	-0.6874405386
C34	-0.1559435729	3.4691975484	-0.9837900046
N1	-1.0842295452	-1.5541214345	1.1573233437
N2	2.0084459572	0.3840444305	0.9039542430
N3	1.7271415066	-2.7327052710	-0.1516418545
P1	-1.5113971635	-0.6619639119	-0.1398240695
P2	1.2122604054	1.0770801897	-0.3403208146
Cl1	1.7097731828	-2.3142838005	3.0135146407
Ti1	1.0580561383	-1.5507018669	0.8693697708
H40	2.7965421079	-4.5217793575	-0.0405626084
H41	3.2093019161	-3.5070442044	-1.4348780383
H42	1.6844370949	-4.4169183386	-1.4180195496