Supporting Information

for

(Arylimido)niobium(V)-Alkylidenes, $Nb(CHSiMe_3)(NAr)[OC(CF_3)_3](PMe_3)_2$, That Enable to Proceed Living Metathesis Polymerization of Internal Alkynes

Itsuki Izawa and Kotohiro Nomura*

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan

Contents

1. Selected NMR spectra for (imido)niobium(V) complexes.

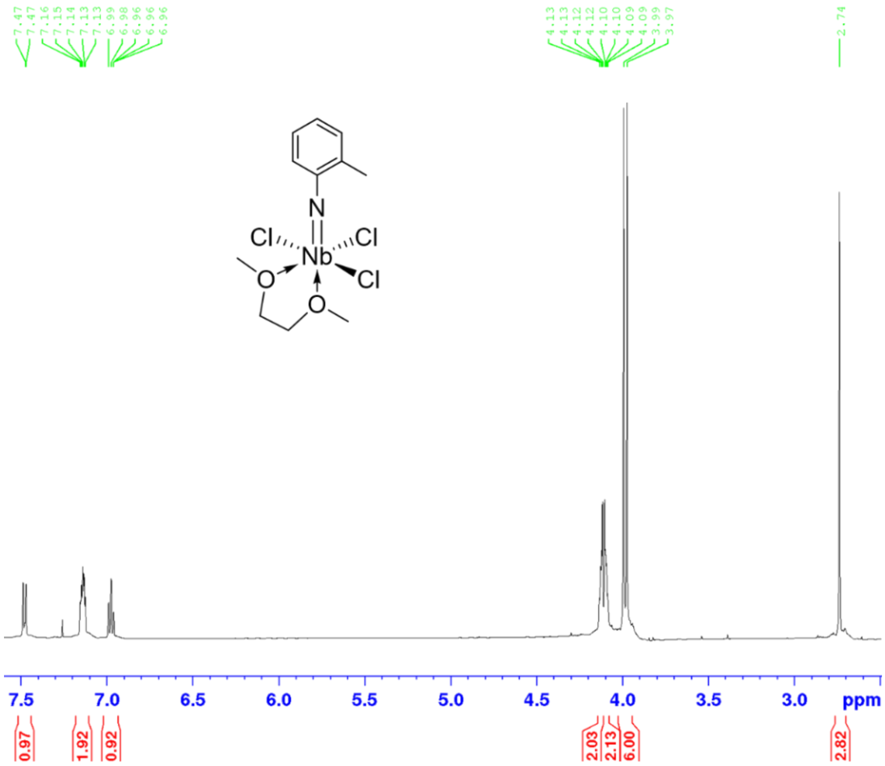

Figure S1-1. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) of **1c**.

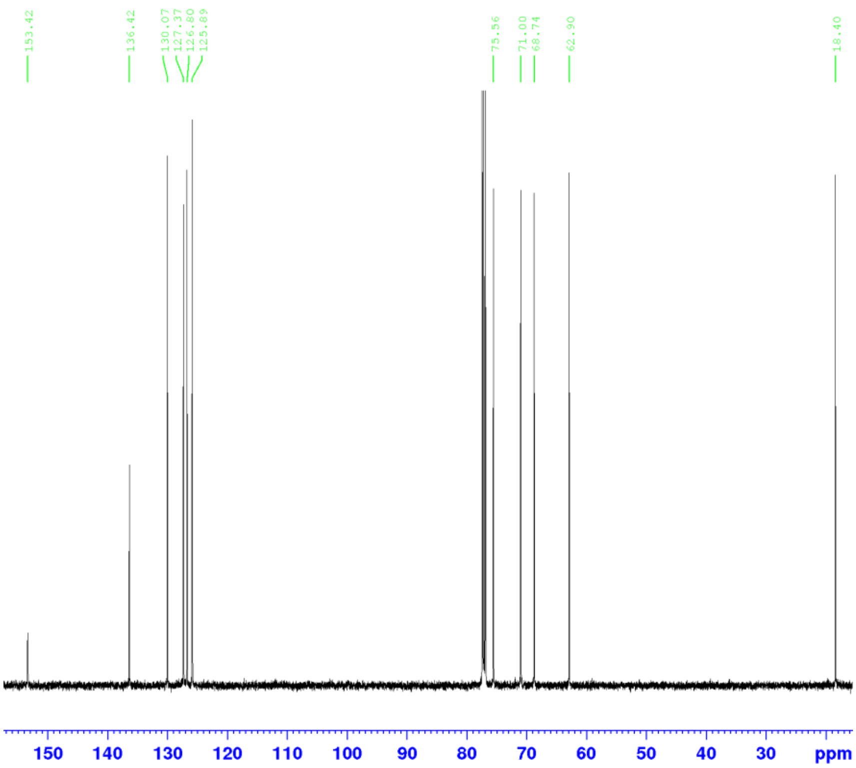

Figure S1-2. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) of **1c**.

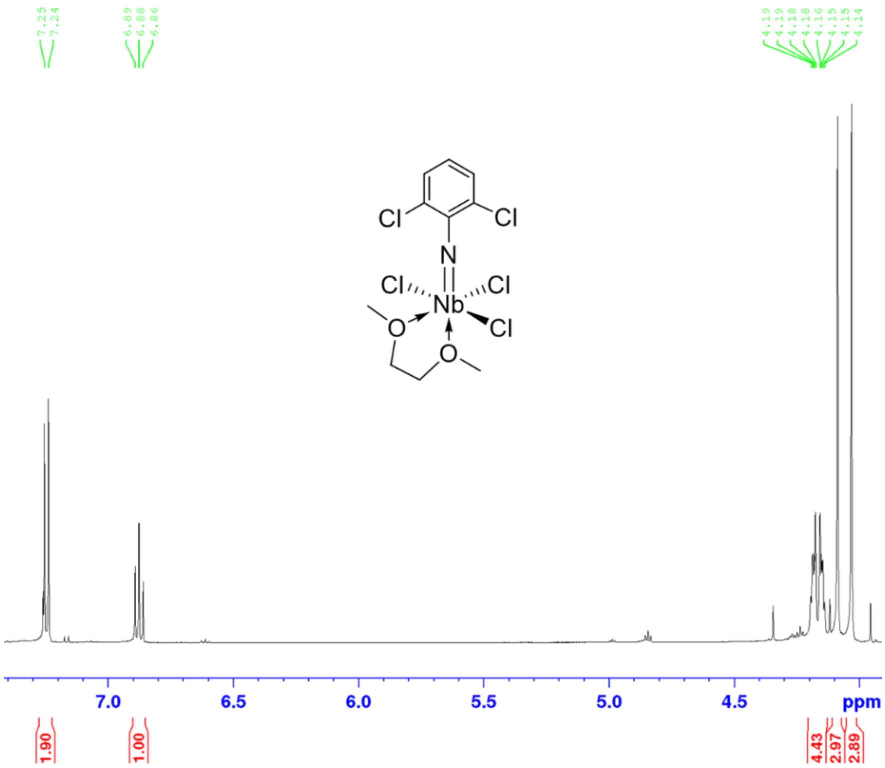

Figure S1-3. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) of **1d**.

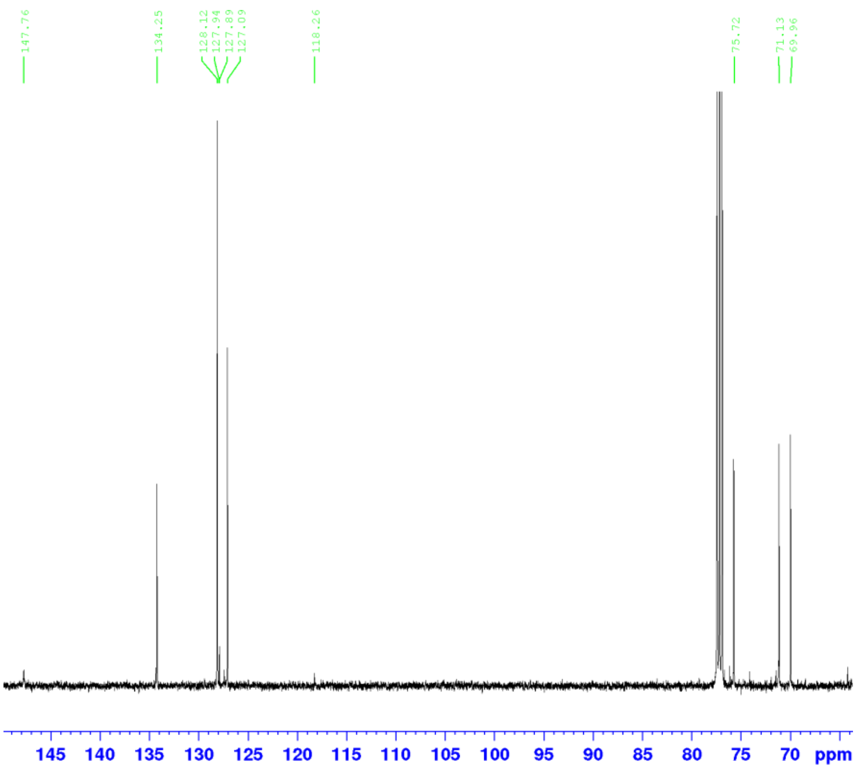

Figure S1-4. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) of **1d**.

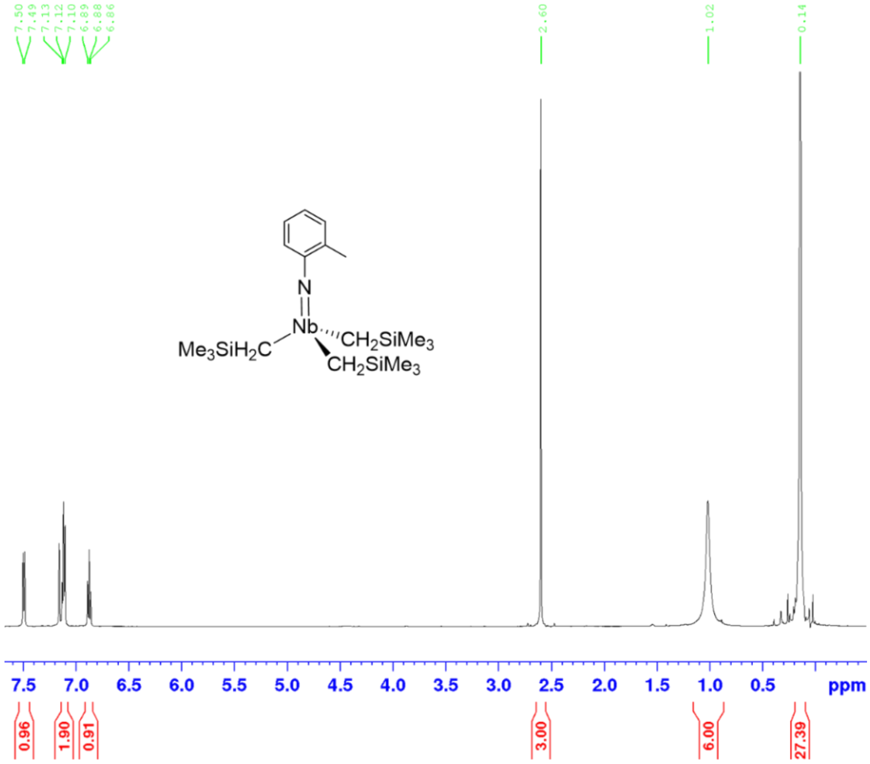

Figure S1-5. ^{1}H NMR spectrum (in C_6D_6 at 25 ºC) of **2c**.

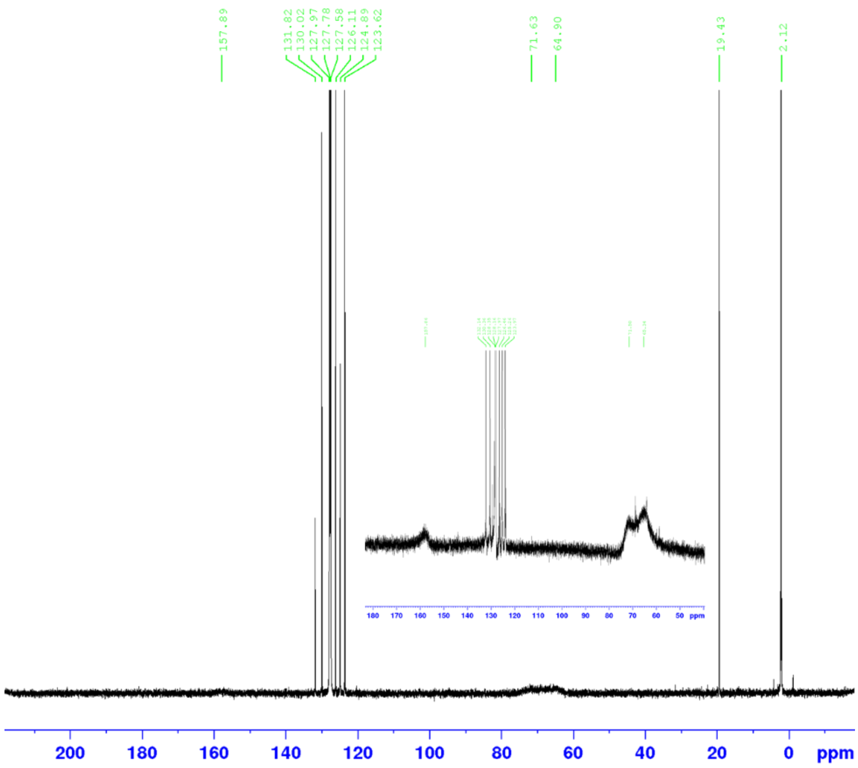

Figure S1-6. ^{13}C NMR spectrum (in C_6D_6 at 25 ºC) of **2c**.

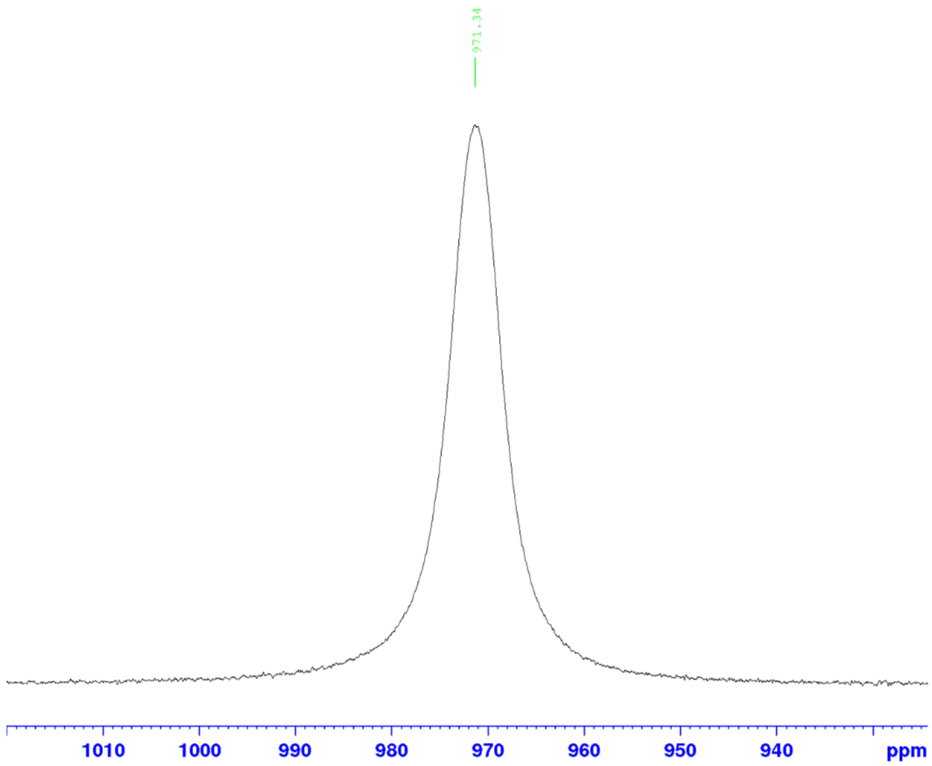

Figure S1-7. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **2c**.

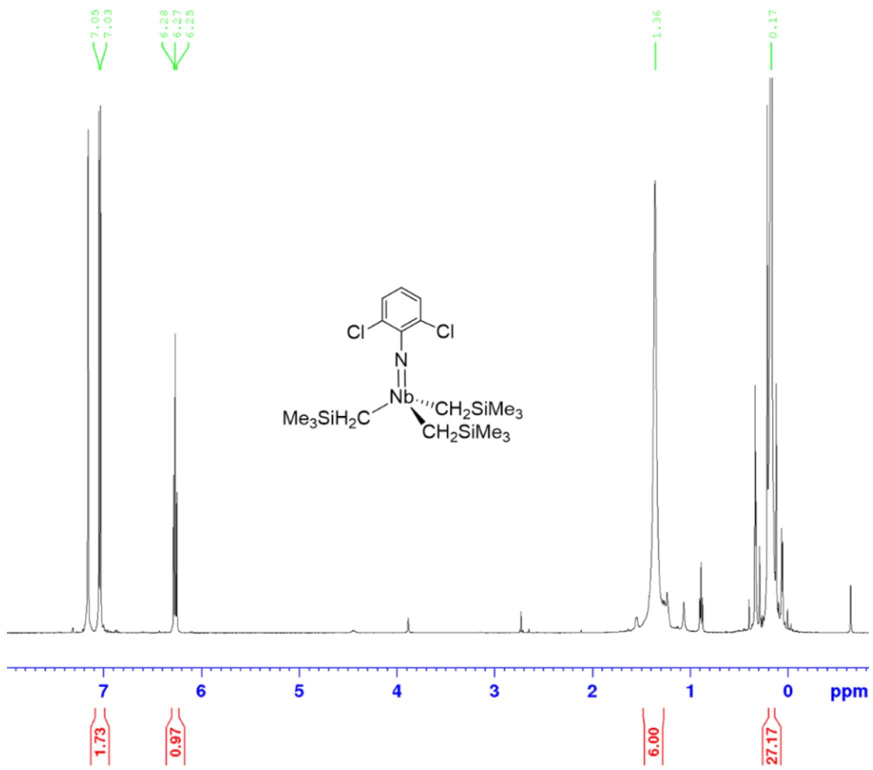

Figure S1-8. ^{1}H NMR spectrum (in C_6D_6 at 25 ºC) of **2d**.

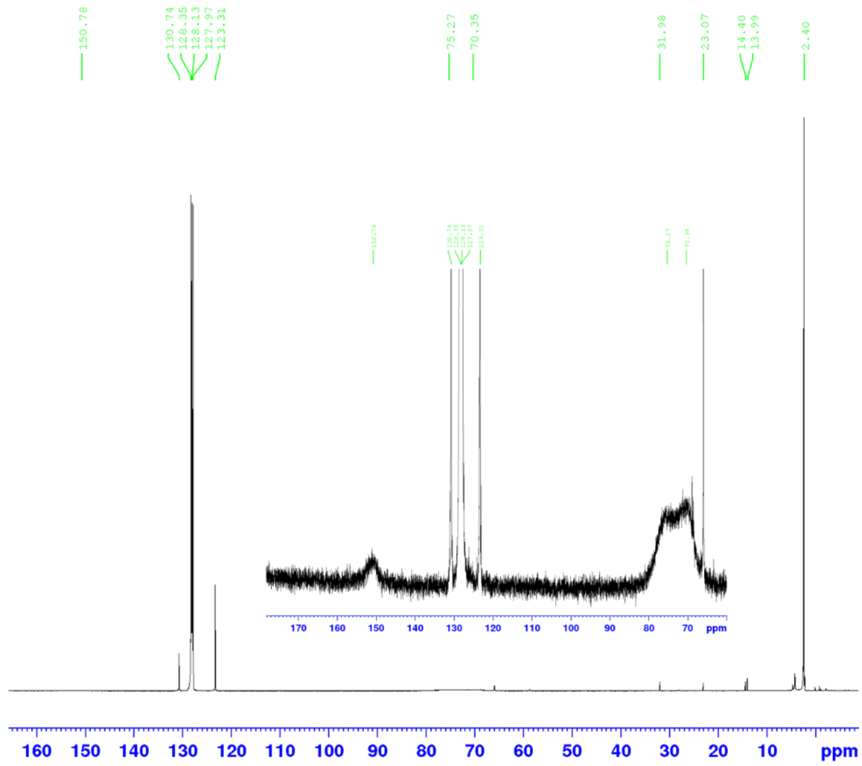

Figure S1-9. ^{13}C NMR spectrum (in C_6D_6 at 25 ºC) of **2d**.

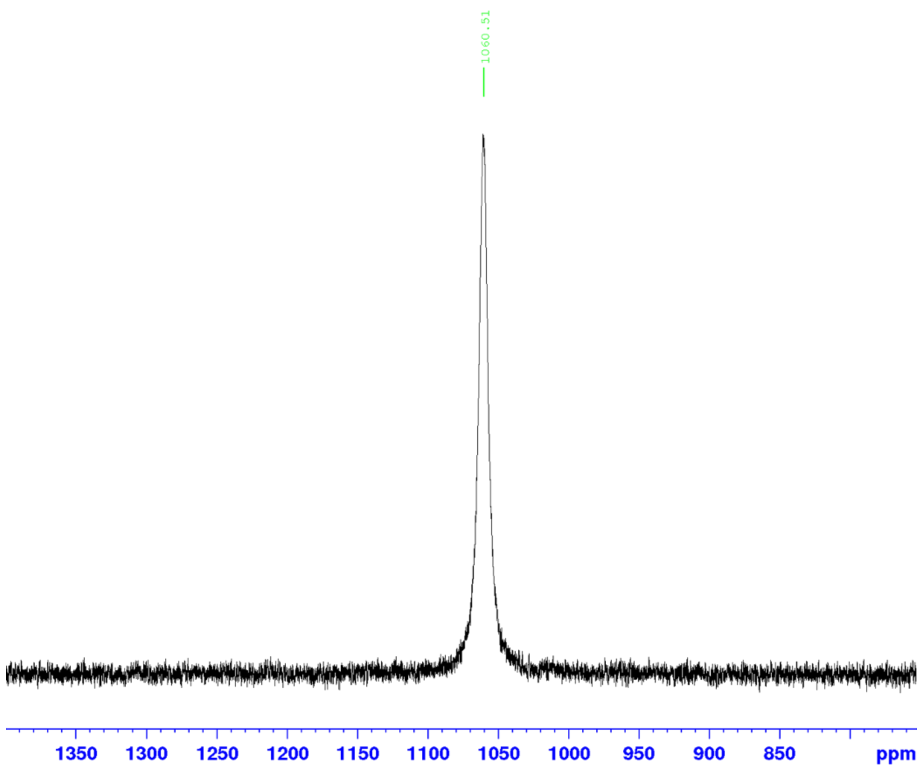

Figure S1-10. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **2d**.

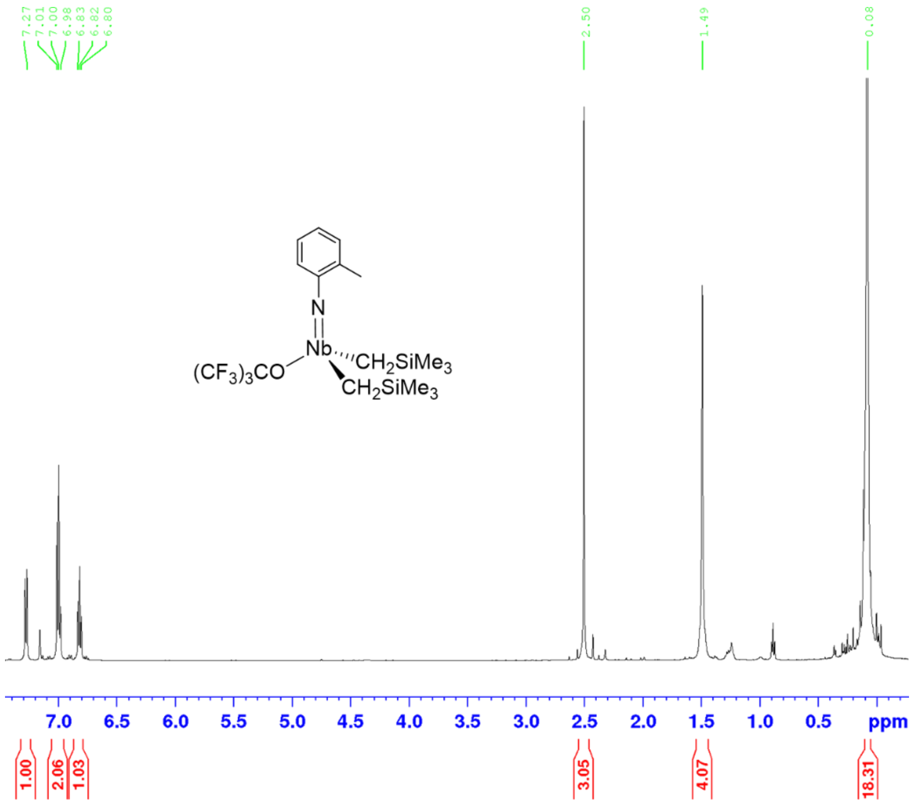

Figure S1-11. ^{1}H NMR spectrum (in C_6D_6 at 25 ºC) of **3c**.

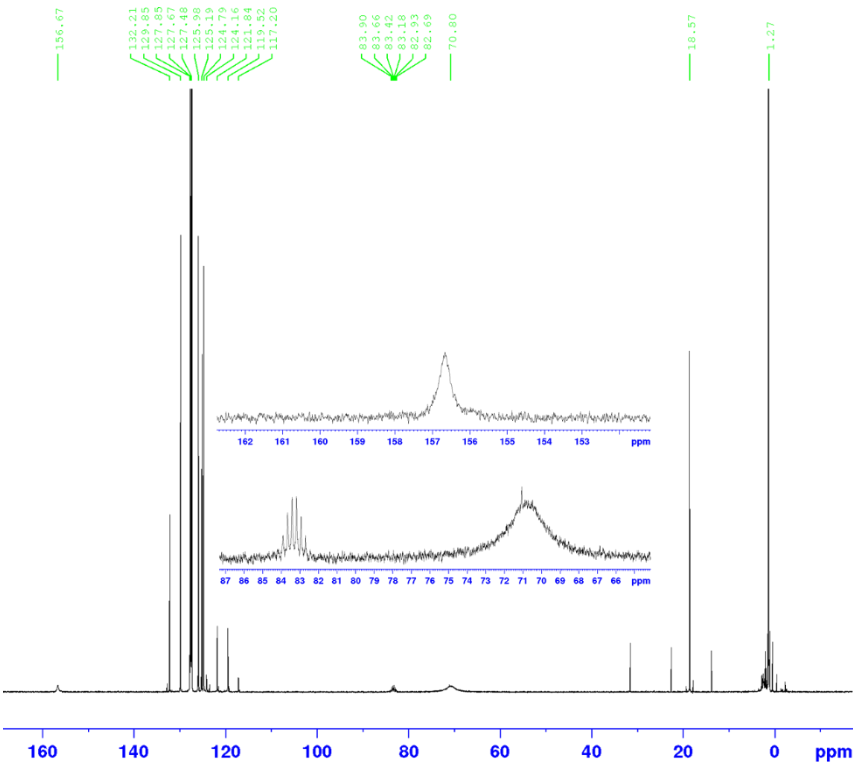

Figure S1-12. ^{13}C NMR spectrum (in C_6D_6 at 25 ºC) of **3c**.

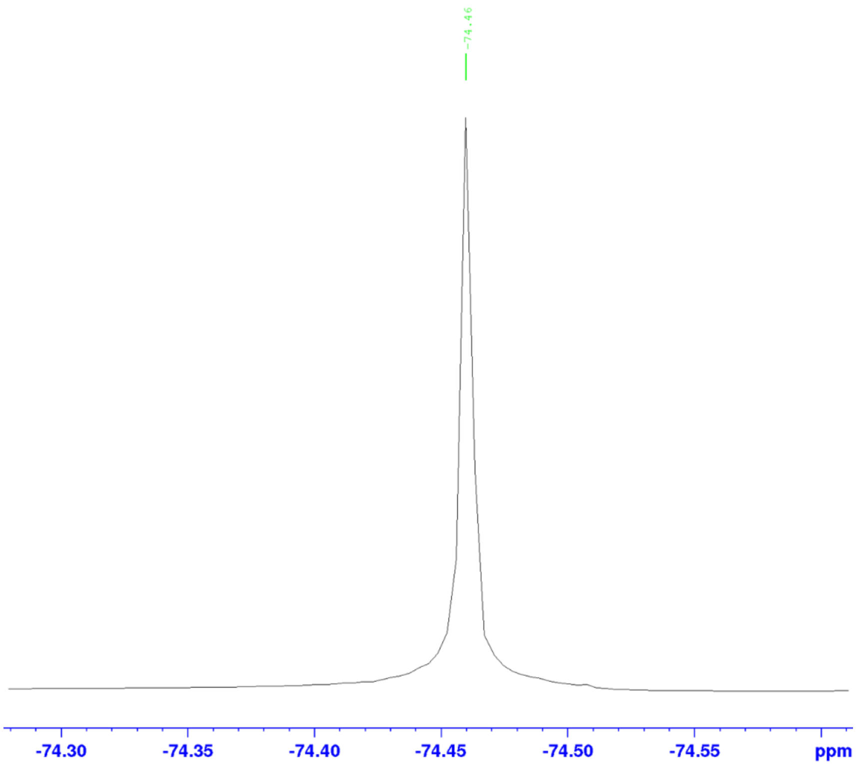

Figure S1-13. ^{19}F NMR spectrum (in C_6D_6 at 25 ºC) of **3c**.

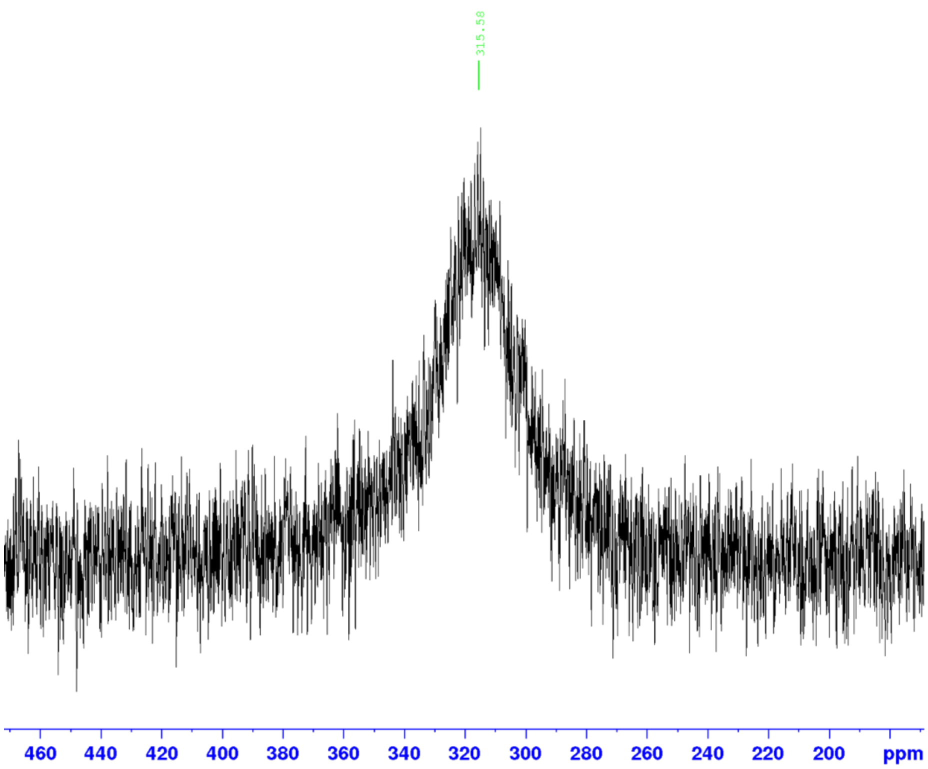

Figure S1-14. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **3c**.

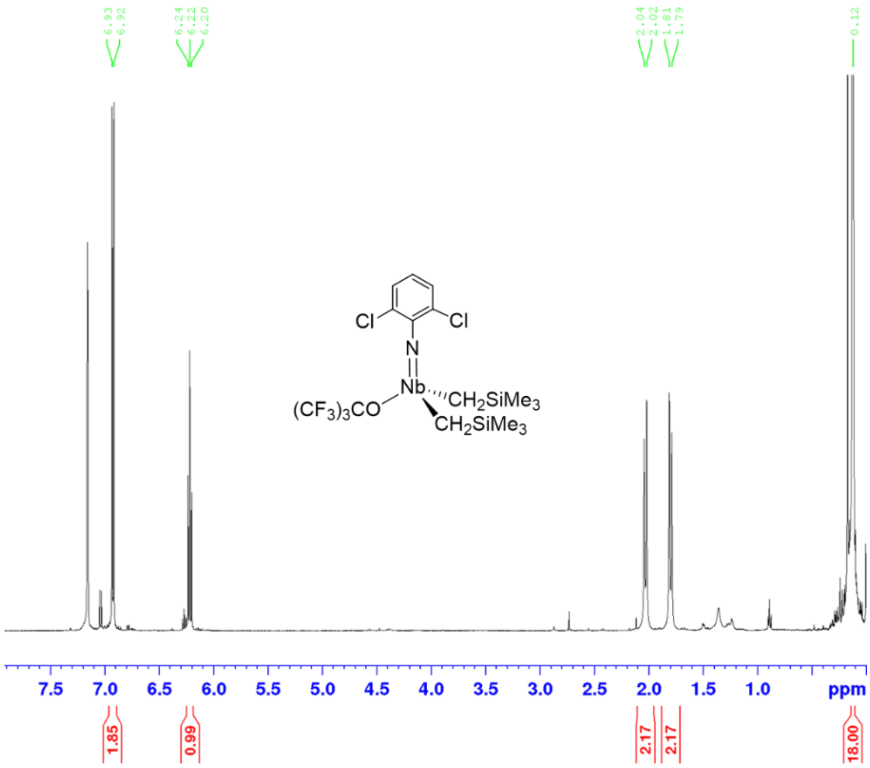

Figure S1-15. ^{1}H NMR spectrum (in C_6D_6 at 25 ºC) of **3d**.

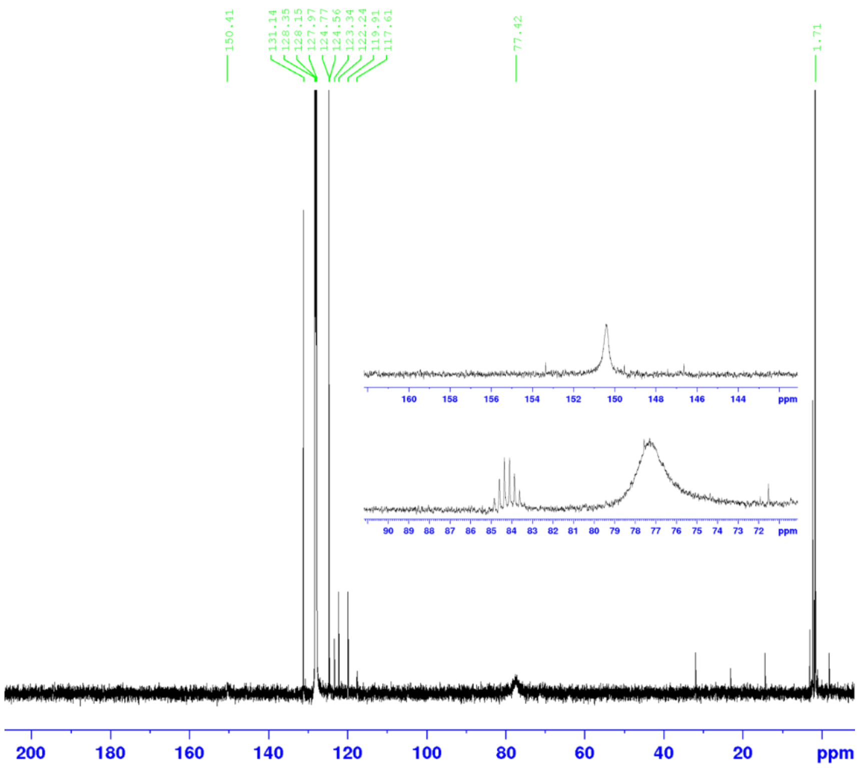

Figure S1-16. ^{13}C NMR spectrum (in C_6D_6 at 25 ºC) of **3d**.

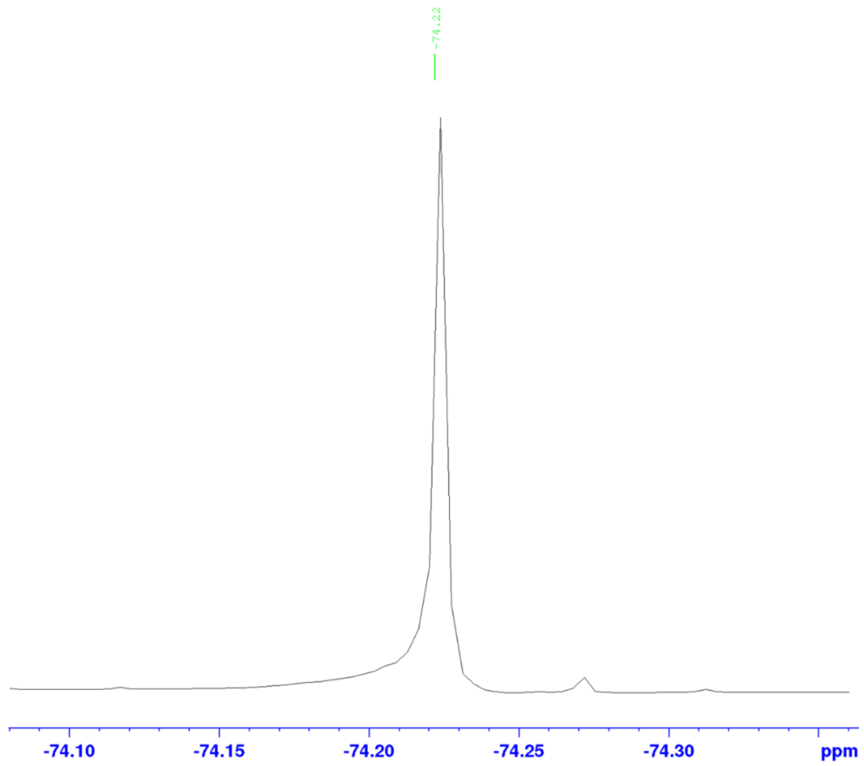

Figure S1-17. ^{19}F NMR spectrum (in C_6D_6 at 25 ºC) of **3d**.

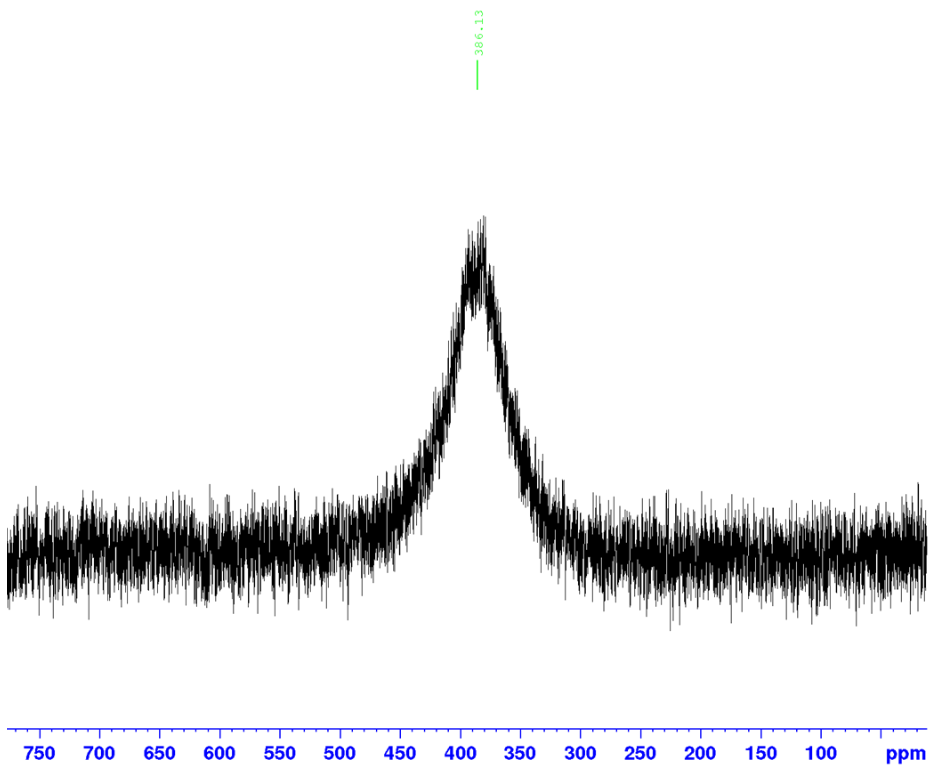

Figure S1-18. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **3d**.

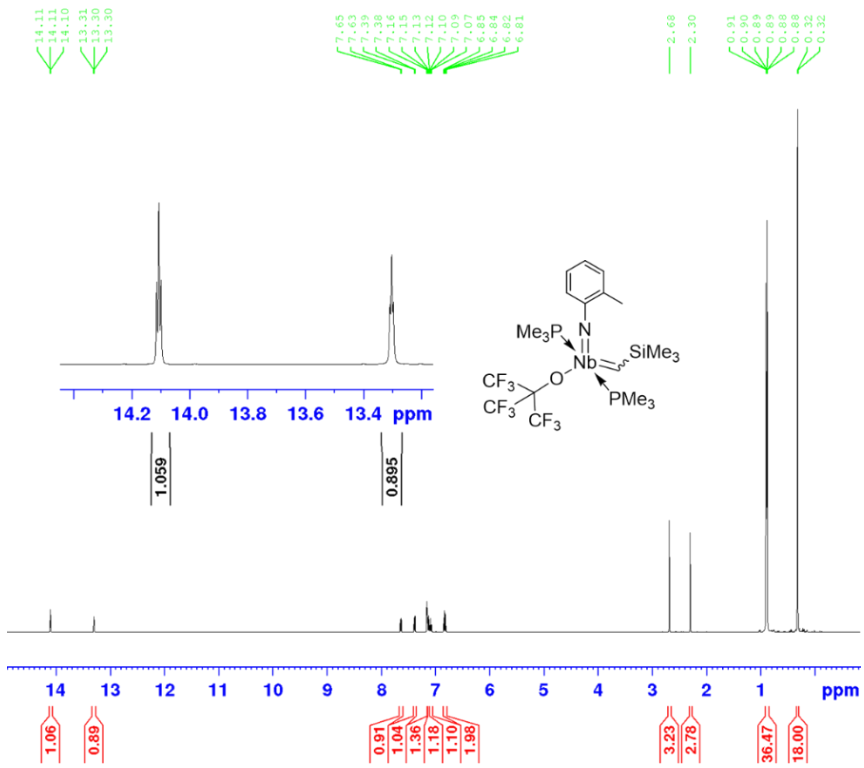

Figure S1-19. ^{1}H NMR spectrum (in C_6D_6 at 25 °C) of **4c**.

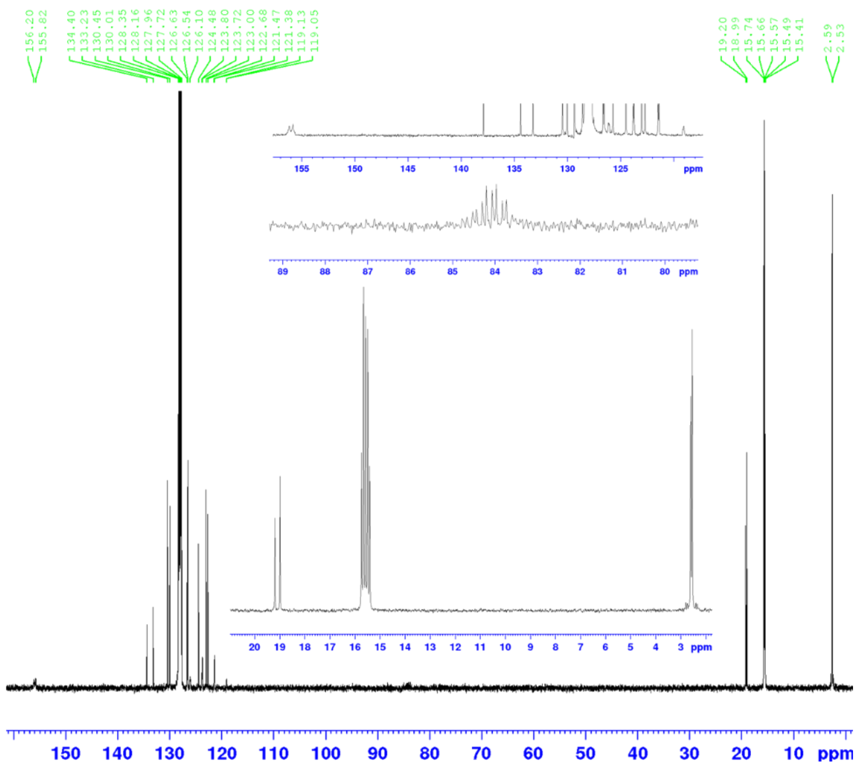

Figure S1-20. ^{13}C NMR spectrum (in C_6D_6 at 25 °C) of **4c**.

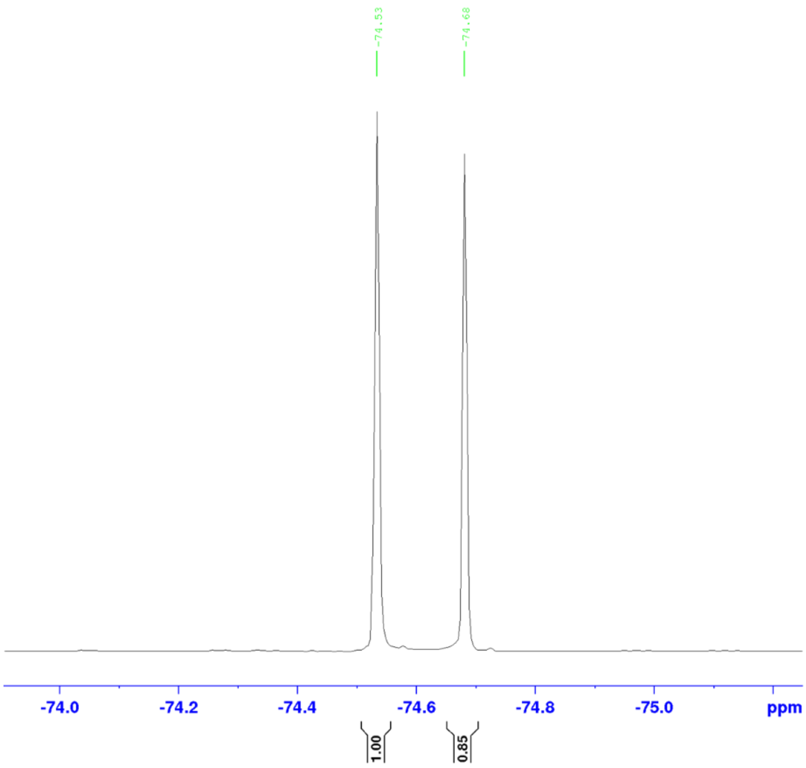

Figure S1-21. ^{19}F NMR spectrum (in C_6D_6 at 25 ºC) of **4c**.

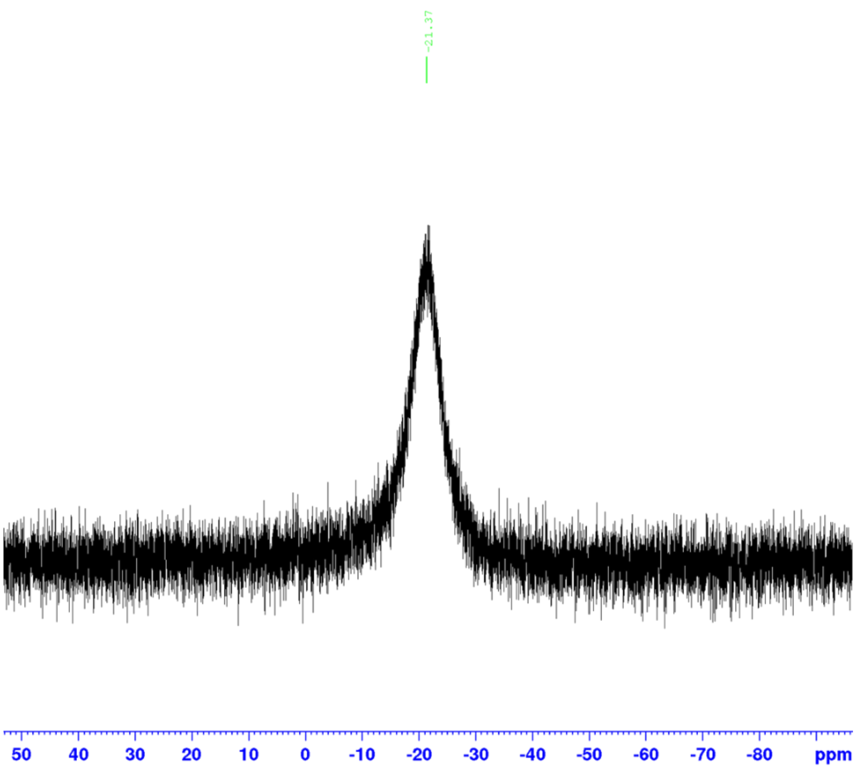

Figure S1-22. ^{31}P NMR spectrum (in C_6D_6 at 25 ºC) of **4c**.

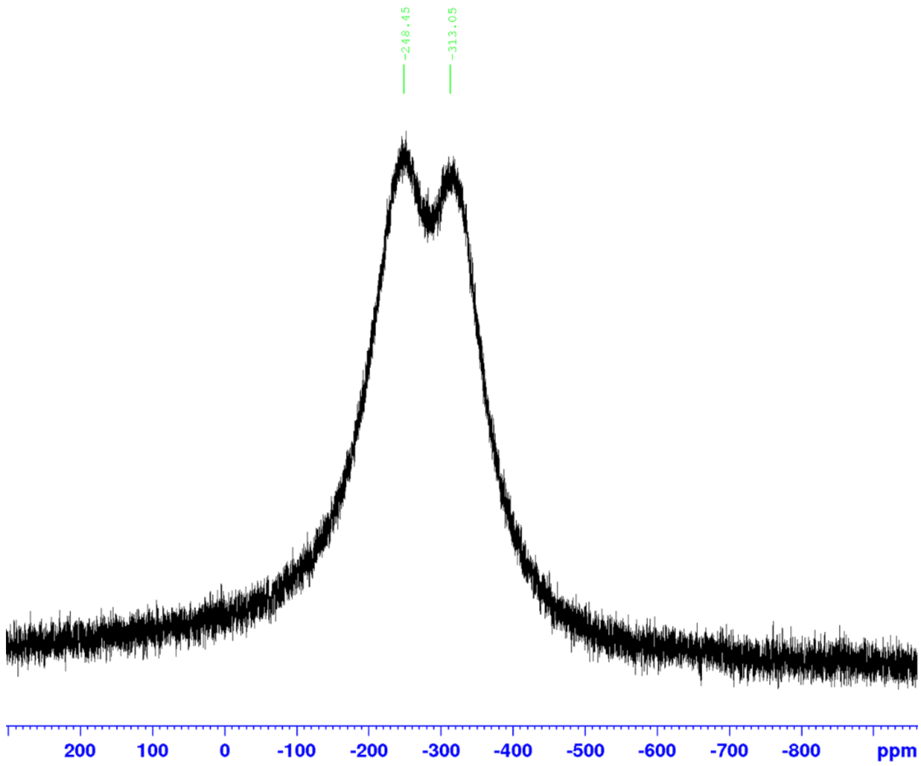

Figure S1-23. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **4c**.

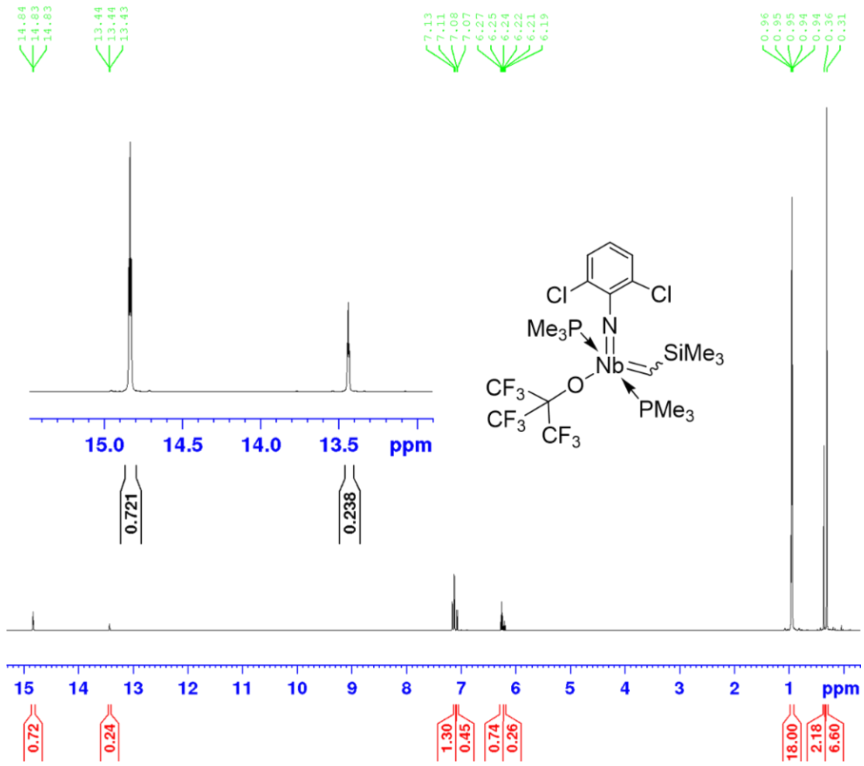

Figure S1-24. ^{1}H NMR spectrum (in C_6D_6 at 25 ºC) of **4d**.

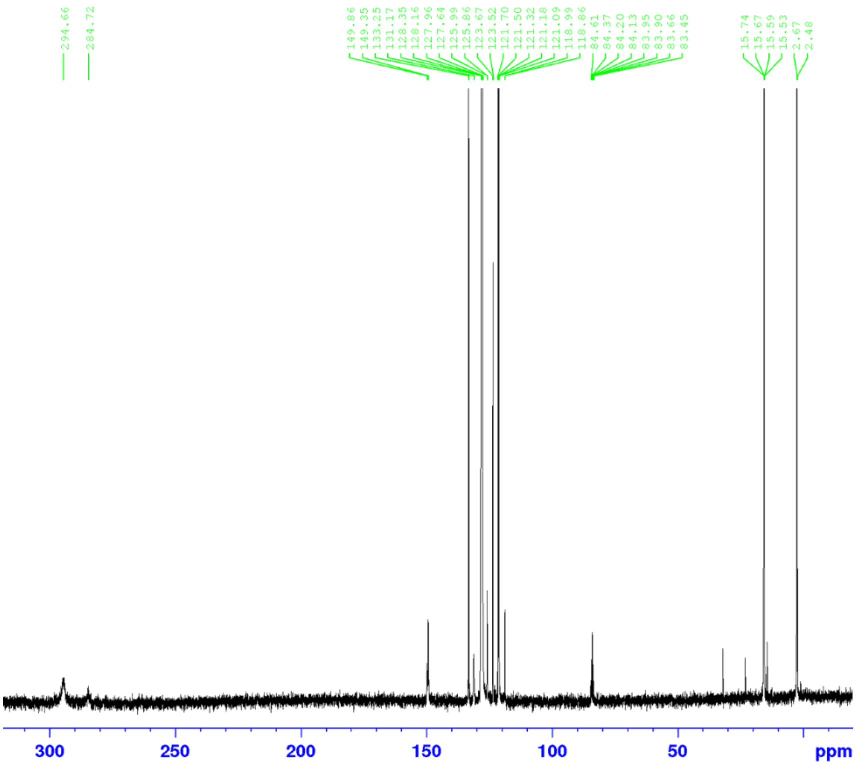

Figure S1-25. ^{13}C NMR spectrum (in C_6D_6 at 25 ºC) of **4d**.

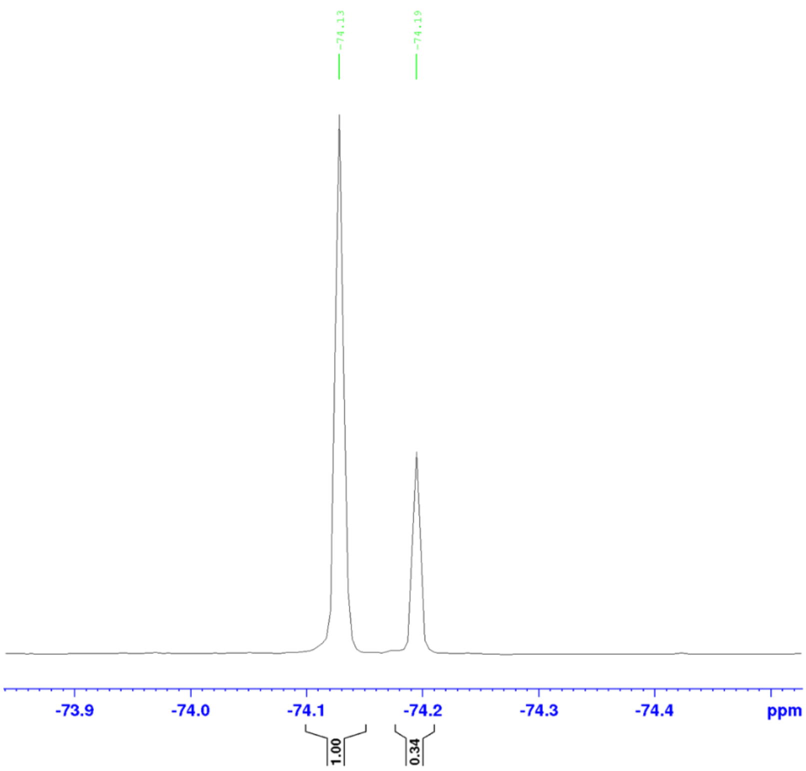

Figure S1-26. ^{19}F NMR spectrum (in C_6D_6 at 25 ºC) of **4d**.

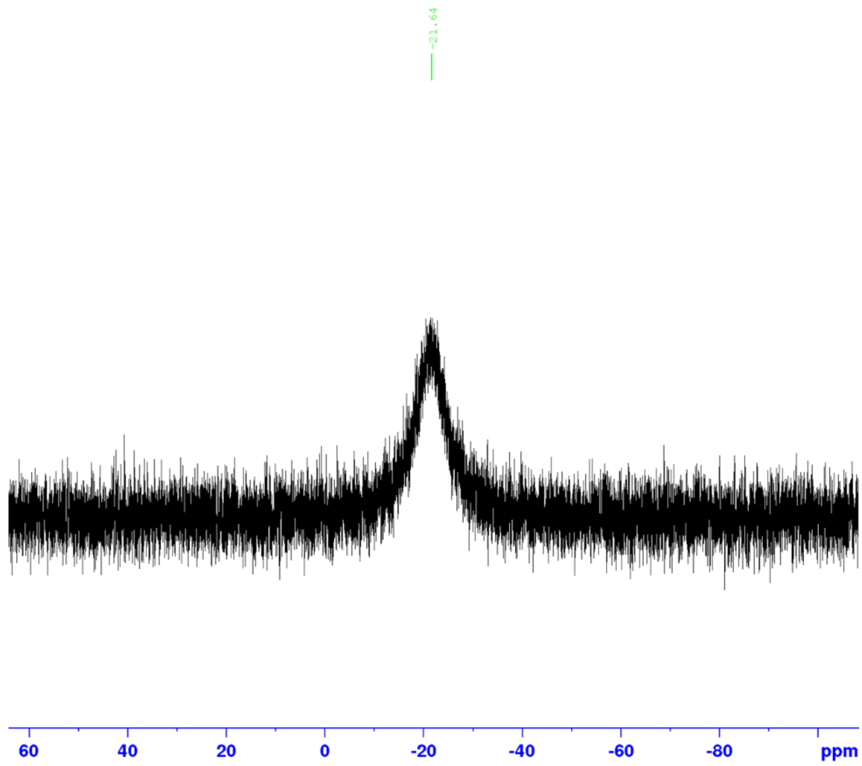

Figure S1-27. ^{31}P NMR spectrum (in C_6D_6 at 25 ºC) of **4d**.

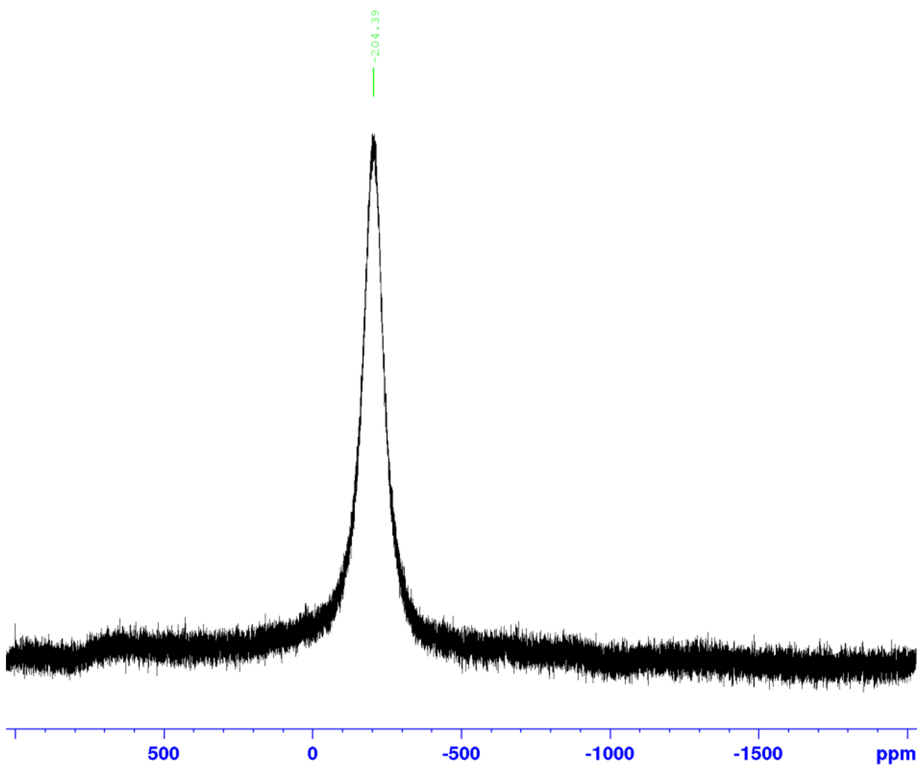

Figure S1-28. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **4d**.

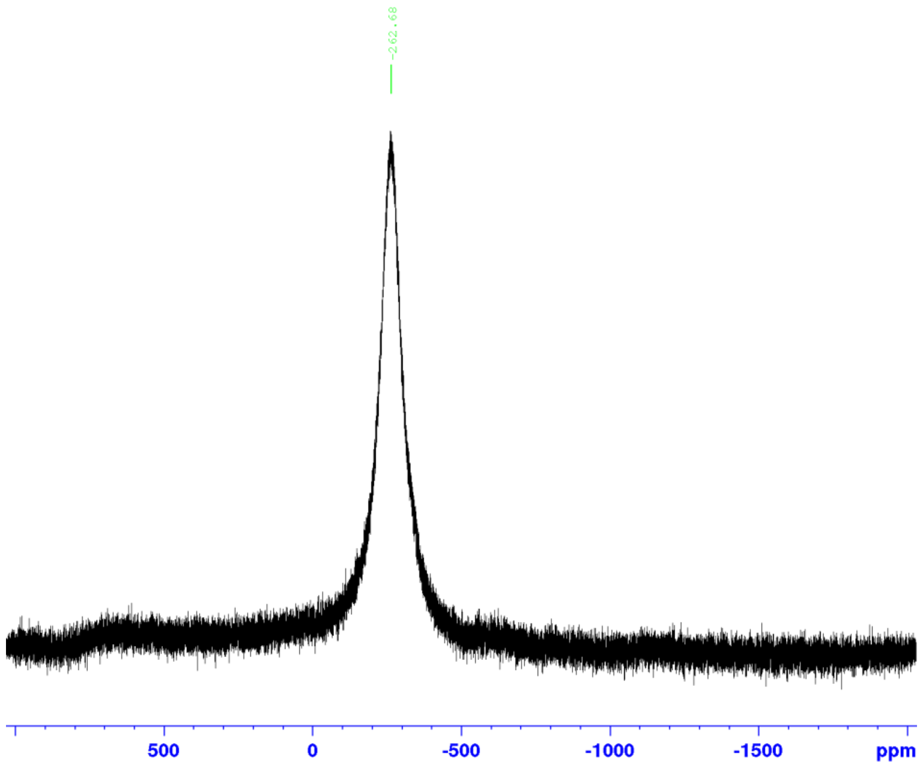

Figure S1-29. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **4a**.

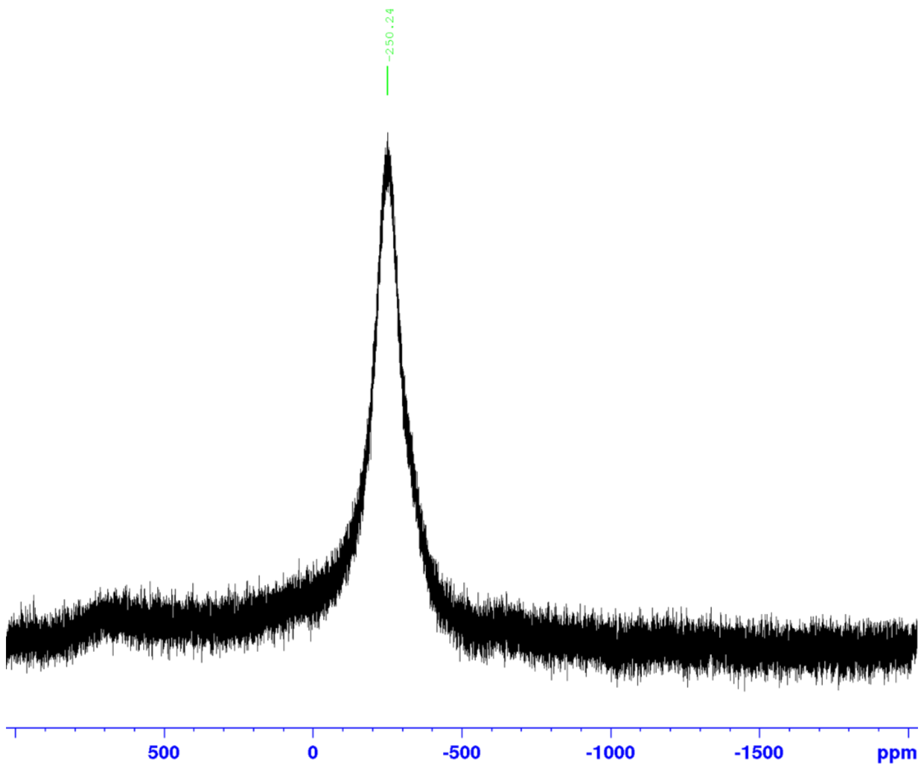

Figure S1-30. ^{93}Nb NMR spectrum (in C_6D_6 at 25 ºC) of **4b**.

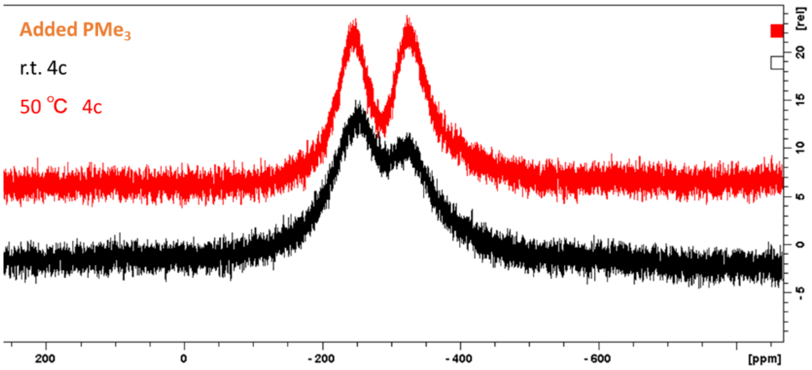

Figure S1-31. ^{93}Nb NMR spectra (in toluene-d_8) of **4c** in the presence of PMe_3 (20 equiv) at different temperature.

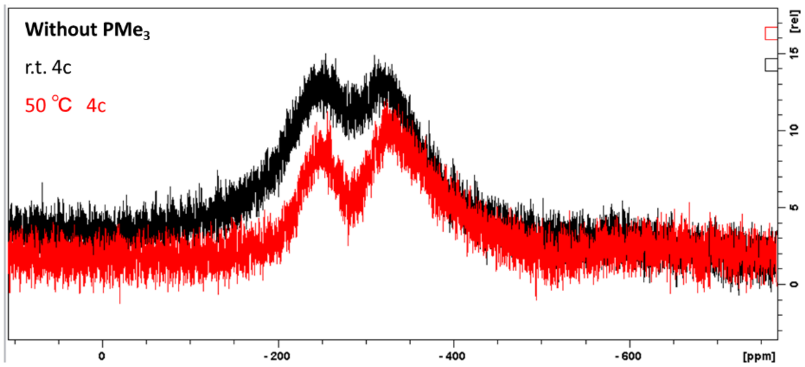

Figure S1-32. ^{93}Nb NMR spectra (in toluene-d_8) of **4c** at different temperature.

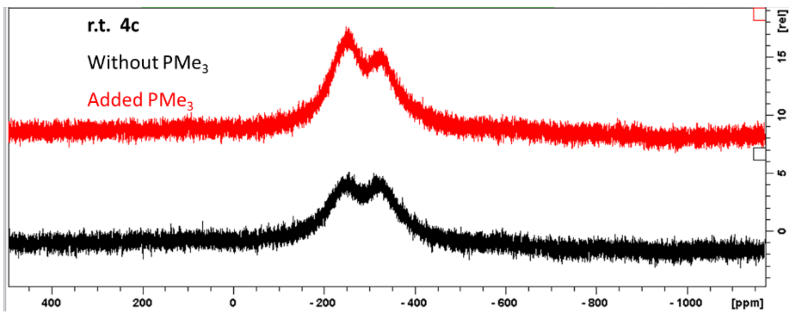

Figure S1-33. ^{93}Nb NMR spectra (in toluene-d_8) of **4c** in the presence PMe_3 (20 equiv) at 25 ºC.

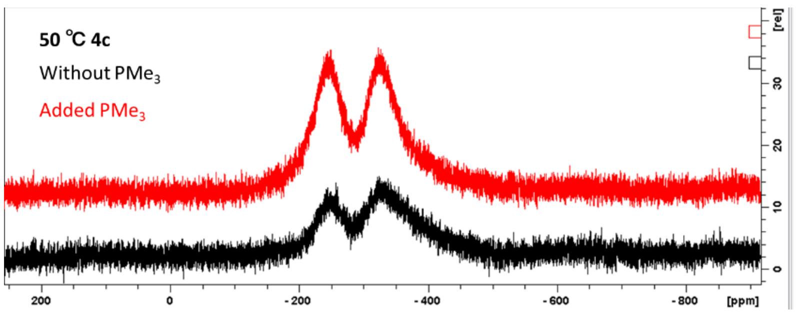

Figure S1-34. ^{93}Nb NMR spectra (in toluene-d_8) of **4c** in the presence PMe_3 (20 equiv) at 50 ºC.

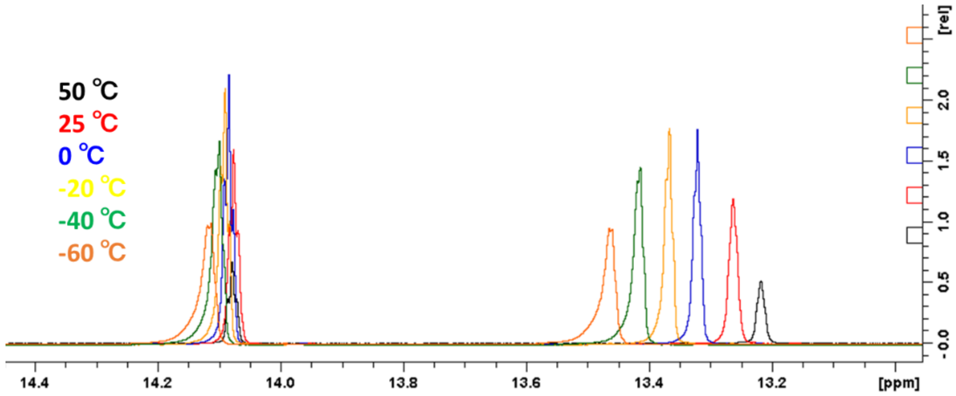

Figure S1-35. ^{1}H NMR spectra (in toluene-d_8) of **4c** at different temperature.

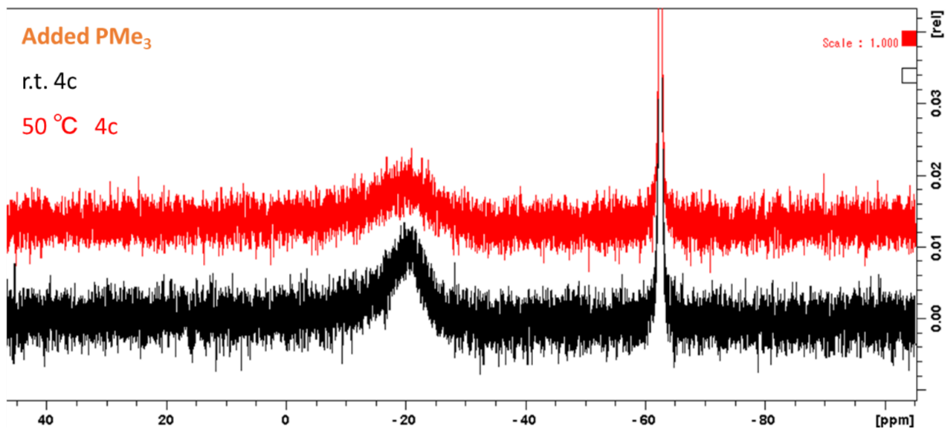

Figure S1-36. ^{31}P NMR spectra (in toluene-d_8) of **4c** in the presence of PMe_3 (20 equiv) at different temperature.

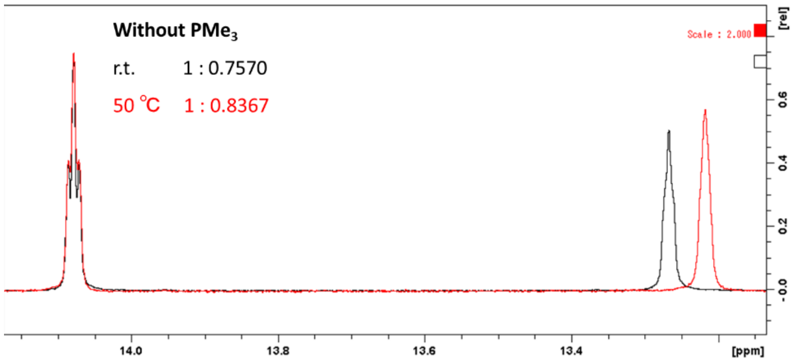

Figure S1-37. ^{1}H NMR spectra (in toluene-d_8) of **4c** at different temperature.

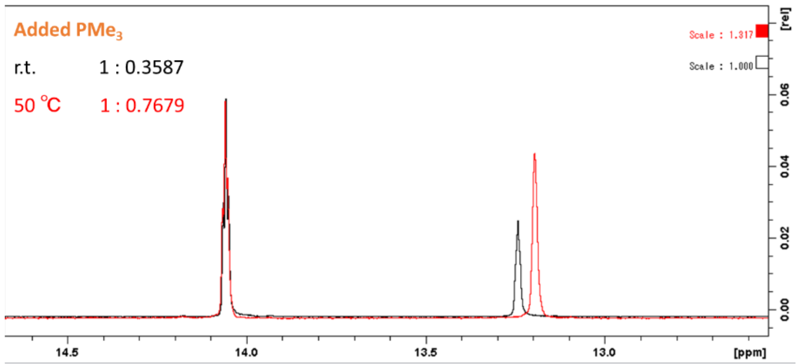

Figure S1-38. ^{1}H NMR spectra (in toluene-d_8) of **4c** in the presence of PMe_3 (20 equiv) at different temperature.

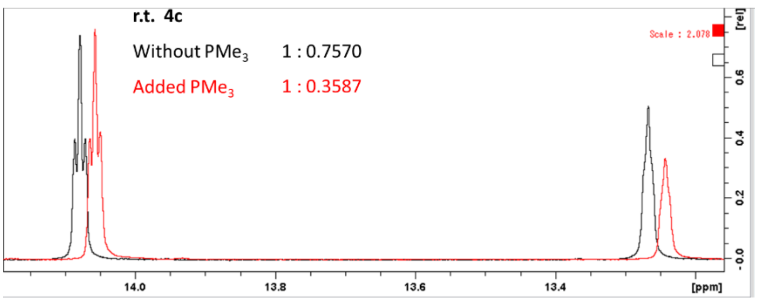

Figure S1-39. ^{1}H NMR spectra (in toluene-d_8) of **4c** in the presence PMe_3 (20 equiv) at 25 ºC.

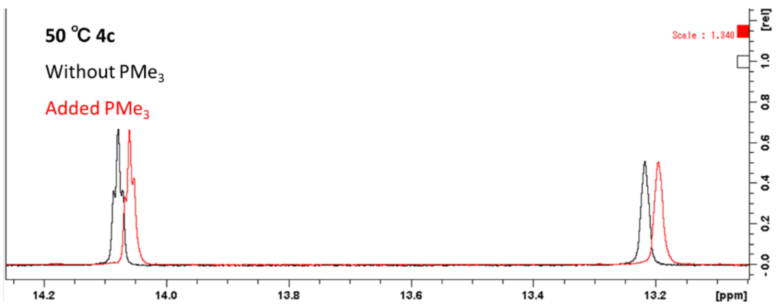

Figure S1-40. ^{1}H NMR spectra (in toluene-d_8) of **4c** in the presence PMe_3 (20 equiv) at 50 ºC.

2. Additional polymerization data.

Table S2-1. 2-Hexyne Polymerization by $Nb(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)[OC(CF_3)_3](PMe_3)_2$ (**4a**) in toluene.[a]

run		cat. / μmol	PMe_3 equiv[b]	temp. / °C	time / h	time / min	yield[c] / mg	yield[c] / %	TON[d]	TOF[e] / h^{-1}	M_n[f]	M_w/M_n[f]
1	**4a**	20	-	25	0.5	30	65	40	40	79.3	29900	1.39
S1	**4a**	20	-	25	0.5	30	58	35	35	71	24900	1.22
2	**4a**	20	-	25	2.0	120	89	54	54	27.1	39200	1.58
3	**4a**	20	-	25	4.0	240	101	62	62	15.4	50600	1.47
S2	**4a**	20	10	25	2.0	120	21	13	13	6.4	6930	1.08
4	**4a**	20	10	25	4.0	240	45	27	27	6.9	14900	1.08
S3	**4a**	10	20	25	1.0	60	19	12	23	23.2	15700	1.11
S4	**4a**	10	20	25	1.0	60	21	13	26	25.6	10100	1.11
5	**4a**	20	-	50	0.5	30	48	29	29	58.5	21700	1.57
6	**4a**	20	-	50	2.0	120	48	29	29	14.6	22700	1.55
S5	**4a**	20	-	50	4.0	240	53	32	32	8.1	22900	1.51
S6	**4a**	10	-	50	0.50	30	17	10	21	41.5	18800	1.76
S7	**4a**	10	-	50	0.75	45	18	11	22	29.3	19500	1.68
S8	**4a**	10	-	50	1.0	60	17	10	21	20.7	17700	1.75
S9	**4a**	20	1	50	2.0	120	49	30	30	14.9	23600	1.58
S10	**4a**	20	3	50	2.0	120	89	54	54	27.1	44500	1.72
S11	**4a**	20	3	50	4.0	240	90	55	55	13.7	43500	1.78
7	**4a**	20	10	50	2.0	120	139	85	85	42.4	63200	1.42
S12	**4a**	20	10	50	4.0	240	159	97	97	24.2	67100	1.48
8	**4a**	20	20	50	2.0	120	127	77	77	38.7	59300	1.21
S13	**4a**	20	20	50	4.0	240	162	99	99	24.7	67600	1.27
S14	**4a**	10	10	50	0.50	30	44	27	54	107	36400	1.55
S15	**4a**	10	10	50	0.50	30	43	26	52	105	33800	1.63
S16	**4a**	10	10	50	0.75	45	50	30	61	81.3	43400	1.61
S17	**4a**	10	10	50	1.0	60	53	32	65	64.6	51900	1.51
S18	**4a**	10	10	50	1.0	60	62	38	76	75.6	45500	1.70
9	**4a**	10	20	50	0.50	30	39	24	48	95.1	37800	1.17
S19	**4a**	10	20	50	0.75	45	47	29	57	76.4	39200	1.34
10	**4a**	10	20	50	1.0	60	56	34	68	68.3	55900	1.24
S20	**4a**	10	20	50	1.25	75	63	38	77	61.5	67100	1.34
11	**4a**	10	20	50	1.25	75	61	37	74	59.5	63600	1.26

To be continued (the next page)

run		cat. / μmol	PMe_3 equiv[b]	temp. / ºC	time / h	/ min	yield[c] / mg	/ %	TON[d]	TOF[e] / h^{-1}	M_n[f]	M_w/ M_n[f]
12	**4a**	10	50	50	0.50	30	27	16	33	65.9	22800	1.10
13	**4a**	10	50	50	0.50	30	28	17	34	68.3	23900	1.12
S21	**4a**	10	50	50	0.75	45	43	26	52	69.9	33700	1.10
S22	**4a**	10	50	50	1.0	60	45	27	55	54.9	36500	1.07
14	**4a**	10	50	50	1.0	60	46	28	56	56.1	41000	1.10
15	**4a**	10	50	50	1.25	75	55	34	67	53.7	49920	1.13
16	**4a**	10	100	50	0.50	30	19	12	23	46.3	14100	1.10
17	**4a**	10	100	50	0.75	45	25	15	30	40.7	19100	1.10
18	**4a**	10	100	50	1.0	60	34	21	41	41.5	25400	1.08
S23	**4a**	20	—	80	0.5	30	37	23	23	45.1	16900	1.55
S24	**4a**	20	—	80	2.0	120	43	26	26	13.1	17500	1.53
S25	**4a**	20	—	80	4.0	240	48	29	29	7.3	17600	1.52
S26	**4a**	20	3	80	0.5	30	49	30	30	59.8	23400	1.57
S27	**4a**	20	3	80	2.0	120	55	34	34	16.8	25900	1.51
S28	**4a**	20	3	80	4.0	240	57	35	35	8.7	26300	1.44
S29	**4a**	20	10	80	2.0	120	84	51	51	25.6	37800	1.73
S30	**4a**	20	10	80	4.0	240	95	58	58	14.5	45300	1.69
S31	**4a**	10	-	80	0.50	30	15	9	18	36.6	17600	1.58
S32	**4a**	10	-	80	0.75	45	16	10	20	26.0	16900	1.59
S33	**4a**	10	-	80	1.0	60	16	10	20	19.5	19700	1.47
S34	**4a**	10	10	80	0.50	30	30	18	37	73.2	29000	1.56
S35	**4a**	10	10	80	0.75	45	29	18	35	47.2	26000	1.64
S36	**4a**	10	10	80	1.0	60	28	17	34	34.1	27200	1.62
S37	**4a**	20	20	80	2.0	120	112	68	68	34.1	48800	1.88
S38	**4a**	20	20	80	4.0	240	112	68	68	17.1	58200	1.58
S39	**4a**	10	20	80	0.50	30	38	23	46	92.7	35100	1.60
S40	**4a**	10	20	80	0.75	45	36	22	44	58.5	35900	1.60
S41	**4a**	10	20	80	1.0	60	39	24	48	47.6	36100	1.61
19	**4a**	10	50	80	0.50	30	61	37	74	149	54800	1.75
S42	**4a**	10	50	80	0.75	45	58	35	71	94.3	53200	1.78
20	**4a**	10	50	80	1.0	60	60	37	73	73.2	58100	1.67
21	**4a**	10	100	80	0.50	30	68	41	83	166	66800	1.30
22	**4a**	10	100	80	0.75	45	75	46	91	122	74400	1.32
23	**4a**	10	100	80	1.0	60	101	62	123	123	88200	1.47

[a]Conditions: 2-Hexyne 2.0 mmol, toluene 1.0 mL. [b]Molar ratio of PMe_3/Nb. [c]Isolated yield (as MeOH insoluble fraction). [d]TON = [2-hexyne reacted (mmol)]/[Nb (mmol)]. [e]TOF = TON/h. [f]GPC data in THF vs polystyrene standards.

Table S2-2. Polymerization of 2-hexyne by $Nb(CHSiMe_3)(NAr)[OC(CF_3)_3](PMe_3)_2$ [Ar = 2,6-$Me_2C_6H_3$ (**4a**), 2,6-$^iPr_2C_6H_3$ (**4b**)] in toluene.[a]

run	cat.		PMe_3	temp.	time		yield[c]		TON[d]	TOF[e]	M_n[f]	M_w/M_n[f]
		/ μmol	equiv[b]	/ ºC	/ h	/ min	/ mg	/ %		/ h^{-1}		
18	**4a**	10	100	50	1.0	60	34	21	41	41.5	25400	1.08
23	**4a**	10	100	80	1.0	60	101	62	123	123	88200	1.47
S43	**BL**[g]	0	100	50	1.0	60	none					
S44	**BL**[g]	0	100	80	1.0	60	none					
S45	**4a**	20	1 (B)[h]	25	2.0	120	14	8.5	8.5	4.3	multi	
S46	**4a**	20	3 (B)[h]	25	2.0	120	15	9.1	9.1	4.6	multi	
S47	**BL**[g]	0	1 (B)[h]	25	2.0	120	none					
S48	**BL**[g]	0	3 (B)[h]	25	2.0	120	none					
24	**4b**	20	--	25	24	1440	22	13	13	0.56	41800	1.66
25	**4b**	20	--	50	2.0	120	13	8	8	4.0	20500	1.62
S49	**4b**	20	--	50	24	1440	16	10	10	0.4	23000	1.41
S50	**4b**	20	1	50	2.0	120	9.0	5	5	2.7	22000	1.51
S51	**4b**	20	3	50	2.0	120	13	8	8	4.0	23700	1.50

[a]Conditions: 2-Hexyne 2.0 mmol, toluene 1.0 mL. [b]Molar ratio of PMe_3/Nb. [c]Isolated yield (as MeOH insoluble fraction). [d]TON = [2-hexyne reacted (mmol)]/[Nb (mmol)]. [e]TOF = TON/h. [f]GPC data in THF vs polystyrene standards. [g]Attemped polymerization without Nb. [h]$B(C_6F_5)_3$ instead of PMe_3.

Table S2-3. Polymerization of 2-hexyne by $Nb(CHSiMe_3)(N\text{-}2\text{-}MeC_6H_4)[OC(CF_3)_3](PMe_3)_2$ (**4c**) in toluene.[a]

run		cat.	PMe_3	temp.	time		yield[c]		TON[d]	TOF[e]	M_n[f]	M_w/M_n[f]
		/ µmol	equiv[b]	/ °C	/ h	/ min	/ mg	/ %		/ h^{-1}		
S52	**4c**	5.0	-	25	0.08	5	34	21	83	1040	60700	1.23
26	**4c**	5.0	-	25	0.08	5	26	16	63	793	49100	1.25
S53	**4c**	5.0	-	25	0.08	5	26	16	63	793		
27	**4c**	5.0	-	25	0.25	15	74	45	180	722	138000	1.41
S54	**4c**	5.0	-	25	0.25	15	68	41	166	663	141000	1.40
S55	**4c**	5.0	-	25	0.33	20	77	47	188	569	158000	1.51
28	**4c**	5.0	-	25	0.50	30	102	62	249	498	172000	1.75
S56	**4c**	5.0	-	25	0.50	30	103	63	251	502		
29	**4c**	5.0	-	25	1.00	60	139	85	339	339	203000	1.76
S57	**4c**	5.0	-	25	1.00	60	136	83	332	332		
30	**4c**	1.5	20	25	1.00	60	32	20	260	260	116000	1.14
31	**4c**	1.5	-	50	0.50	30	7.6	5	62	124	64000	2.03
S58	**4c**	1.5	-	50	1.00	60	7.9	5	64	64.2	67800	1.94
S59	**4c**	1.5	20	50	0.50	30	12	7	98	195	116000	2.29
S60	**4c**	1.5	20	50	0.75	45	25	15	203	271	186000	2.06
S61	**4c**	1.5	20	50	1.00	60	26	16	211	211	192000	2.09
S62	**4c**	1.5	20	50	1.25	75	29	18	236	189	204000	2.18
32	**4c**	1.5	50	50	0.50	30	45	27	366	732	195000	1.57
S63	**4c**	1.5	50	50	0.50	30	48	29	390	781	213000	1.73
S64	**4c**	1.5	50	50	0.75	45	55	34	447	596	236000	1.75
S65	**4c**	1.5	50	50	1.00	60	69	42	561	561	253000	2.01
S66	**4c**	1.5	50	50	1.25	75	72	44	585	468	284000	1.83
S67	**4c**	1.5	100	50	0.50	30	20	12	163	325	103000	1.27
33	**4c**	1.5	100	50	0.50	30	23	14	187	374	120000	1.26
S68	**4c**	1.5	100	50	0.50	30	26	16	211	423	133000	1.35
S69	**4c**	1.5	100	50	0.75	45	35	21	285	379	169000	1.39
S70	**4c**	1.5	100	50	1.00	60	50	30	407	407	194000	1.55
S71	**4c**	1.5	100	50	1.25	75	71	43	577	462	234000	1.65
34	**4c**	1.5	200	50	0.50	30	12	7	98	195	67700	1.17
35	**4c**	1.5	200	50	0.75	45	20	12	163	217	113000	1.28
36	**4c**	1.5	200	50	1.00	60	32	20	260	260	152000	1.33
37	**4c**	1.5	200	50	1.25	75	42	26	341	273	168000	1.36

[a]Conditions: 2-Hexyne 2.0 mmol, toluene 1.0 mL. [b]Molar ratio of PMe_3/Nb. [c]Isolated yield (as MeOH insoluble fraction). [d]TON = [2-hexyne reacted (mmol)]/[Nb (mmol)]. [e]TOF = TON/h. [f]GPC data in THF vs polystyrene standards.

Table S2-4. Polymerization of 2-hexyne by $Nb(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)[OC(CF_3)_3](PMe_3)_2$ (**4d**) in toluene.[a]

run	cat.	/ μmol	PMe_3 equiv[b]	temp. / °C	time / h	time / min	yield[c] / mg	yield[c] / %	TON[d]	TOF[e] /h $^{-1}$	M_n[f]	M_w/M_n[f]
38	**4d**	5.0	-	25	0.08	5	16	10	39	468	17000	1.39
39	**4d**	5.0	-	25	0.25	15	36	22	88	351	31000	1.37
40	**4d**	5.0	-	25	0.33	20	42	26	102	310	43400	1.56
41	**4d**	5.0	-	25	0.50	30	46	28	111	222	44900	1.67
S72	**4d**	5.0	-	25	0.50	30	47	29	115	229		
42	**4d**	5.0	-	25	1.00	60	53	32	129	129	50800	1.59
S73	**4d**	5.0	-	25	1.00	60	51	31	124	124		
43	**4d**	5.0	-	25	1.25	75	55	34	134	107	53400	1.64
44	**4d**	5.0	20	25	1.00	60	28	17	68	68	21500	1.12
45	**4d**	5.0	-	50	0.50	30	34	21	83	166	30300	1.79
S74	**4d**	5.0	-	50	1.00	60	34	21	83	82.9	34000	1.71
46	**4d**	5.0	20	50	0.50	30	63	38	154	307	41200	1.27
S75	**4d**	5.0	20	50	0.50	30	64	39	156	312		
47	**4d**	5.0	20	50	0.75	45	77	47	188	250	51100	1.41
48	**4d**	5.0	20	50	1.00	60	90	55	220	220	53500	1.44
49	**4d**	5.0	20	50	1.25	75	96	59	234	187	55600	1.45
50	**4d**	5.0	50	50	0.50	30	44	27	107	215	29200	1.14
51	**4d**	5.0	50	50	0.75	45	60	37	146	195	38000	1.17
52	**4d**	5.0	50	50	1.00	60	68	41	166	166	41800	1.21
53	**4d**	5.0	50	50	1.25	75	77	47	188	150	45800	1.23
54	**4d**	5.0	100	50	0.50	30	23	14	56	112	15100	1.10
S76	**4d**	5.0	100	50	0.50	30	25	15	61	122	17800	1.12
55	**4d**	5.0	100	50	0.75	45	34	21	83	111	22100	1.09
56	**4d**	5.0	100	50	1.00	60	48	29	117	117	28300	1.12
57	**4d**	5.0	100	50	1.25	75	52	32	127	102	29700	1.11

[a]Conditions: 2-Hexyne 2.0 mmol, toluene 1.0 mL. [b]Molar ratio of PMe_3/Nb. [c]Isolated yield (as MeOH insoluble fraction). [d]TON = [2-hexyne reacted (mmol)]/[Nb (mmol)]. [e]TOF = TON/h. [f]GPC data in THF vs polystyrene standards.

Table S2-5. Polymerization of 4-methyl-2-pentyne by $Nb(CHSiMe_3)(NAr)[OC(CF_3)_3](PMe_3)_2$ [Ar = 2,6-$Me_2C_6H_3$ (**4a**), 2,6-$^{i}Pr_2C_6H_3$ (**4b**), 2,6-$Cl_2C_6H_3$ (**4d**)] in toluene.[a]

run	cat.	/ µmol	PMe_3 equiv[b]	temp. / ºC	time / h	yield[c] / mg	TON[d]	M_n[e]	M_w/M_n[e]
S77	**4a**	20	--	25	2.0	trace	-	-	-
58	**4a**	20	--	25	12	trace			
59	**4c**	20	--	25	6.0	7.0	4	4600	1.34
60	**4c**	20	--	25	12	12	7	8200	1.38
61	**4c**	20	--	25	24	25	15	11200	1.55
62	**4c**	20	20	25	24	10	6	2700	1.20
S78	**4c**	20	20	25	24	10	6	2900	1.21
63	**4c**	20	--	50	6.0	6.0	4	7100	1.69
64	**4c**	20	20	50	3.0	10	6	3400	1.22
65	**4c**	20	20	50	6.0	18	11	4500	1.24
66	**4c**	20	20	50	12	28	17	6300	1.39
67	**4c**	20	20	50	24	39	24	10000	1.51
68	**4c**	20	50	50	6.0	13	8	2900	1.22
69	**4c**	20	50	50	12	24	15	4300	1.26
70	**4c**	20	50	50	24	38	23	6800	1.29
71	**4c**	20	50	50	36	48	29	8900	1.37
S79	**4d**	20	--	25	6.0	1.0		2600	1.12
S80	**4d**	20	--	25	12	2.0	1	3500	1.28
72	**4d**	20	--	25	24	3.0	2	3800	1.25
S81	**4d**	20	20	25	24	5.0	3	1700	1.11
73	**4d**	20	20	25	24	7.0	4	1800	1.16
74	**4d**	20	--	50	6.0	1.0	1	3200	1.21
75	**4d**	20	20	50	6.0	11	7	2700	1.19
76	**4d**	20	20	50	6.0	11	7	2700	1.18
77	**4d**	20	20	50	12	16	10	3500	1.28
78	**4d**	20	20	50	24	19	12	4400	1.47
79	**4d**	20	20	50	24	19	12	4300	1.47
80	**4d**	20	50	50	6.0	6.0	4	1800	1.14
81	**4d**	20	50	50	12	11	7	2700	1.14
82	**4d**	20	50	50	24	21	13	3900	1.22
S82	**4d**	20	50	50	24	21	13	3800	1.23

[a]Conditions: 4-methyl-2-pentyne 2.0 mmol, toluene 1.0 mL. [b]Molar ratio of PMe_3/Nb. [c]Isolated yield (as MeOH insoluble fraction). [d]TON = [4-methyl-2-pentyne reacted (mmol)]/[Nb (mmol)]. [e]GPC data in THF vs polystyrene standards.

Table S2-6. Polymerization of 3-hexyne, 4-octyne, and 5-decyne by $Nb(CHSiMe_3)(NAr)[OC(CF_3)_3](PMe_3)_2$ [Ar = 2,6-$Me_2C_6H_3$ (**4a**), 2,6-$Cl_2C_6H_3$ (**4d**)] in toluene.[a]

run	monomer	cat.	/ μmol	PMe_3 equiv[b]	temp. / °C	time / h	yield[c] / mg	TON[d]	M_n[e]	M_w/M_n[e]
S83	3-hexyne	**4a**	20	--	25	48	7.0	4.3	insoluble	
83	3-hexyne	**4c**	10	--	25	24	2.0	2	6800	1.48
84	3-hexyne	**4c**	20	50	50	6.0	8.0	5	11000	1.13
85	3-hexyne	**4c**	20	50	50	12	18	11	16600	1.17
86	3-hexyne	**4c**	20	50	50	24	23	14	18200	1.33
87	3-hexyne	**4c**	10	50	50	24	10	12	17500	1.57
88	4-octyne	**4c**	20	50	50	6.0	2.0	1	6200	1.10
89	4-octyne	**4c**	20	50	50	12	3.3	2	11000	1.09
90	4-octyne	**4c**	20	50	50	24	5.5	3	22000	1.09
91	4-octyne	**4c**	30	20	50	24	11	3.3	28900	1.34
92	4-octyne	**4c**	30	20	50	48	16	4.8	33500	1.72
S84	5-decyne	**4c**	20	50	50	6.0	trace			
S85	5-decyne	**4c**	20	50	50	12	trace			
93	5-decyne	**4c**	20	50	50	24	trace			

[a]Conditions: alkyne (3-hexyne, 4-octyne, 5 -decyne) 2.0 mmol, toluene 1.0 mL. [b]Molar ratio of PMe_3/Nb. [c]Isolated yield (as MeOH insoluble fraction). [d]TON = [alkyne reacted (mmol)]/[Nb (mmol)]. [e]GPC data in THF vs polystyrene standards.

Table S2-7. Polymerization of 1-phenyl-1-propyne by [Ar = 2,6-$Me_2C_6H_3$ (**4a**), 2,6-$^iPr_2C_6H_3$ (**4b**), 2,6-$Cl_2C_6H_3$ (**4d**)] in toluene.[a]

run	cat.	PMe_3 equiv[b]	temp. / °C	time / h	yield[c] / mg	yield[c] / %	TON[d]	M_n[f] ×10^{-3}	M_w/M_n[f]
94	**4a**	--	25	6	14	6	6	6900	1.51
95	**4a**	--	25	6	10	4	4	5400	1.46
96	**4a**	--	25	12	18	7.8	8	7900	1.74
97	**4a**	--	25	24	20	8.6	9	8400	1.82
98	**4a**	20	25	6	25	11	11	6200	1.48
99	**4a**	20	25	12	59	25	25	12200	1.64
100	**4a**	20	25	24	69	30	30	14300	1.80
101	**4a**	--	50	6	18	7.8	8	9800	1.86
S86	**4a**	--	50	12	18	7.8	8	9300	1.89
102	**4a**	--	50	24	18	7.8	8	9100	1.93
S87	**4a**	20	50	6	51	22	22	16500	2.04
S88	**4a**	20	50	6	50	22	22	16100	2.06
S89	**4a**	20	50	12	51	22	22	16500	2.04
S90	**4a**	20	50	24	51	22	22	16000	2.13
S91	**4a**	20	50	24	50	22	22	16800	2.01
103	**4a**	50	50	6	59	25	25	16600	1.92
S92	**4a**	50	50	6	63	27	27	18100	2.17
S93	**4a**	50	50	12	57	25	25	16000	2.00
104	**4a**	50	50	24	60	26	26	16100	2.02
S94	**4a**	50	50	24	62	27	27	19800	2.06
105	**4c**	20	25	6	30	13	13	5700	1.27
S95	**4c**	20	25	12	46	20	20	8200	1.48
106	**4c**	20	25	24	57	25	25	9700	1.63
108	**4d**	--	25	6	118	51	51	24800	1.33
109	**4d**	--	25	6	119	51	51	25700	1.31
110	**4d**	--	25	12	165	71	71	33200	1.51
111	**4d**	--	25	24	186	80	80	36900	1.62
112	**4d**	20	25	6	11	5.0	5	2900	1.22
S96	**4d**	20	25	6	10	4.0	4	2900	1.21
113	**4d**	20	25	12	29	13	13	4100	1.26
114	**4d**	20	25	24	50	22	22	6600	1.27

To be continued (the next page)

Run	cat.	PMe_3 equiv[b]	temp. / ºC	time / h	yield[c] / mg	/ %	TON[d]	M_n[f] $\times 10^{-3}$	M_w/M_n[f]
115	**4d**	--	50	6.0	115	50	50	24600	1.80
S97	**4d**	--	50	6.0	110	47	47	25000	1.85
S98	**4d**	--	50	12	120	52	52	25400	1.82
116	**4d**	--	50	24	131	56	56	25100	1.79
S99	**4d**	--	50	24	136	59	59	25600	1.75
S100	**4d**	20	50	6.0	119	51	51	20400	1.48
117	**4d**	20	50	6.0	122	53	53	19600	1.57
118	**4d**	20	50	12	157	68	68	27900	1.63
S101	**4d**	20	50	24	173	75	75	31600	1.84
119	**4d**	20	50	24	177	76	76	31300	1.90
120	**4d**	50	50	6.0	76	33	33	12900	1.34
S102	**4d**	50	50	6.0	81	35	35	13600	1.34
121	**4d**	50	50	12	117	50	50	18600	1.46
122	**4d**	50	50	24	157	68	68	24000	1.64

[a]Conditions: Nb complex 20 μmol, 1-phenyl-1-propyne 2.0 mmol, toluene 1.0 mL. [b]Molar ratio of PMe_3/Nb. [c]Isolated yield (as MeOH insoluble fraction). [d]TON = [1-phenyl-1-propyne reacted (mmol)]/[Nb (mmol)]. [e]GPC data in THF vs polystyrene standards.

3. Additional analysis results for polymerization of internal alkynes by Nb(CHSiMe$_3$)(NAr)[OC(CF$_3$)$_3$] Nb(CHSiMe$_3$)(NAr)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [Ar = 2,6-Me$_2$C$_6$H$_3$ (4a), 2-MeC$_6$H$_4$ (4c), 2,6-Cl$_2$C$_6$H$_3$ (4d)].

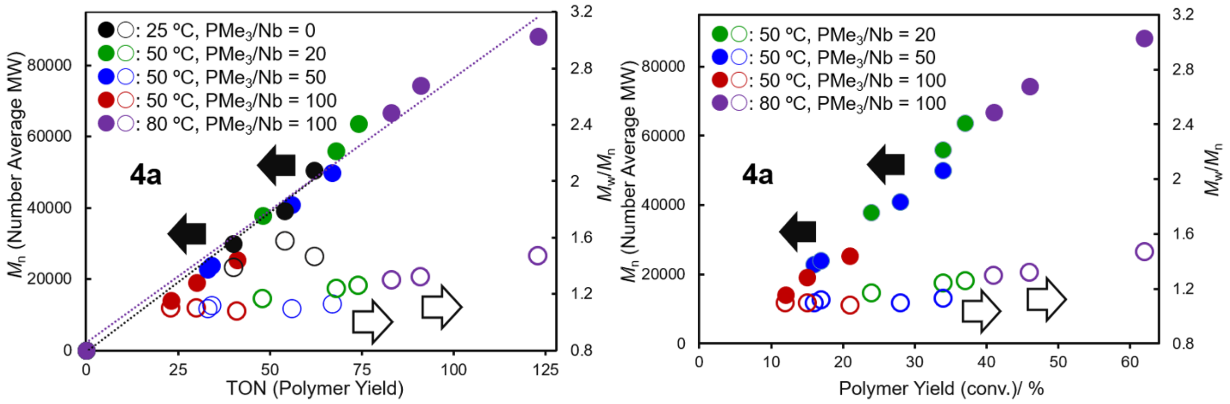

Figure S3-1. Plots of M_n (number average molecular weight), M_w/M_n vs polymer yield (TON, turnover number) in 2-hexyne polymerization by Nb(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$]-(PMe$_3$)$_2$ (**4a**) in toluene. The data are also shown in Table 1.

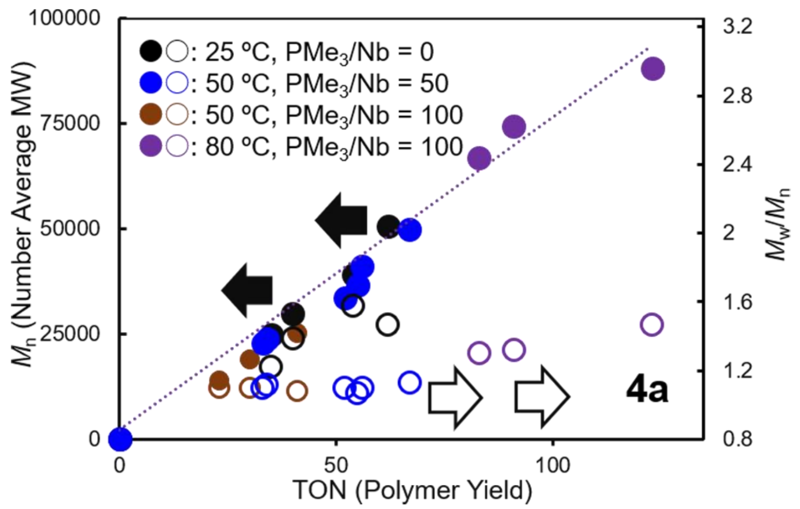

Figure S3-2. Plots of M_n (number average molecular weight), M_w/M_n vs polymer yield (TON, turnover number) in 2-hexyne polymerization by Nb(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$]-(PMe$_3$)$_2$ (**4a**) in toluene. The data are also shown in Tables 1 and S2-1. Plots with additional polymerization data.

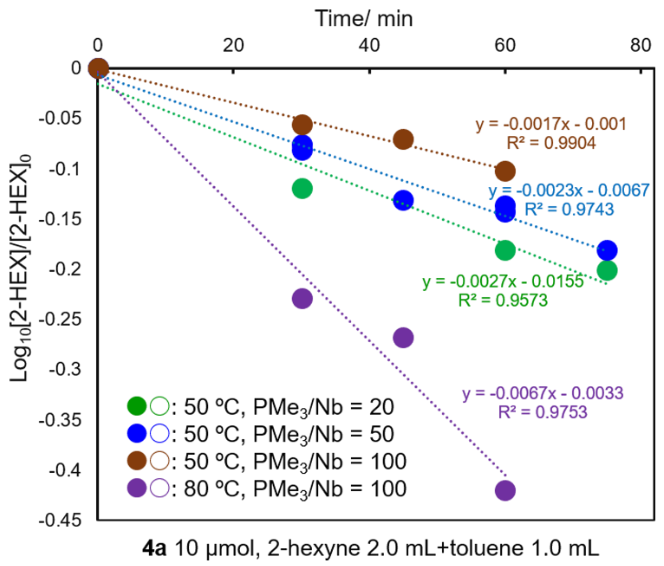

Figure S3-3. Time-course plots versus $\log_{10}[M]/[M]_0$ in 2-hexyne (M) polymerization by $Nb(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)[OC(CF_3)_3](PMe_3)_2$ (**4a**) in toluene. The data are also shown in Tables 1 and S2-1.

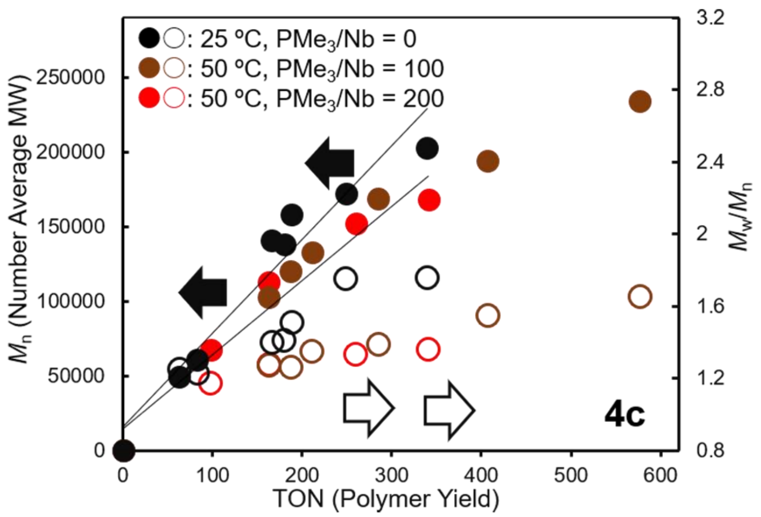

Figure S3-4. Plots of M_n (number average molecular weight), M_w/M_n vs polymer yield (TON, turnover number) in 2-hexyne polymerization by $Nb(CHSiMe_3)(N\text{-}2\text{-}MeC_6H_4)[OC(CF_3)_3](PMe_3)_2$ (**4c**). The data are also shown in Tables 2 and S2-3.

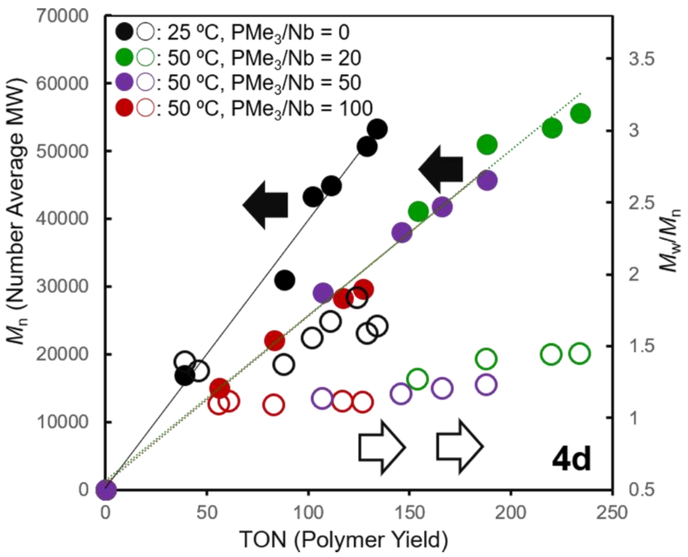

Figure S3-5. Plots of M_n (number average molecular weight), M_w/M_n vs polymer yield (TON, turnover number) in 2-hexyne polymerization by $Nb(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)[OC(CF_3)_3](PMe_3)_2$ (**4d**). The data are also shown in Tables 2 and S2-3.

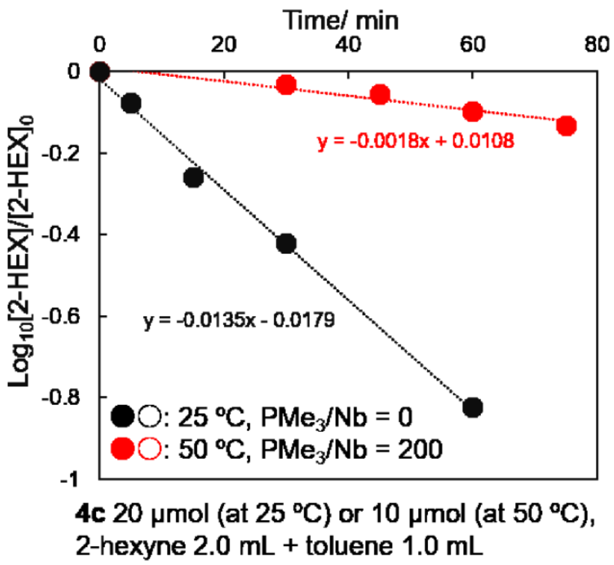

Figure S3-6. Time-course plots versus $\log_{10}[M]/[M]_0$ in 2-hexyne (M) polymerization by $Nb(CHSiMe_3)(N\text{-}2\text{-}MeC_6H_4)[OC(CF_3)_3](PMe_3)_2$ (**4c**) in toluene. The data are also shown in Tables 2 and S2-3.

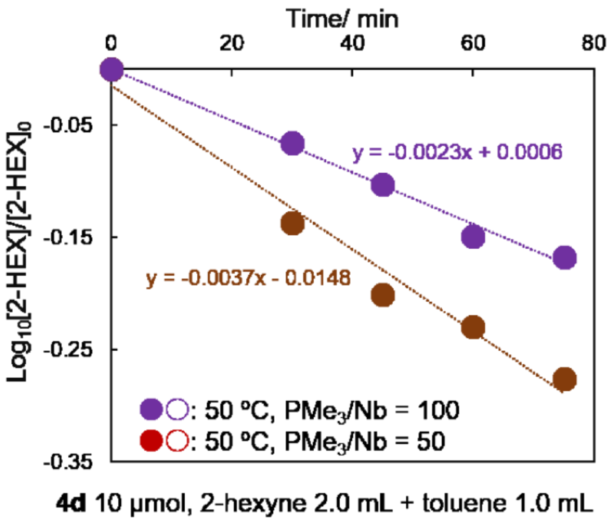

Figure S3-7. Time-course plots versus $\log_{10}[M]/[M]_0$ in 2-hexyne (M) polymerization by $Nb(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)[OC(CF_3)_3](PMe_3)_2$ (**4d**) in toluene. The data are also shown in Tables 2 and S2-4.

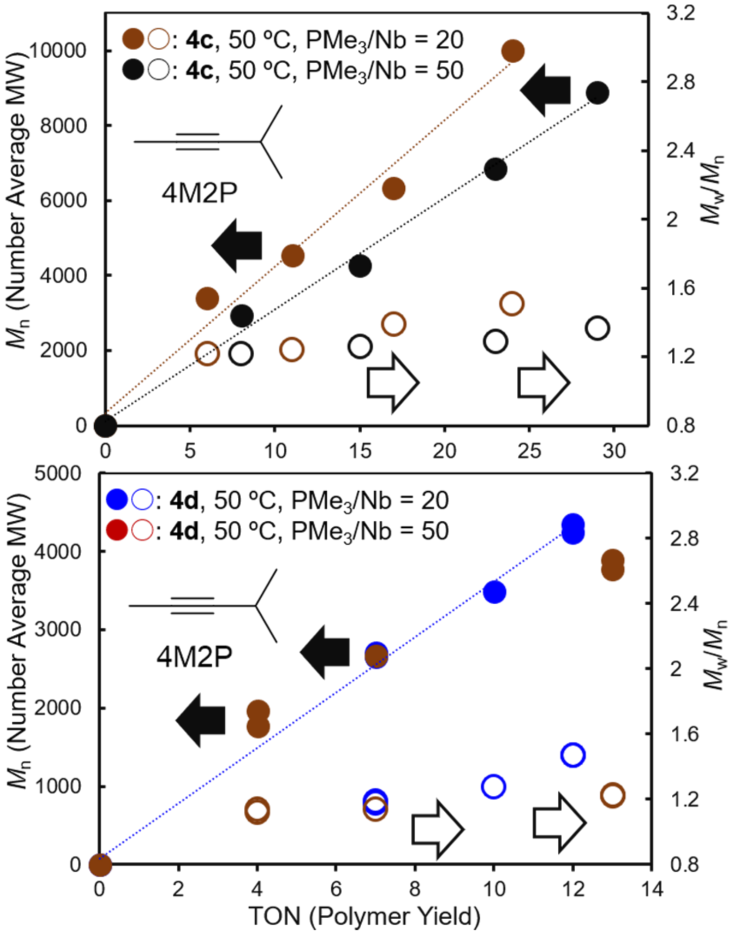

Figure S3-8. Plots of M_n, M_w/M_n vs polymer yield (TON, turnover number) in 4-methy-2-pentyne polymerization by $Nb(CHSiMe_3)(NAr)[OC(CF_3)_3](PMe_3)_2$ [Ar = 2-MeC_6H4 (**4c**), 2,6-$Cl_2C_6H_3$ (**4d**)] in toluene. The data are also shown in Tables 3 and S2-5.

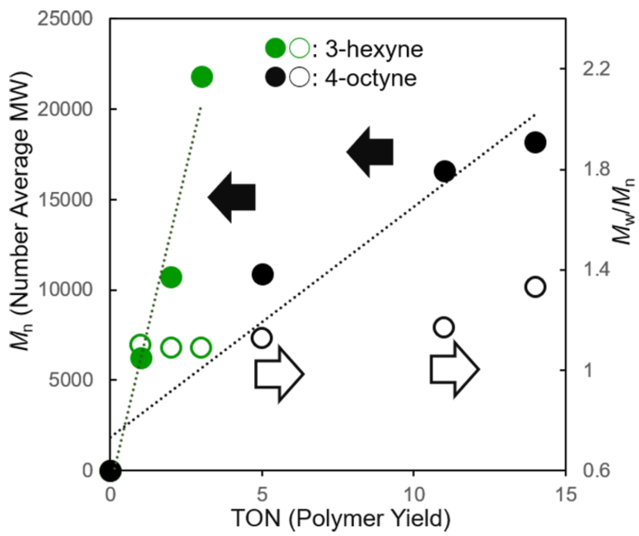

Figure S3-9. Plots of M_n (number average molecular weight), M_w/M_n vs polymer yield (TON, turnover number) in polymerization of 3-hexyne, 4-octyne by Nb(CHSiMe$_3$)(N-2-MeC$_6$H$_4$)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ (**4c**). The data are also shown in Tables 4 and S2-6.

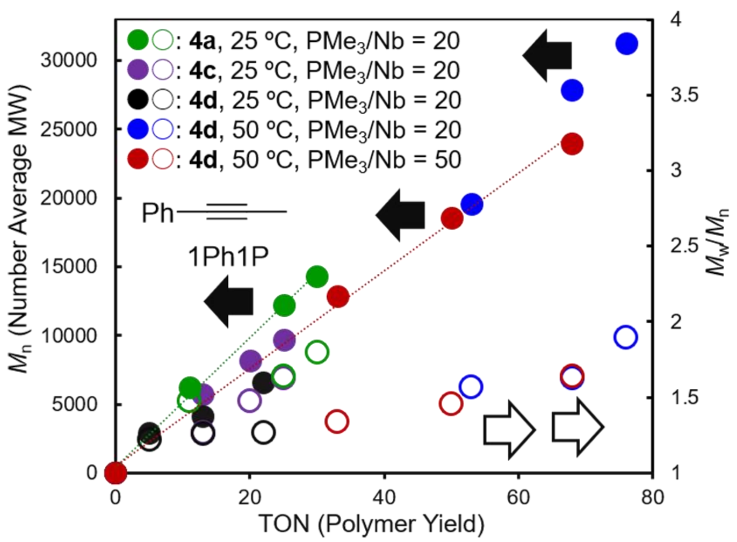

Figure S3-10. Plots of M_n, M_w/M_n vs polymer yield (TON, turnover number) in 1-phenyl-1-propyne polymerization by Nb(CHSiMe$_3$)(NAr)[OC(CF$_3$)$_3$](PMe$_3$)$_2$ [Ar = 2,6-Me$_2$C$_6$H$_3$ (**4a**), 2-MeC$_6$H$_4$ (**4c**),, 2,6-Cl$_2$C$_6$H$_3$ (**4d**)] in toluene. The data are also shown in Tables 5 and S2-7.

4. Selected NMR spectra for prepared poly(2-hexyne), poly(4-methyl-2-pentyne), and poly(1-phenyl-1-propyene).

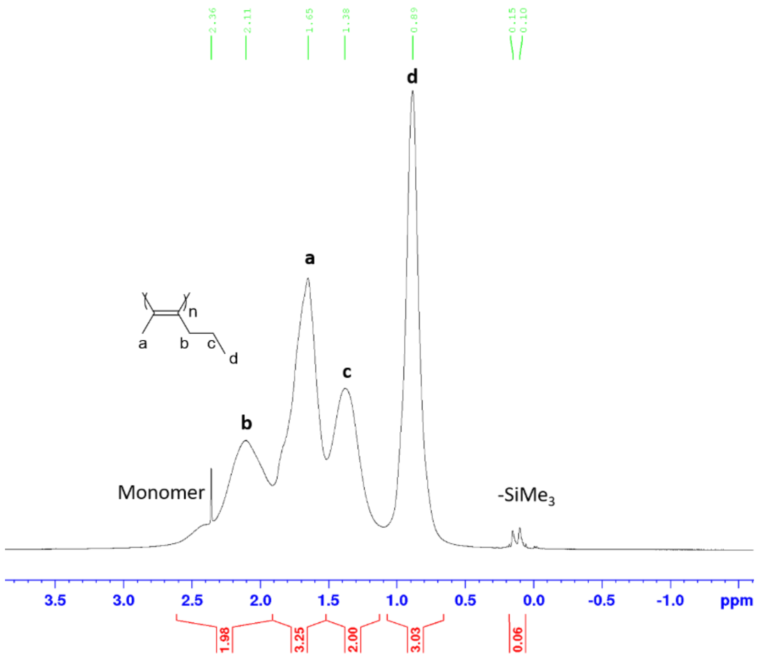

Figure S4-1. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) of poly(2-hexyne) (run S1, Table S2-1). ^{1}H NMR ($CDCl_3$): δ 0.89 (br. 3H), 1.38 (br. 2H), 1.65 (br 3H), 2.11 (br 2H).

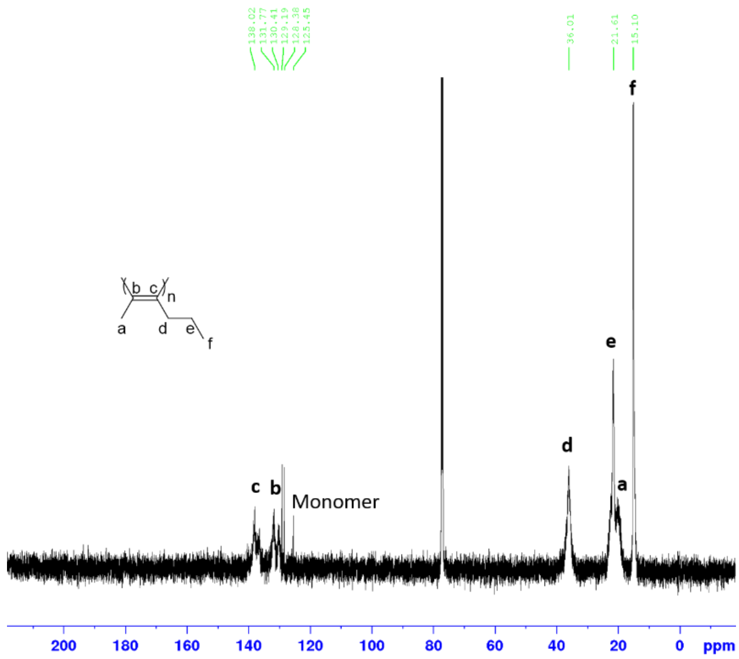

Figure S4-2. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) of poly(2-hexyne) (run S1, Table S2-1). ^{13}C NMR ($CDCl_3$): δ 15.1, 20.5, 21.6, 36.0, 125.5, 128.4, 129.1, 130.4, 131.8, 138.0.

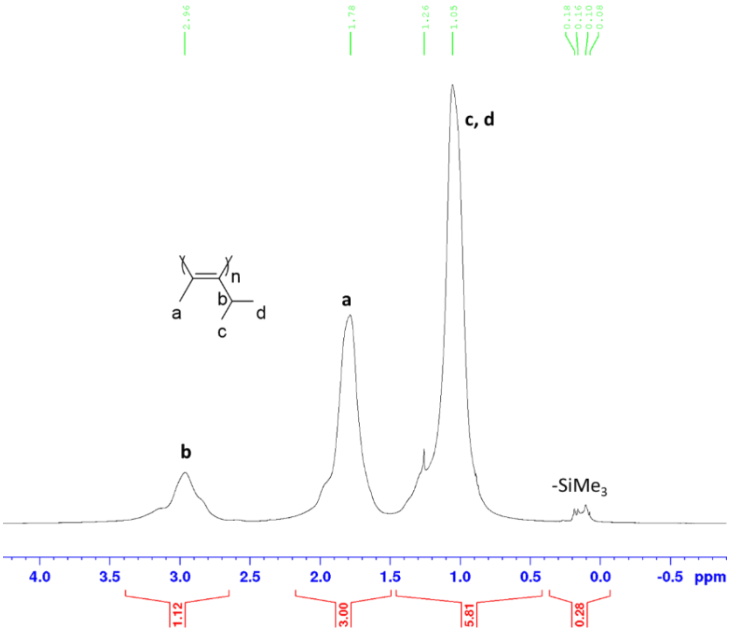

Figure S4-3. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) of poly(4-methyl-2-pentyne) (run 71, Table 3). ^{1}H NMR ($CDCl_3$): δ 1.05 (br. 6H), 1.78 (br. 3H), 2.96 (br 1H).

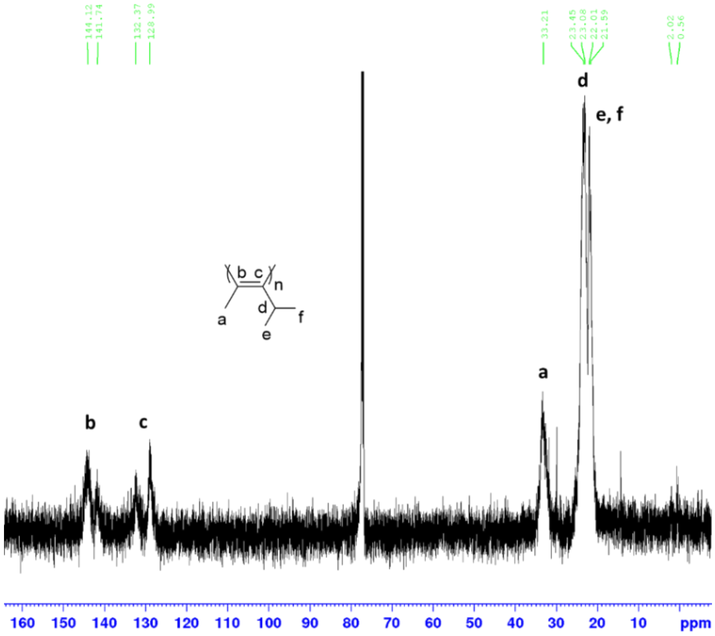

Figure S4-4. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) of poly(4-methyl-2-pentyne) (run 71, Table 3). ^{13}C NMR ($CDCl_3$): δ 21.6, 22.0, 23.1, 23.5, 33.2, 129.0, 132.4, 141.7, 144.1.

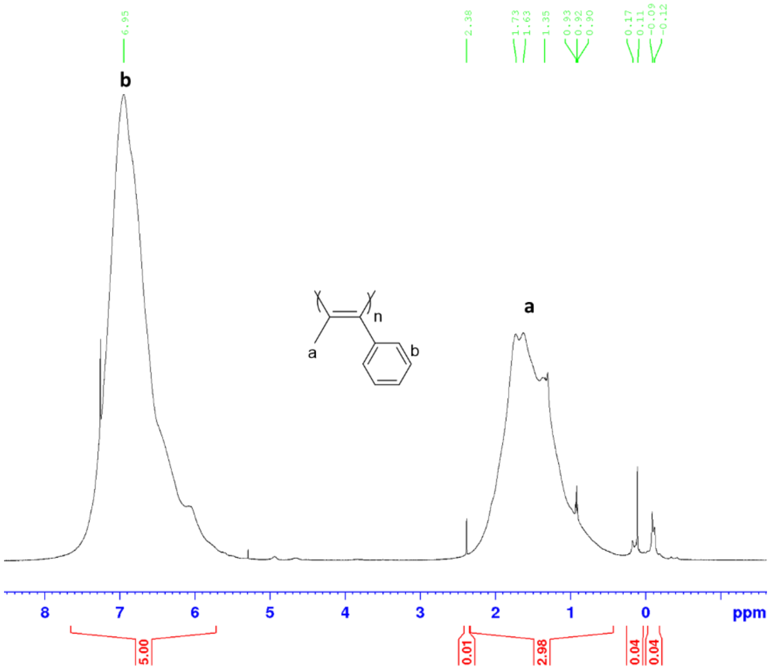

Figure S4-5. ^{1}H NMR spectrum (in $CDCl_3$ at 25 ºC) of poly(1-phenyl-1-propyne) (run 103, Table 5). ^{1}H NMR ($CDCl_3$): δ 0.90-1.73 (br. 3H), 6.95 (br. 5H).

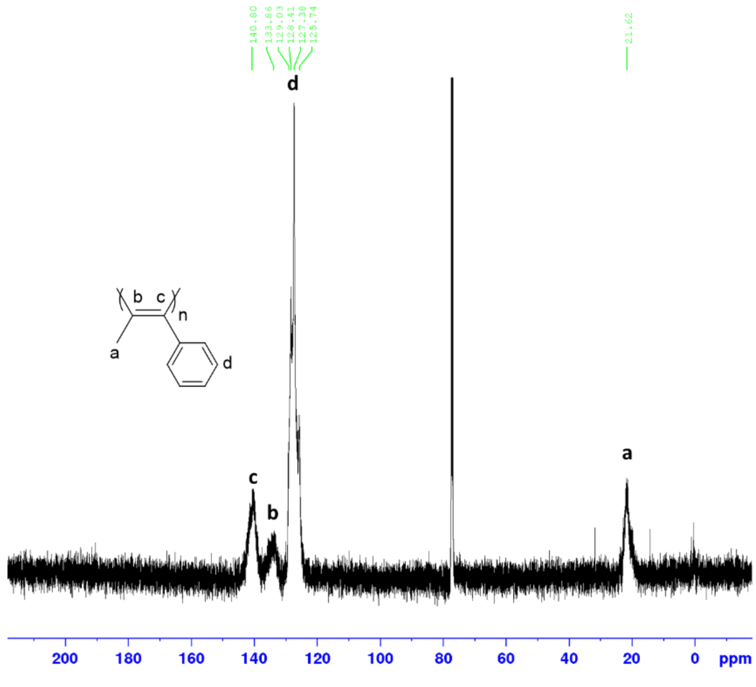

Figure S4-6. ^{13}C NMR spectrum (in $CDCl_3$ at 25 ºC) of poly(1-phenyl-1-propyne) (run 103, Table 5). ^{13}C NMR ($CDCl_3$): δ 21.6, 125.7, 127.4, 128.4, 129.0, 133.9, 140.8.

5. Selected NMR spectra for reaction of Nb(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)[OC(CF$_3$)$_3$]-(PMe$_3$)$_2$ (4a) with diphenylacetylene in toluene-*d*$_8$ in the presence of PMe$_3$.

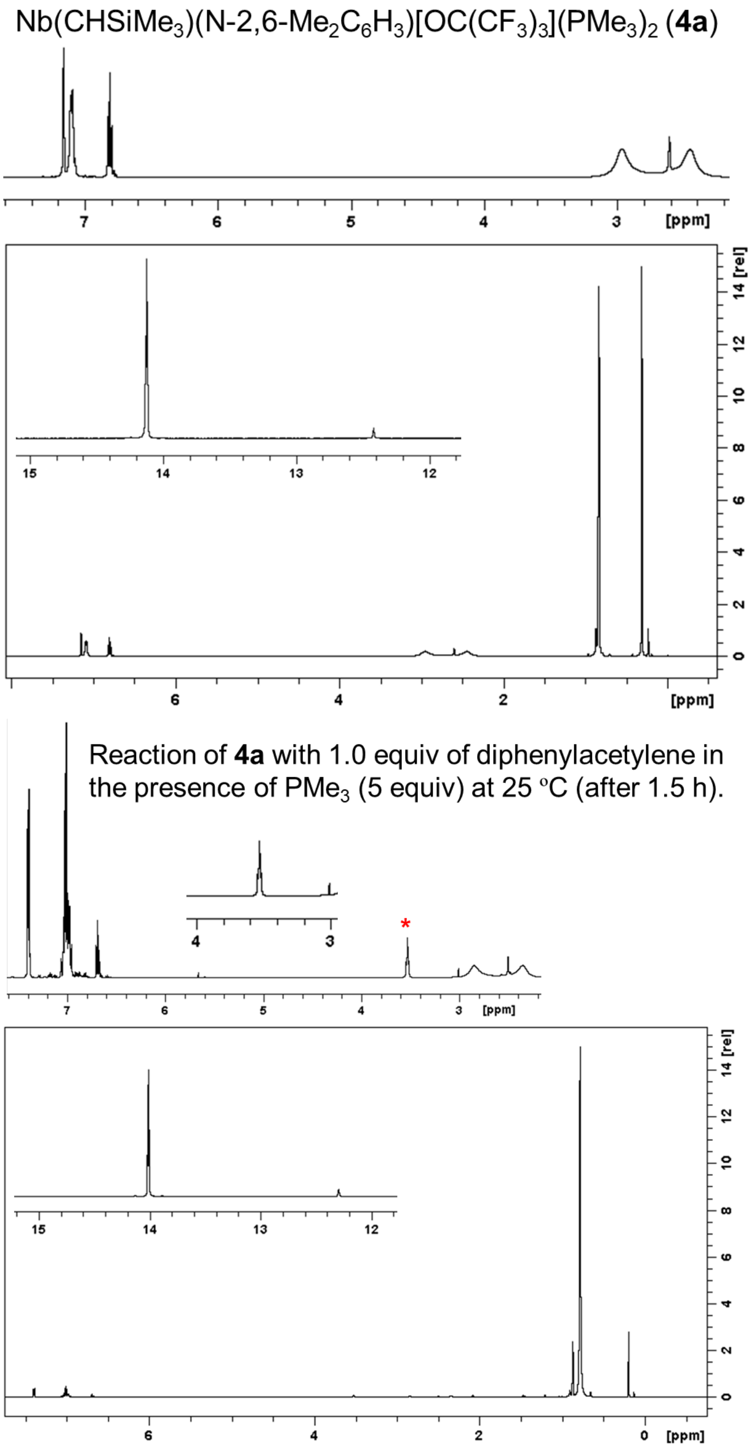

Figure S5-1. ^{1}H NMR spectra (in toluene-*d*$_8$) for (top) Nb(CHSiMe$_3$)(N-2,6-Me$_2$C$_6$H$_3$)-[OC(CF$_3$)$_3$](PMe$_3$)$_2$ (**4a**), and (bottom) reaction of **4a** with 1.0 equiv of diphenylacetylene in the presence of PMe$_3$ (5 equiv). * Marked in red is resonance newly observed in the reaction.

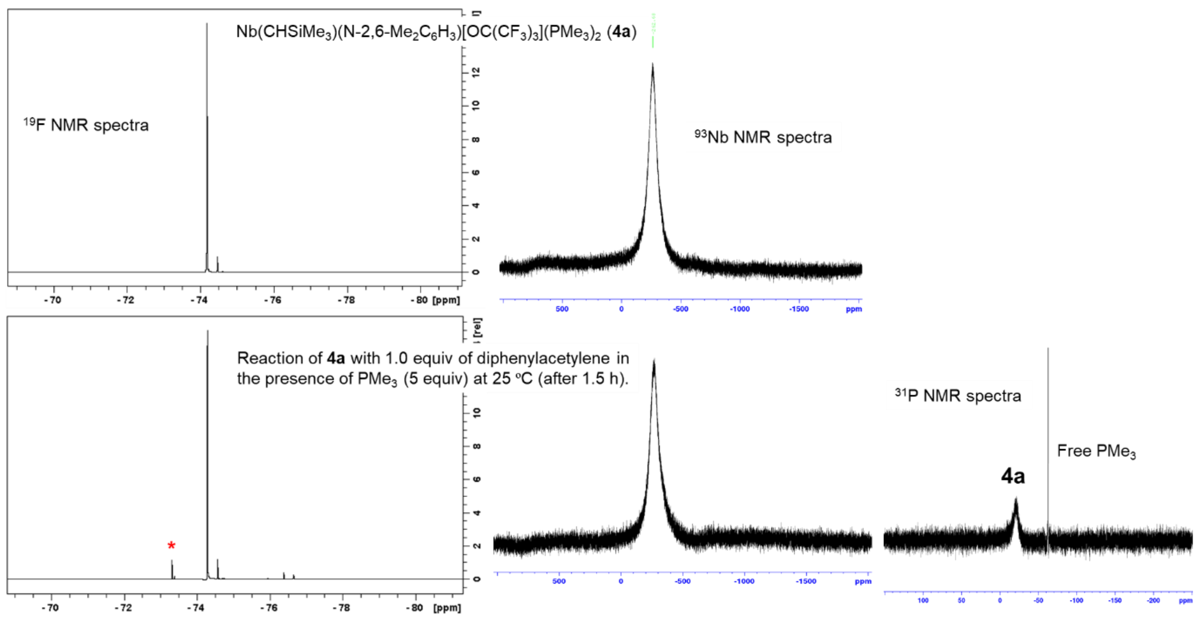

Figure S5-2. [19]F-, [93]Nb-, and [31]P-NMR spectra (in toluene-d_8) for (top) $Nb(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)\text{-}[OC(CF_3)_3](PMe_3)_2$ (**4a**), and (bottom) reaction of **4a** with 1.0 equiv of diphenylacetylene in the presence of PMe_3 (5 equiv). * Marked in red is resonance newly observed in the reaction.

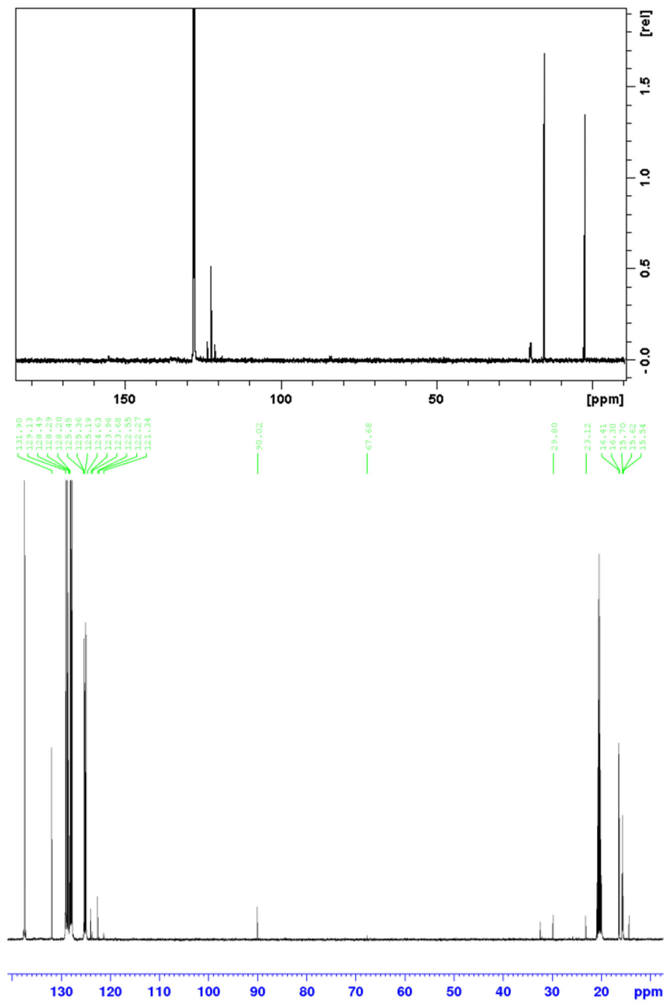

Figure S5-3. [13]C-NMR spectrum (in toluene-d_8) for (top) $Nb(CHSiMe_3)(N\text{-}2,6\text{-}Me_2C_6H_3)$-$[OC(CF_3)_3](PMe_3)_2$ (**4a**), and (bottom) reaction of **4a** with 1.0 equiv of diphenylacetylene in the presence of PMe_3 (20 equiv).