Supporting Information for the Paper Entitled:

Reactivity of Tuck-over Titanium Oxo Complexes with Isocyanides

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Table S1.- Experimental data for the X-ray diffraction studies on complexes **3**, **4**, **5**, **7** and **9**.

	3	**4**	**5**	**7**	**9**
formula	$C_{50}H_{59}NOTi_2$	$C_{46}H_{61}NOSiTi_2$	$C_{46}H_{59}NOTi_2$	$C_{39}H_{59}NOTi_2$	$C_{40}H_{68}N_2OTi_2$
M	785.78	767.84	737.74	653.67	688.76
T [K]	200	200	200	200	200
λ[Å]	0.71073	0.71073	0.71073	0.7013	0.71073
crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	*P-1*	*P-1*	$P2_1$	$P2_1/n$	*P-1*
a [Å]; α [º]	11.475(2), 72.42(1)	12.20(2), 113.03(8)	12.063(1)	15.478(3)	9.017(4), 86.70(4)
b [Å]; β [º]	12.514(2), 75.63(1)	13.18(2), 97.86(8)	15.222(1), 116.406(5)	15.369(3), 100.38(1)	12.793(6), 76.00(5)
c [Å]; γ [º]	16.677(3), 66.62(1)	15.835(9), 100.41(7)	12.113(1)	15.729(2)	18.40(1), 72.39(3)
V [Å^3]	2072.8(7)	2243(5)	1992.1(3)	3680(1)	1963(2)
Z	2	2	2	4	2
ρ_{calcd} [g cm^{-3}]	1.259	1.137	1.23	1.18	1.165
μ [mm^{-1}]	0.424	0.414	0.435	0.464	0.441
F(000)	836	820	788	1408.0	748.0
crystal size [mm^3]	0.18 x 0.12 x 0.07	0.22x0.13x0.10	0.19 x 0.15 x 0.10	0.37 × 0.22 × 0.15	0.15 × 0.10 × 0.04
θ range [deg]	3.00 to 25.35°	3.05 to 25.35°	3.20 to 27.50°	3.04 to 27.51°	3.00 to 25.03°
index ranges	-13 to 13, -15 to 15, -20 to 20	-14 to 14, -15 to 15, -19 to 19	-15 to 15, -19 to 19, -15 to 15	-20 to 20, -19 to 19, -20 to 20	-10 to 10, -15 to 15, -21 to 21
reflections collected	39155	22675	37883	62606	18359
unique data	7567	8198	9117	8365	6891
reflections [I>2σ(I)]	4893	4479	6390	5258	4309
goodness-of-fit on F^2	1.12	1.089	1.11	1.27	1.081
final *R* indices [$I>2\sigma(I)$]	0.077 / 0.132	0.087 / 0.145	0.060 / 0.097	0.072 / 0.141	0.081 / 0.155
R indices (all data)	0.138 / 0.155	0.175 / 0.177	0.112 / 0.118	0.136 / 0.177	0.143 / 0.184
largest diff. peak/hole [e·Å^{-3}]	0.432 / - 0.457	0.405 / -0.319	0.56 / -0.507	0.678 / -0.716	0.654 / -0.487

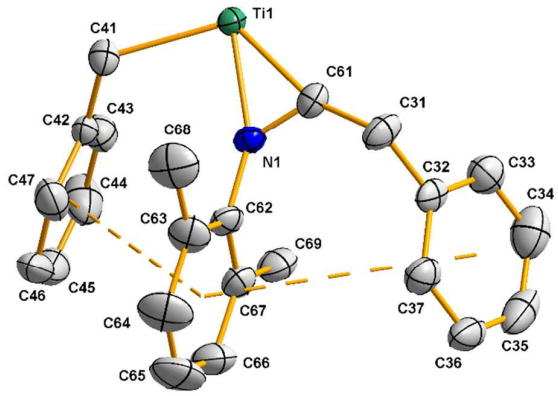
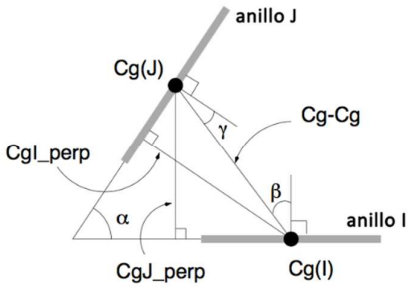


Figure S1. π-stacking interactions in compound **3**.

Table S2. Structural parameters related to the π-stacking interaction in **3**. [1]



Cg(I)	C32-C37	C42-C47
Cg(J)	C62-C67	C62-C67
Cg-Cg	4.671(3) Å	4.039(4) Å
α	24.5(3)°	16.4(3)°
β	54.2°	39.3°
γ	40.0°	30.5°
CgI_Perp	3.579(2)Å	-3.482(2)Å
CgJ_Perp	-2.729(2)Å	3.128(2)Å

[1] a) Hunter, C. A., Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525-5534. b) Steed, J. W., Atwood, J. L. *Supramolecular Chemistry*, 2ª edición, John Wiley & Sons, United Kingdom, **2009**.

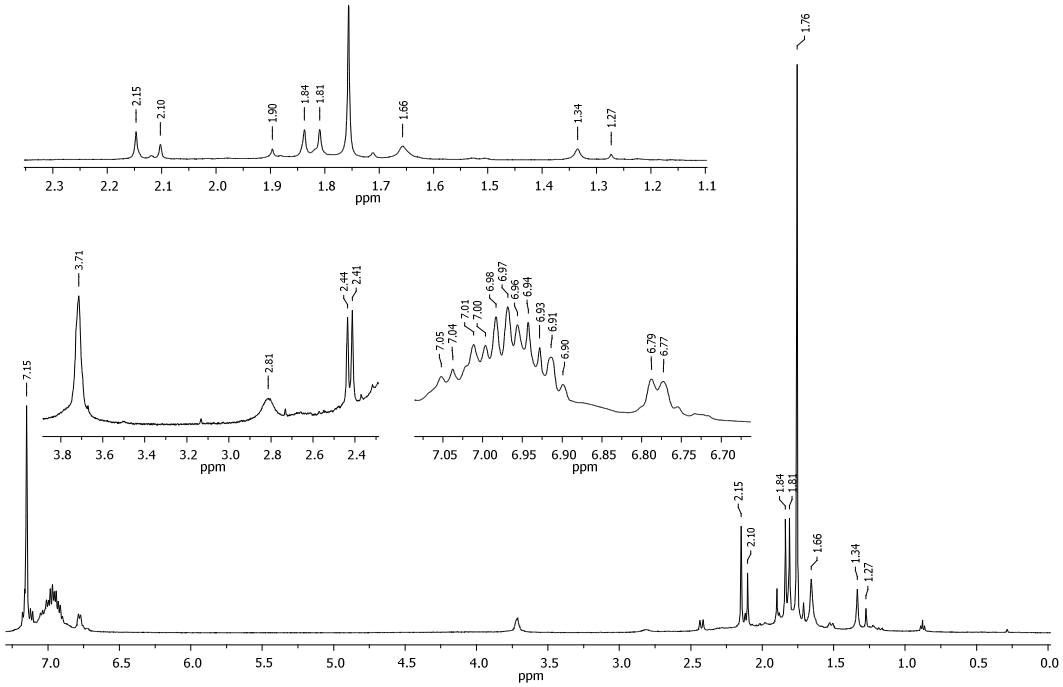


Figure S2. ^{1}H-NMR spectrum of **3** in C_6D_6 (500 MHz at 298 K)

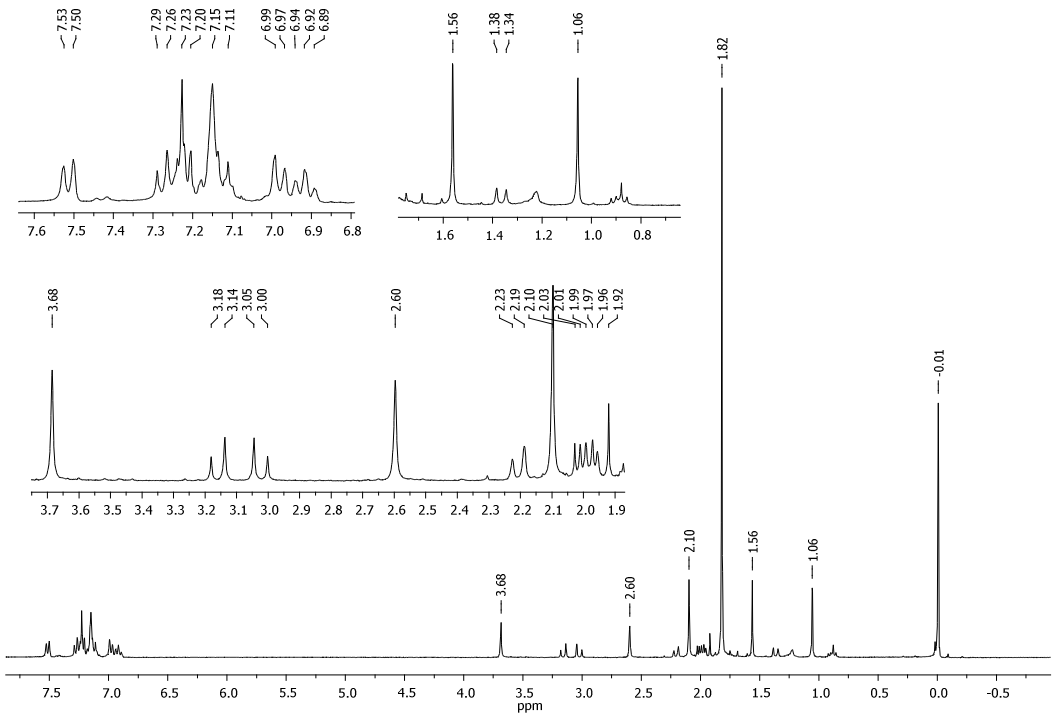


Figure S3. ^{1}H-NMR spectrum of **4** in C_6D_6 (500 MHz at 298 K).

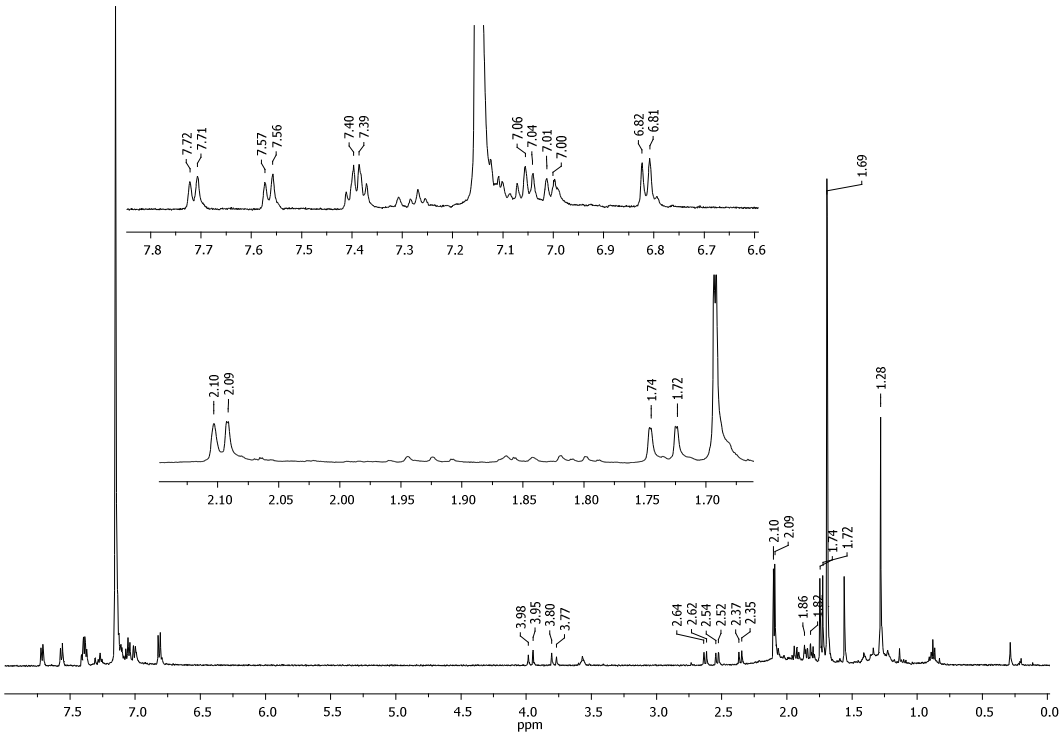


Figure S4. ^{1}H-NMR spectrum of **5** in C_6D_6 (500 MHz at 298 K).

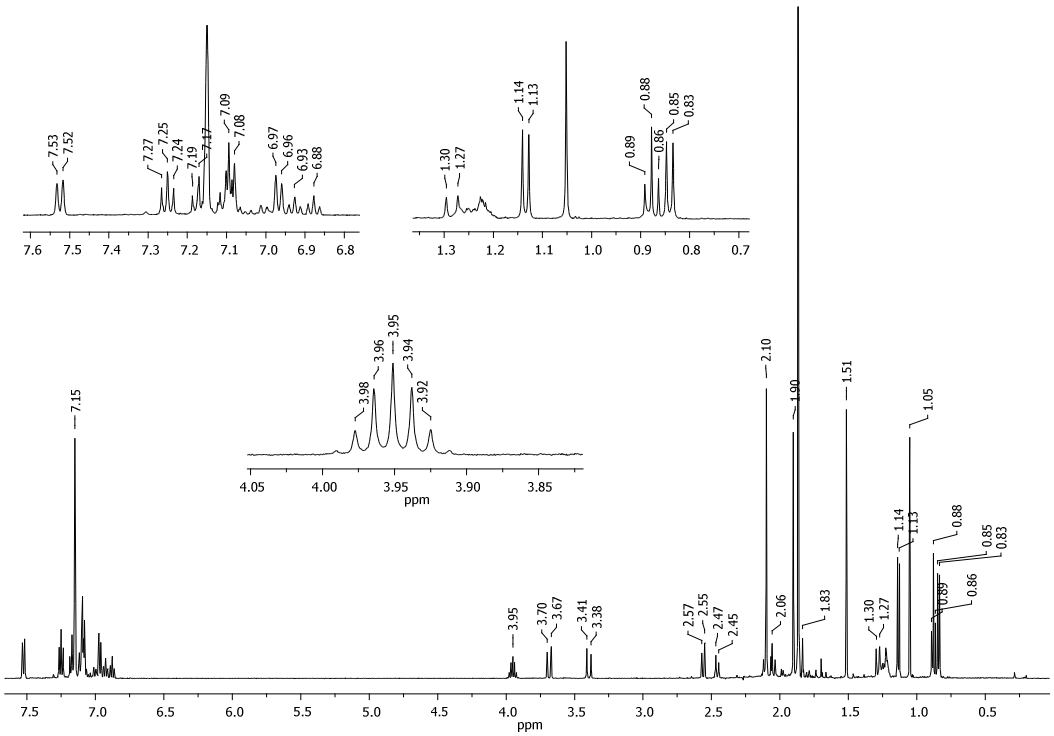


Figure S5. ^{1}H-NMR spectrum of **6** in C_6D_6 (500 MHz at 298 K).

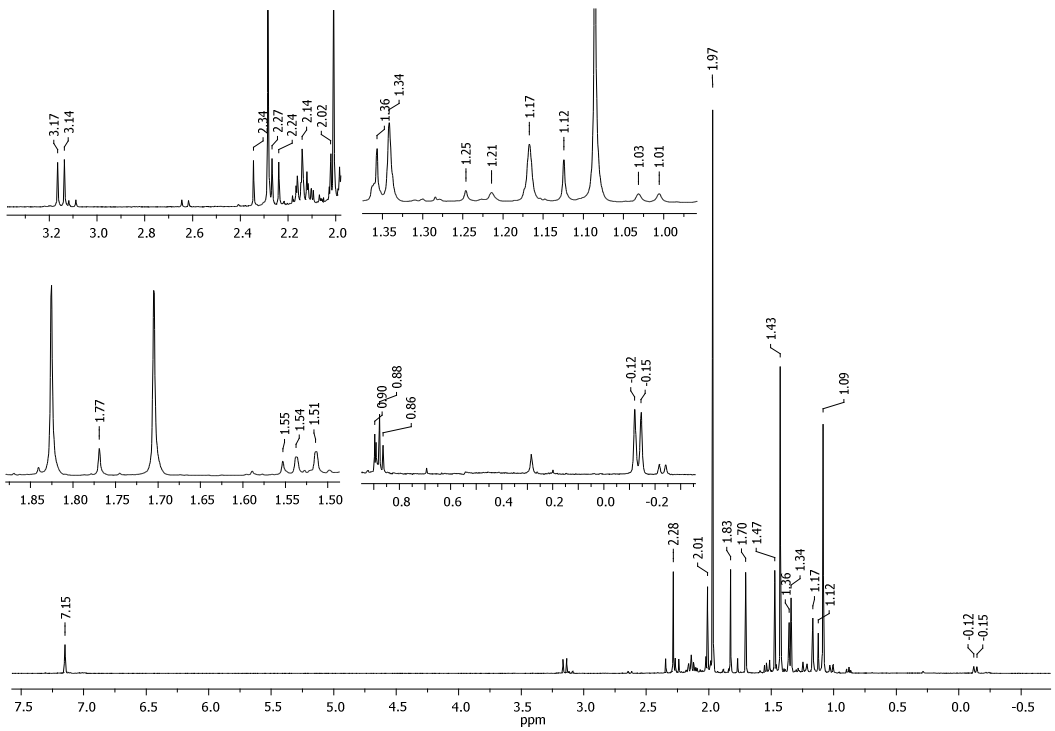


Figure S6. ^{1}H-NMR spectrum of **7** in C_6D_6 (500 MHz at 298 K).

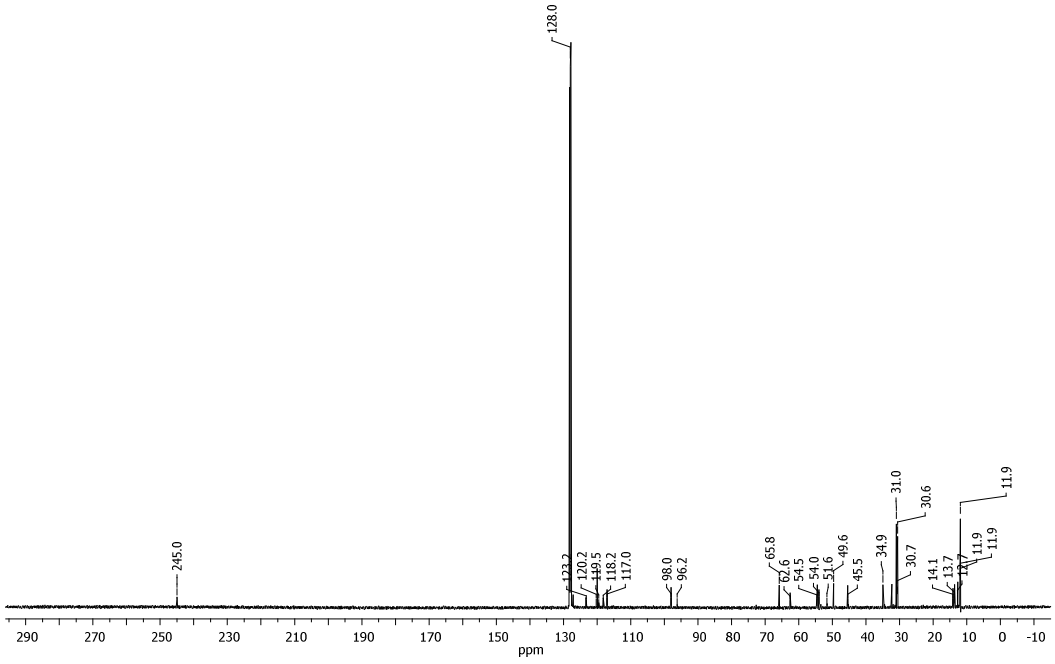


Figure S7. ^{13}C{^{1}H}-NMR spectrum of **7** in C_6D_6 (125 MHz at 298 K).

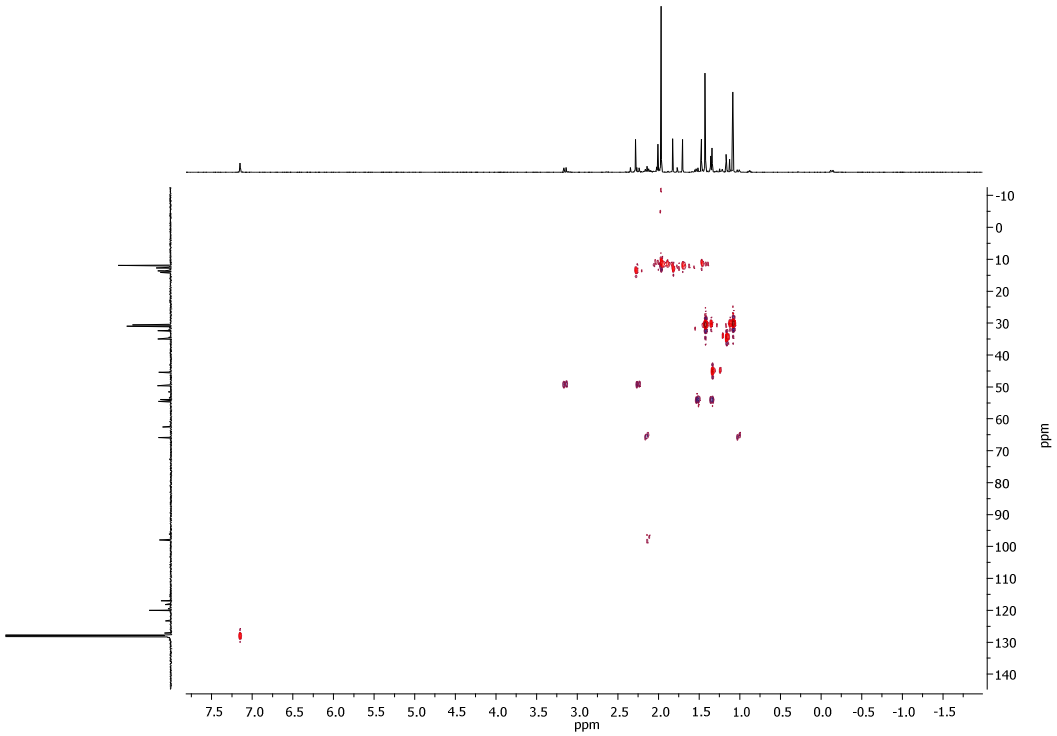


Figure S8. ^{1}H-^{13}C HSQC-NMR spectrum of **7** in C_6D_6 (500 MHz at 298 K, X axis: ^{1}H, Y axis: ^{13}C NMR).

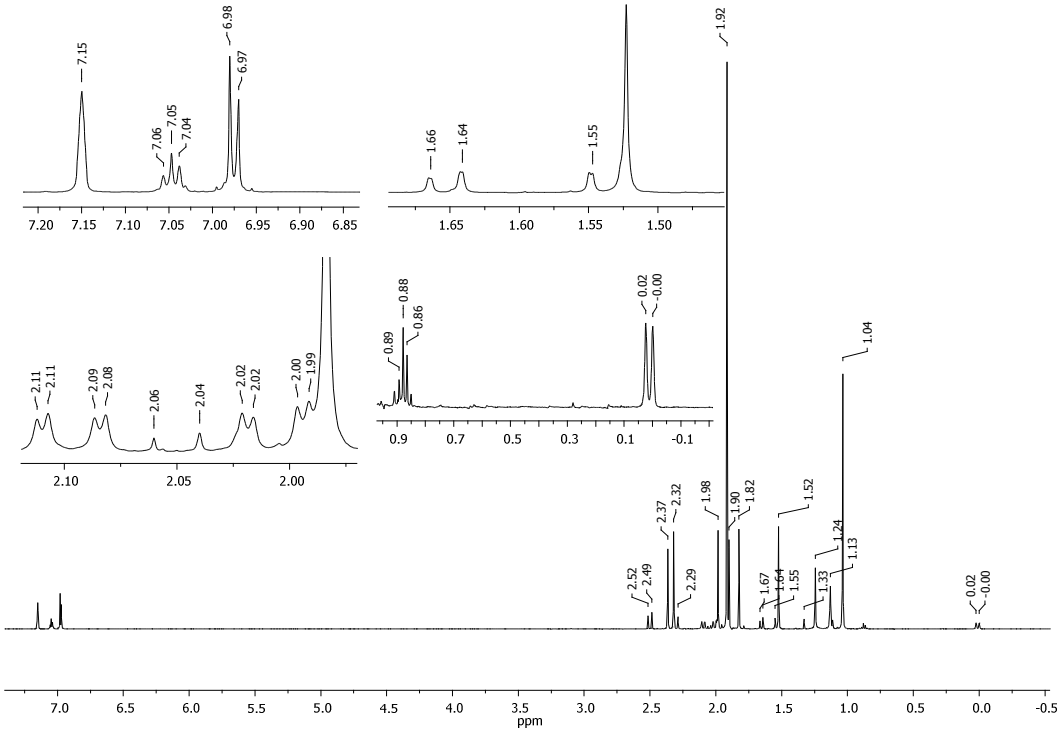


Figure S9. ^{1}H-NMR spectrum of **8** in C_6D_6 (500 MHz at 298 K).

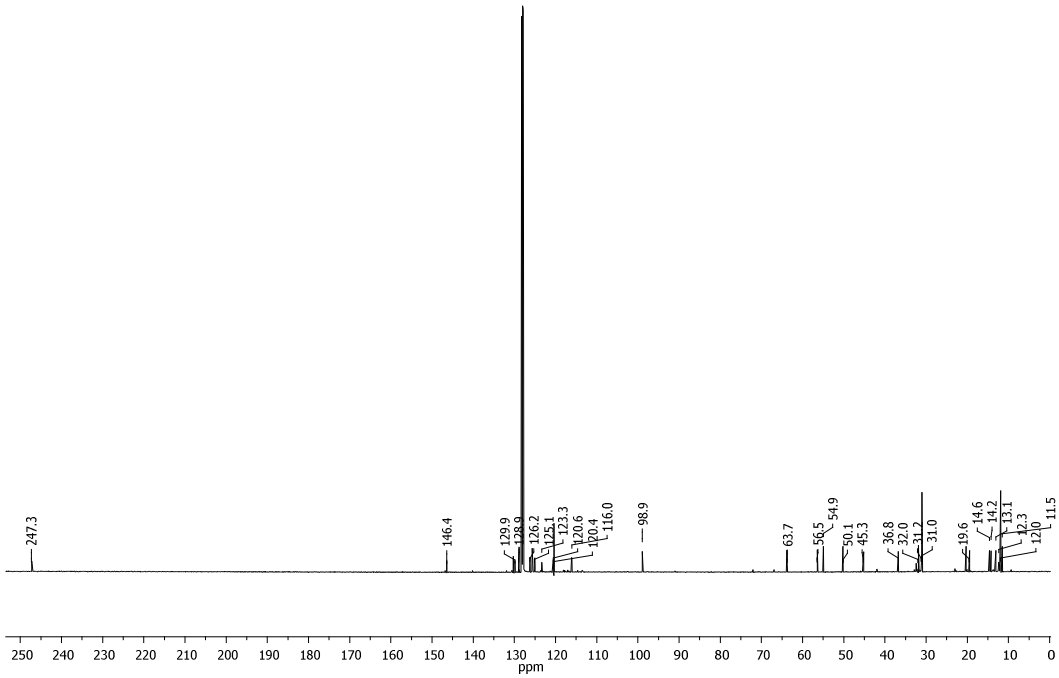


Figure S10. $^{13}C\{^{1}H\}$-NMR spectrum of **8** in C_6D_6 (125 MHz at 298 K).

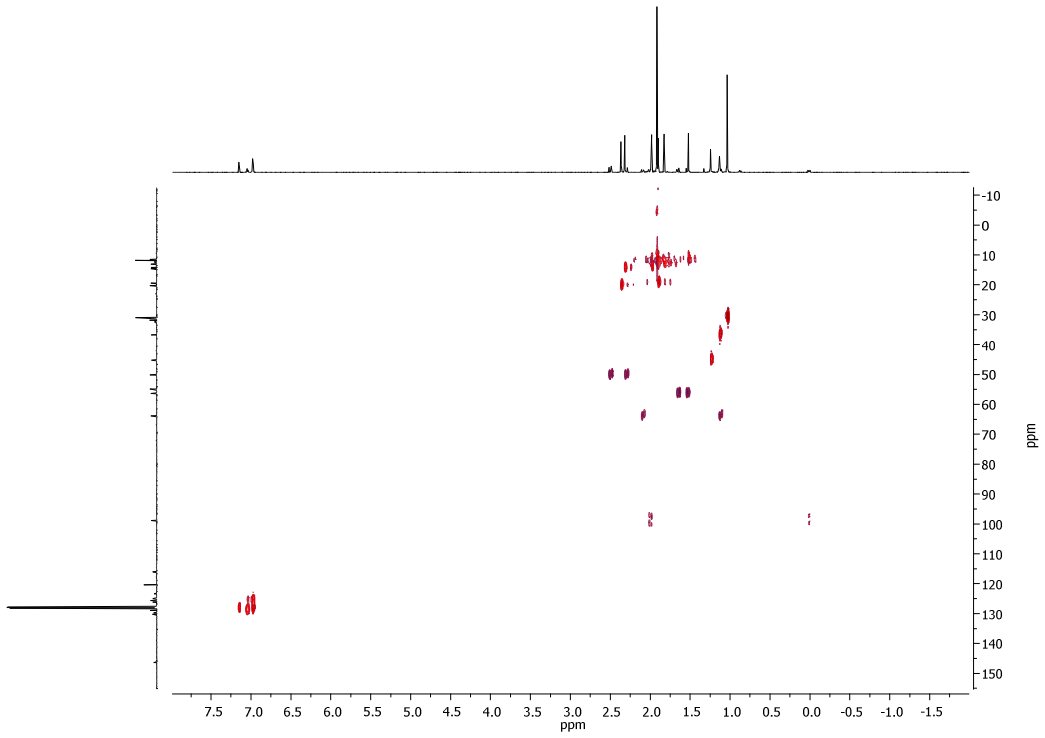


Figure S11. ^{1}H-^{13}C HSQC-NMR spectrum of **8** in C_6D_6 (500 MHz at 298 K, X axis: ^{1}H, Y axis: ^{13}C NMR).

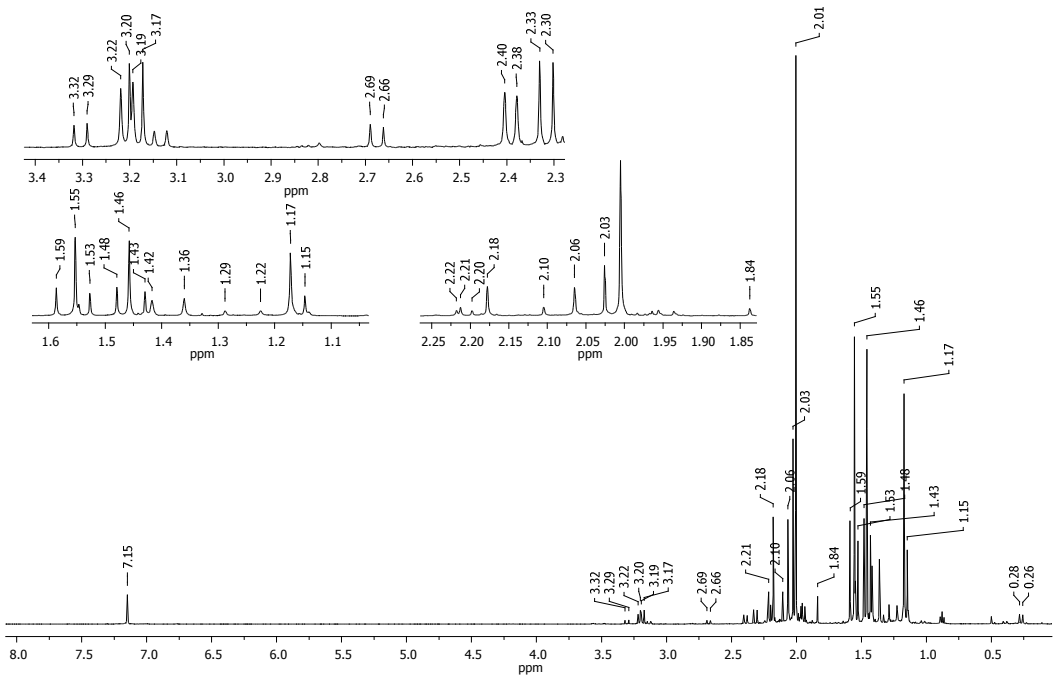


Figure S12. ^{1}H-NMR spectrum of **9** in C_6D_6 (500 MHz at 298 K)

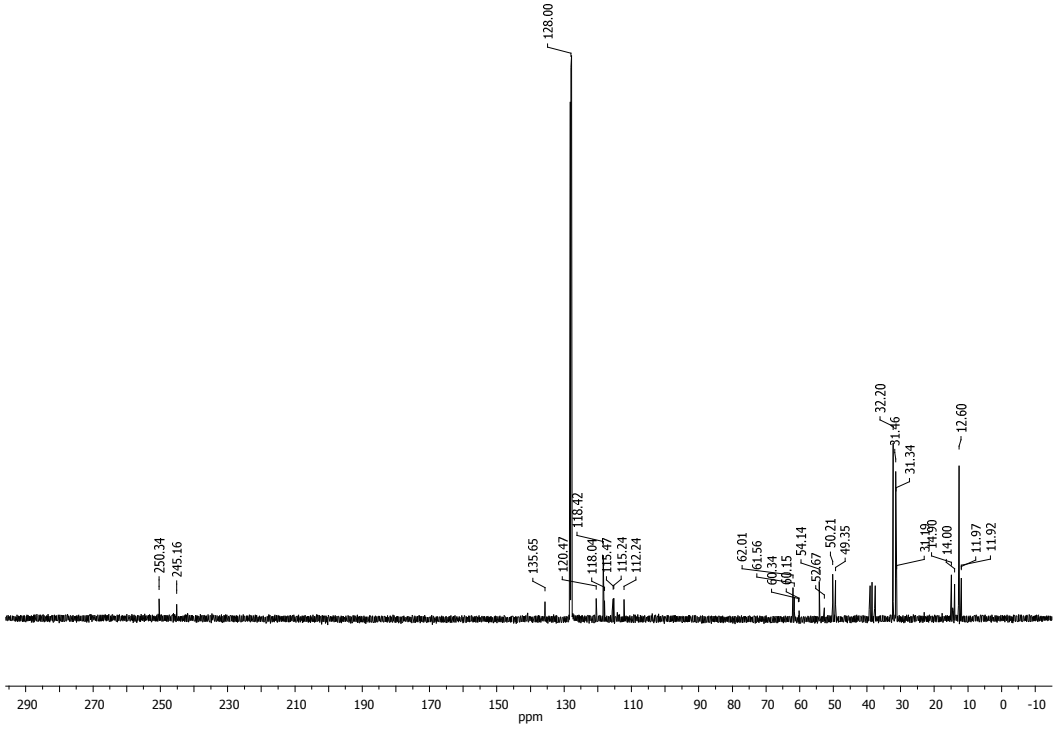


Figure S13. $^{13}C\{^{1}H\}$-NMR spectrum of **9** in C_6D_6 (125 MHz at 298 K)

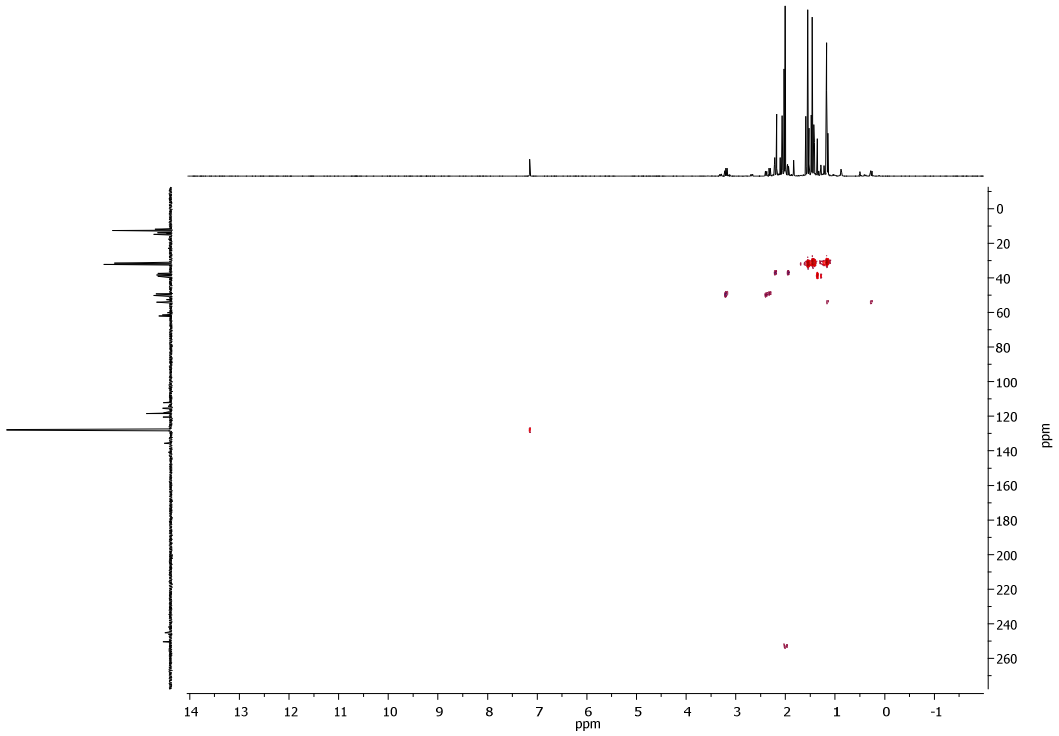


Figure S14. ^{1}H-^{13}C HSQC-NMR spectrum of **9** in C_6D_6 (500 MHz at 298 K, X axis: ^{1}H, Y axis: ^{13}C NMR)

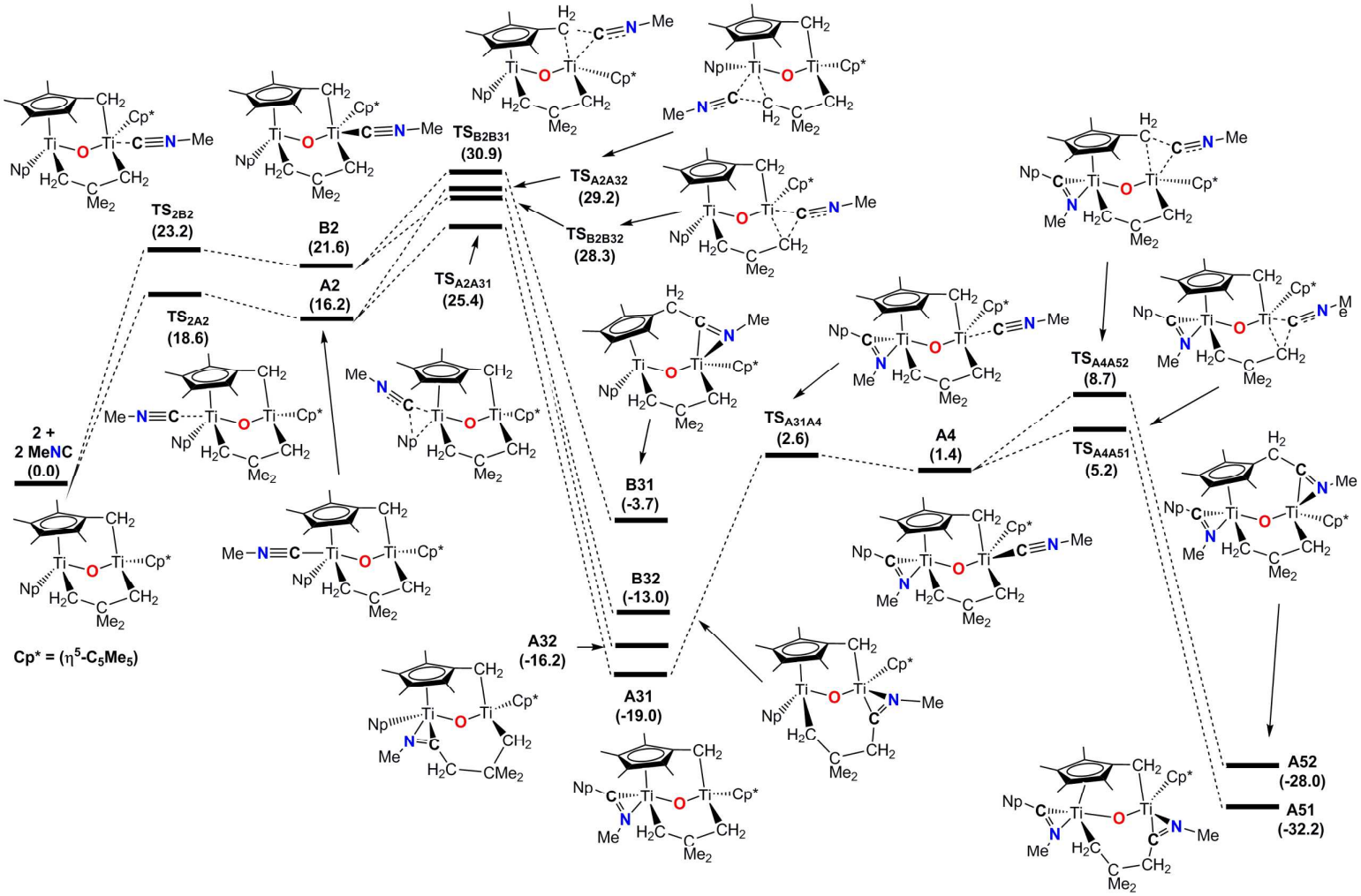


Figure S15. Full Gibbs energy profile at 25°C (kcal·mol^{-1}) for the insertion steps of MeNC on complex **2**.