

Supporting Information

Syntheses and Coordination Chemistry of Thiosemicarbazone-based Titanium Complexes

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NMR Spectra of complexes

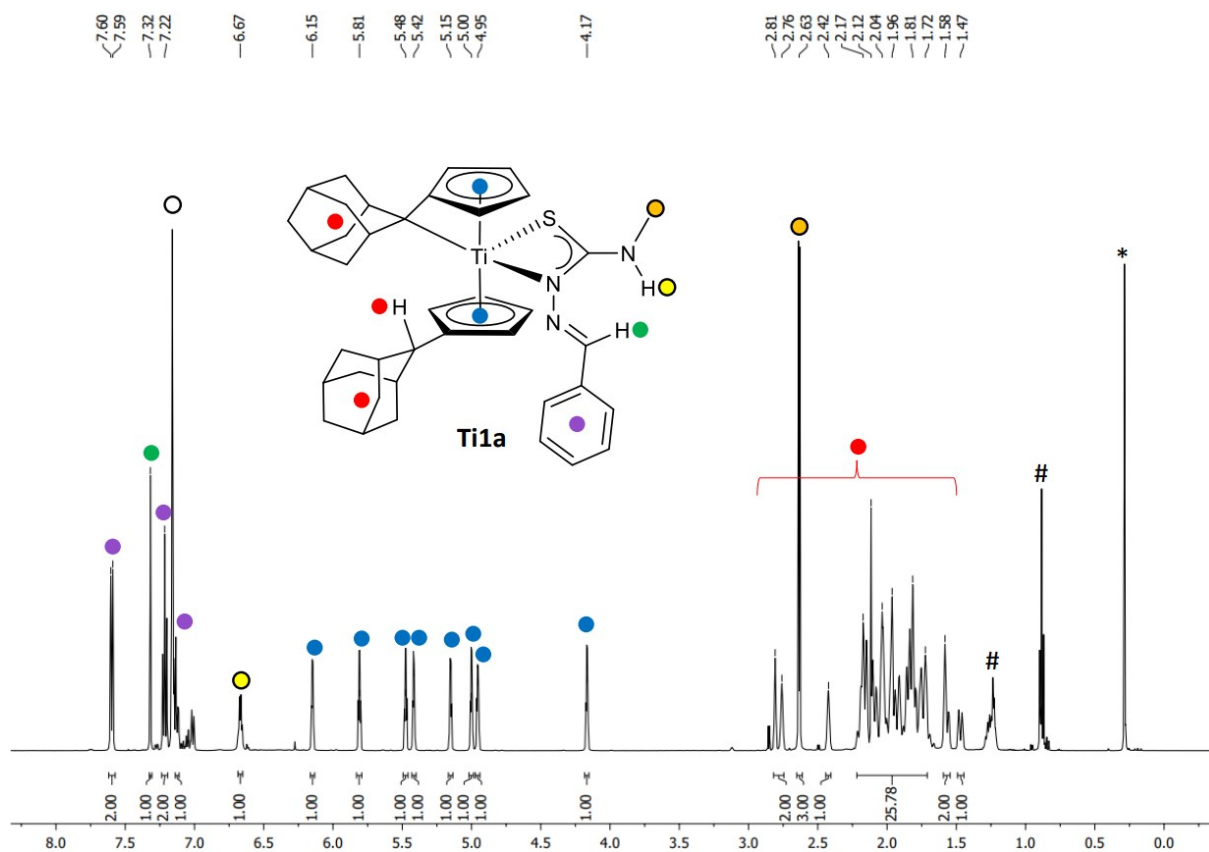


Figure S1: ¹H NMR spectrum (500 MHz, C₆D₆, 305 K) of **Ti1a**. Product signals given in colours (° = C₆H₅D, # = *n*-hexane, * = grease).

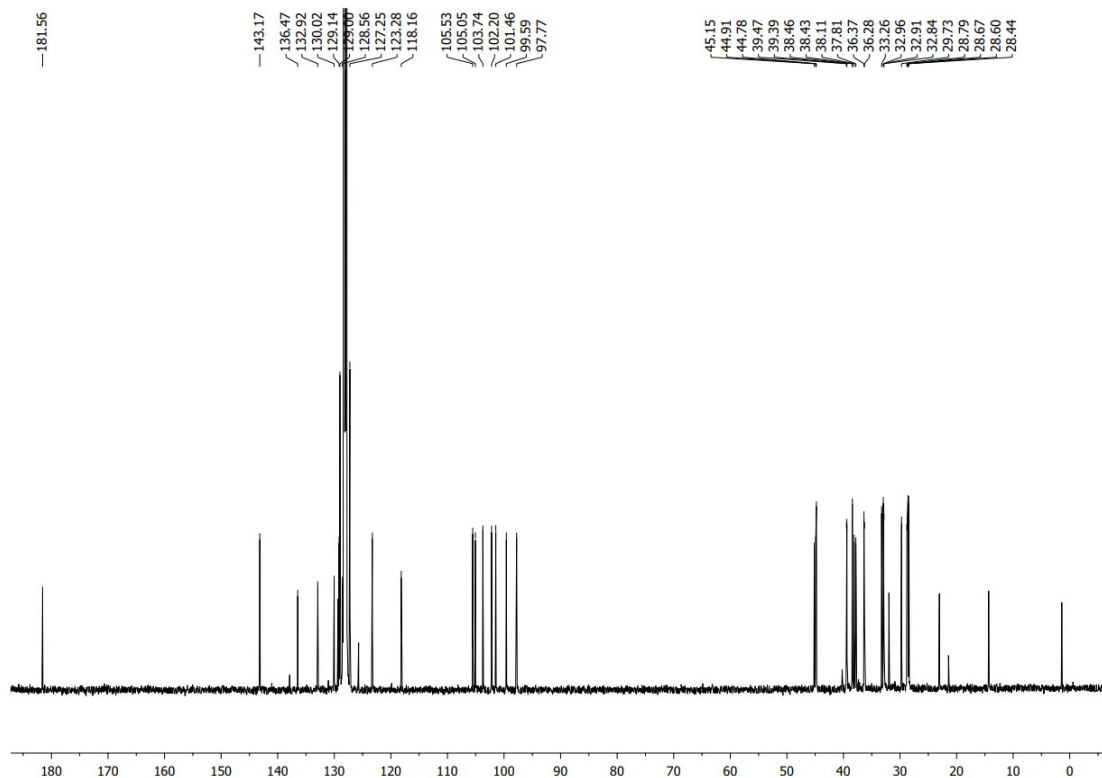


Figure S2: ¹³C NMR spectrum (125 MHz, C₆D₆, 305 K) of **Ti1a**.

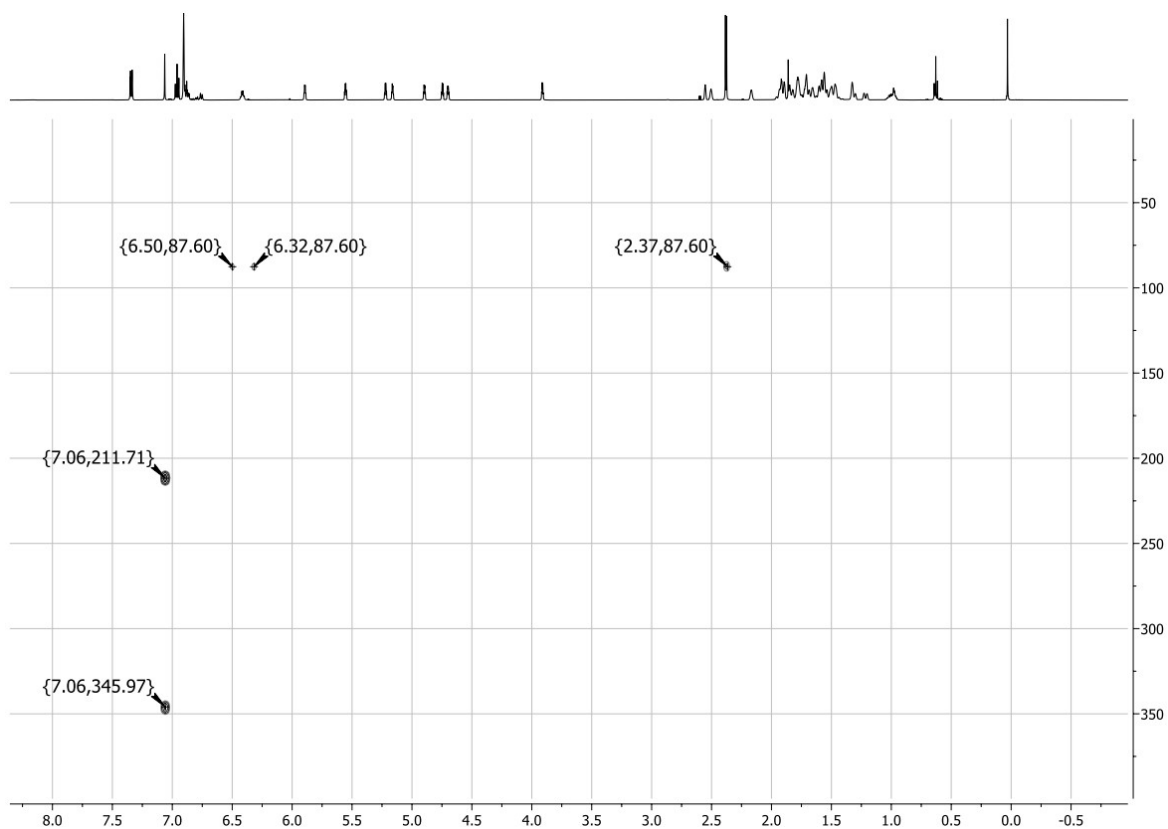


Figure S3: ^1H - ^{15}N -HMBC NMR spectrum (51 MHz, C_6D_6 , 305 K) of **Ti1a**.

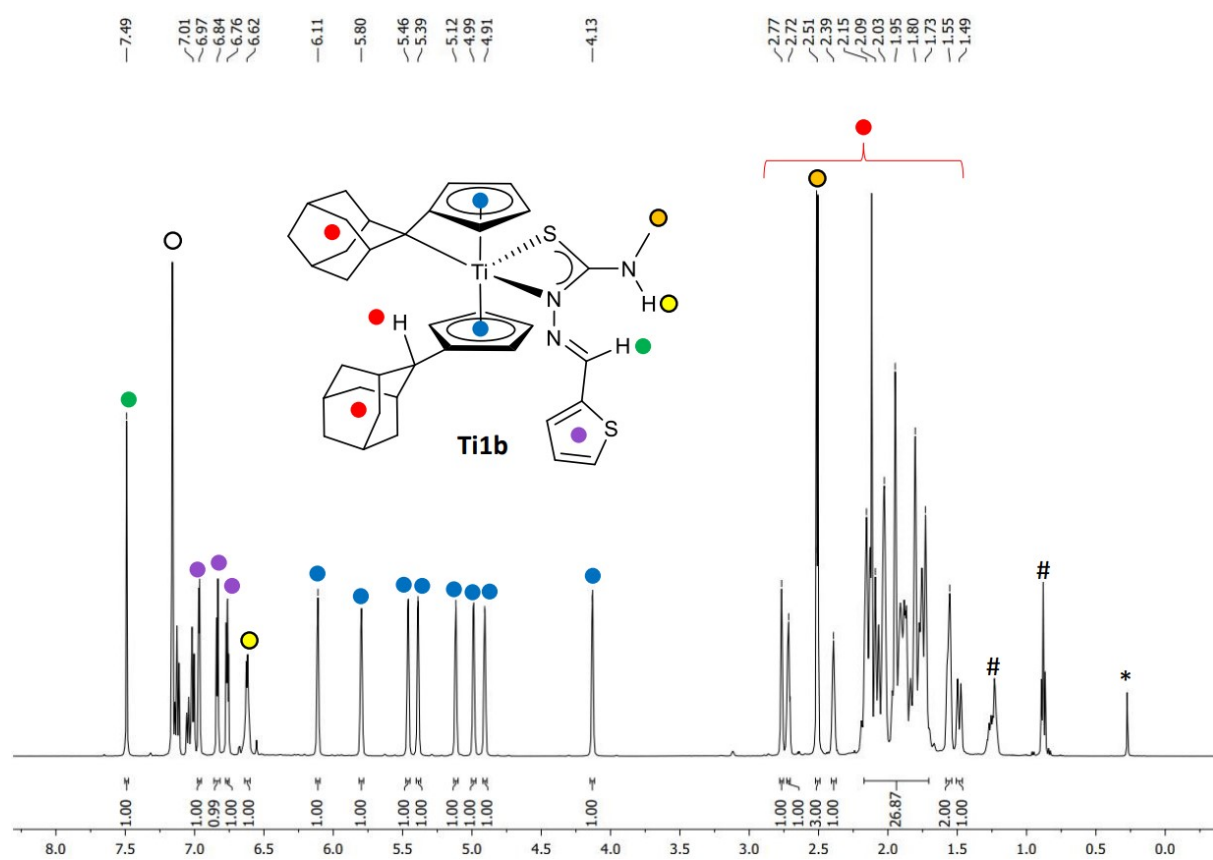


Figure S4: ^1H NMR spectrum (500 MHz, C_6D_6 , 305 K) of **Ti1b**. Product signals given in colours ($^{\circ}$ = $\text{C}_6\text{H}_5\text{D}$, # = n -hexane, * = grease).

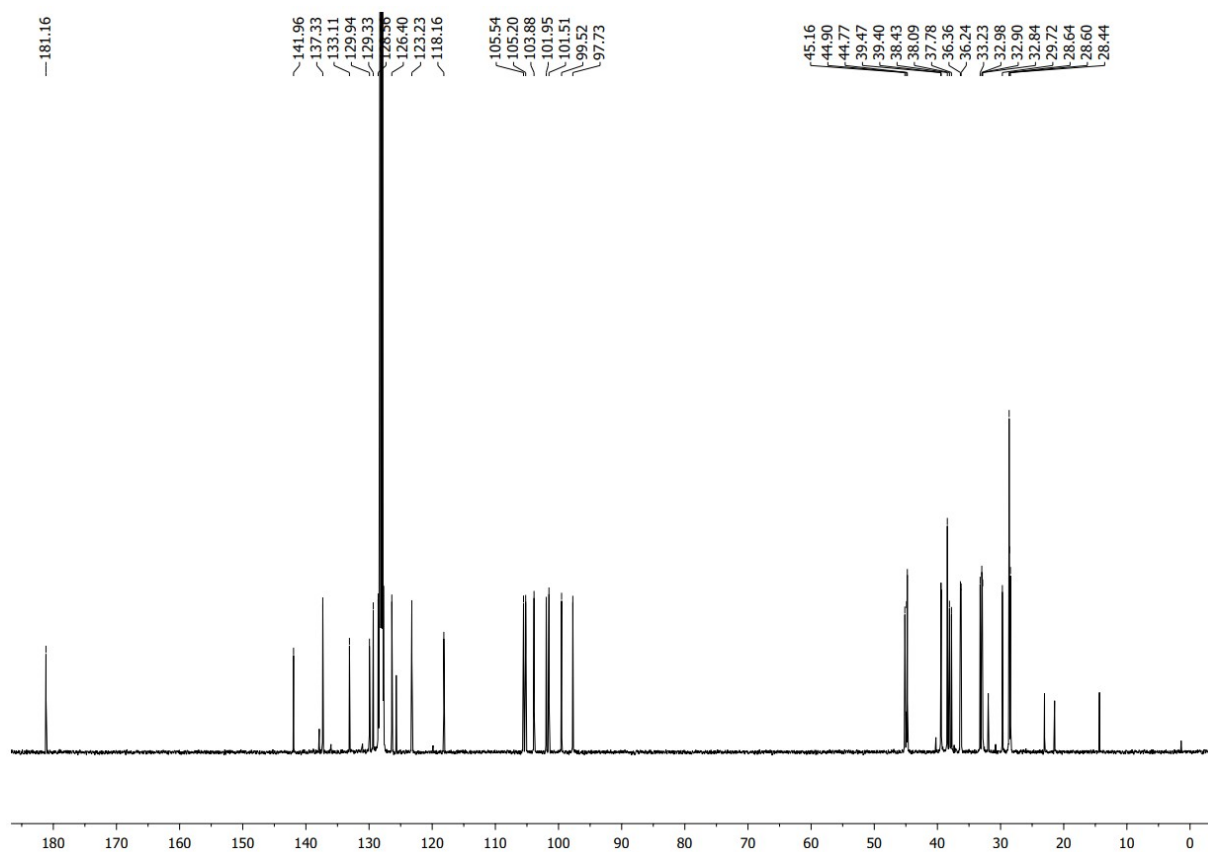


Figure S5: ^{13}C NMR spectrum (125 MHz, C_6D_6 , 305 K) of **Ti1b**.

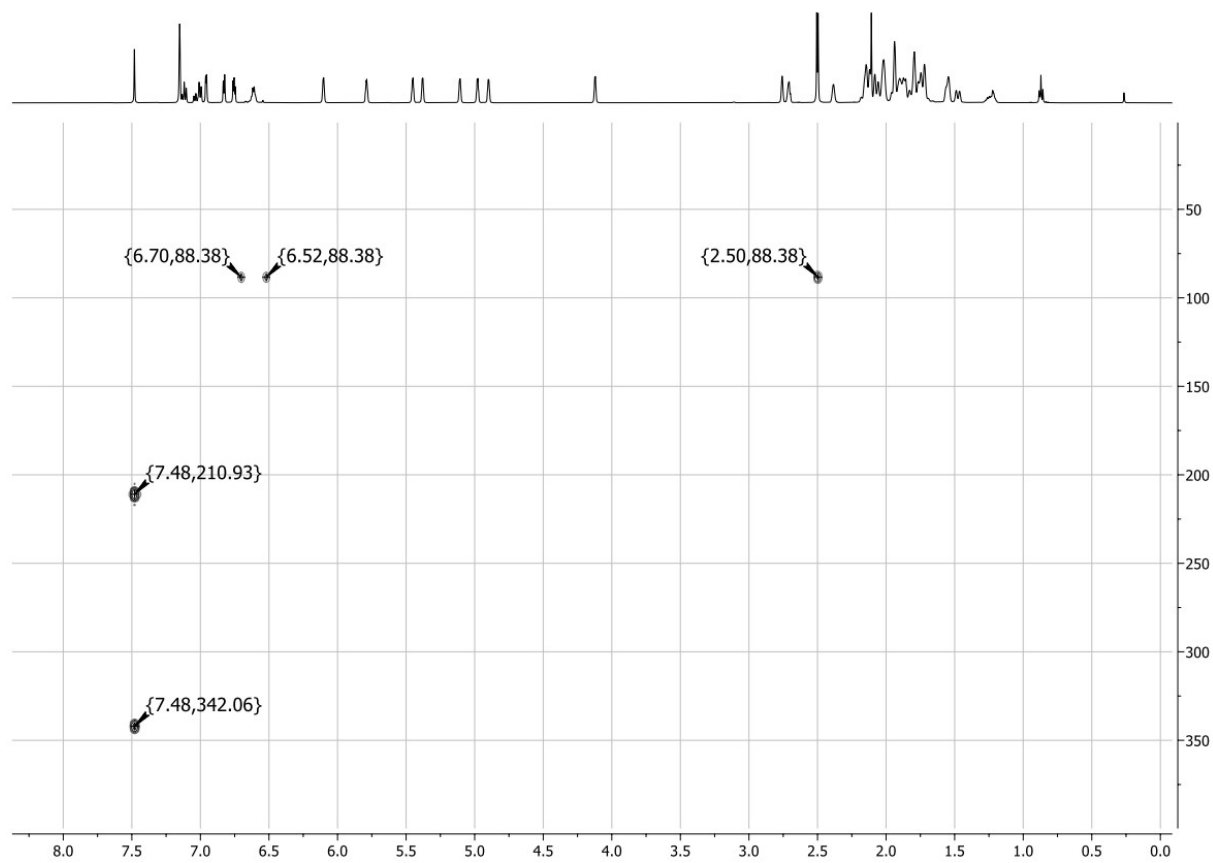


Figure S6: ^1H - ^{15}N -HMBC NMR spectrum (51 MHz, C_6D_6 , 305 K) of **Ti1b**.

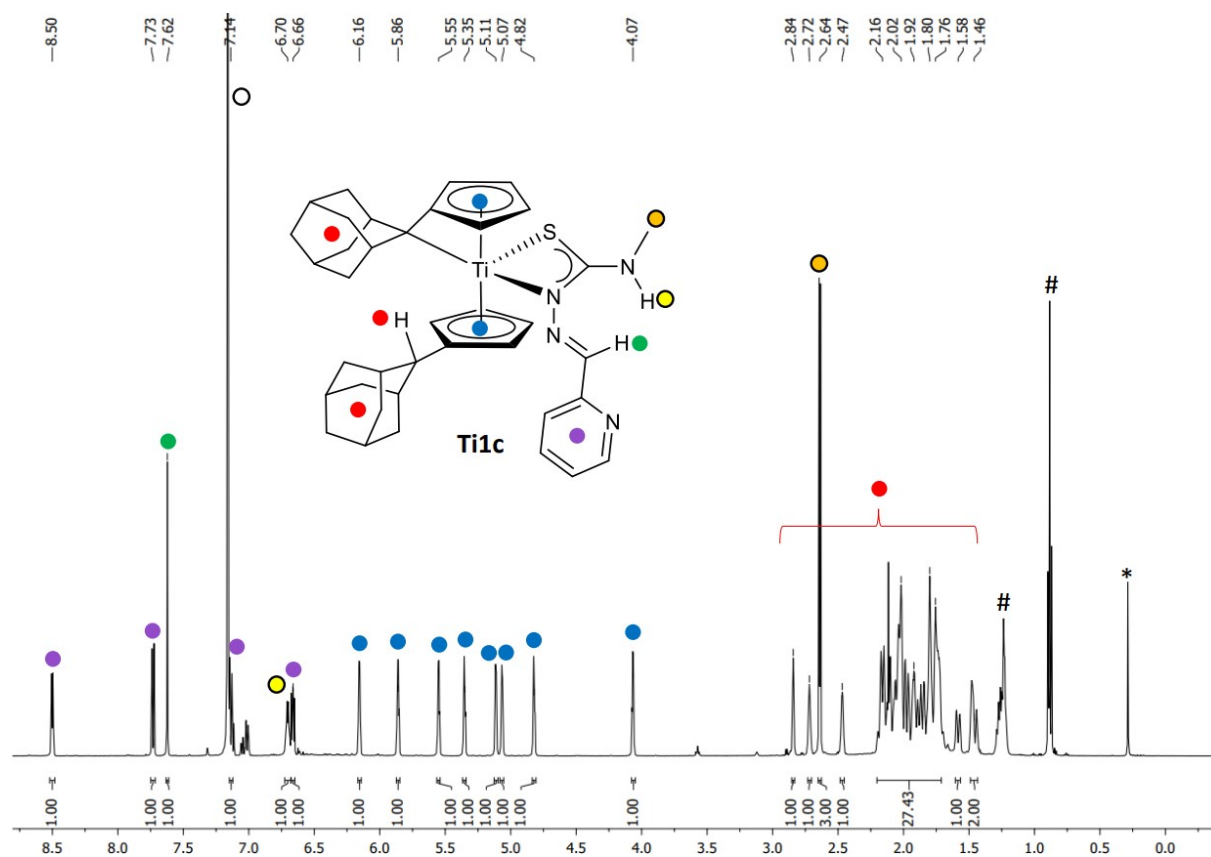


Figure S7: ^1H NMR spectrum (500 MHz, C_6D_6 , 305 K) of **Ti1c**. Product signals given in colours ($^{\circ}$ = $\text{C}_6\text{H}_5\text{D}$, # = *n*-hexane, * = grease).

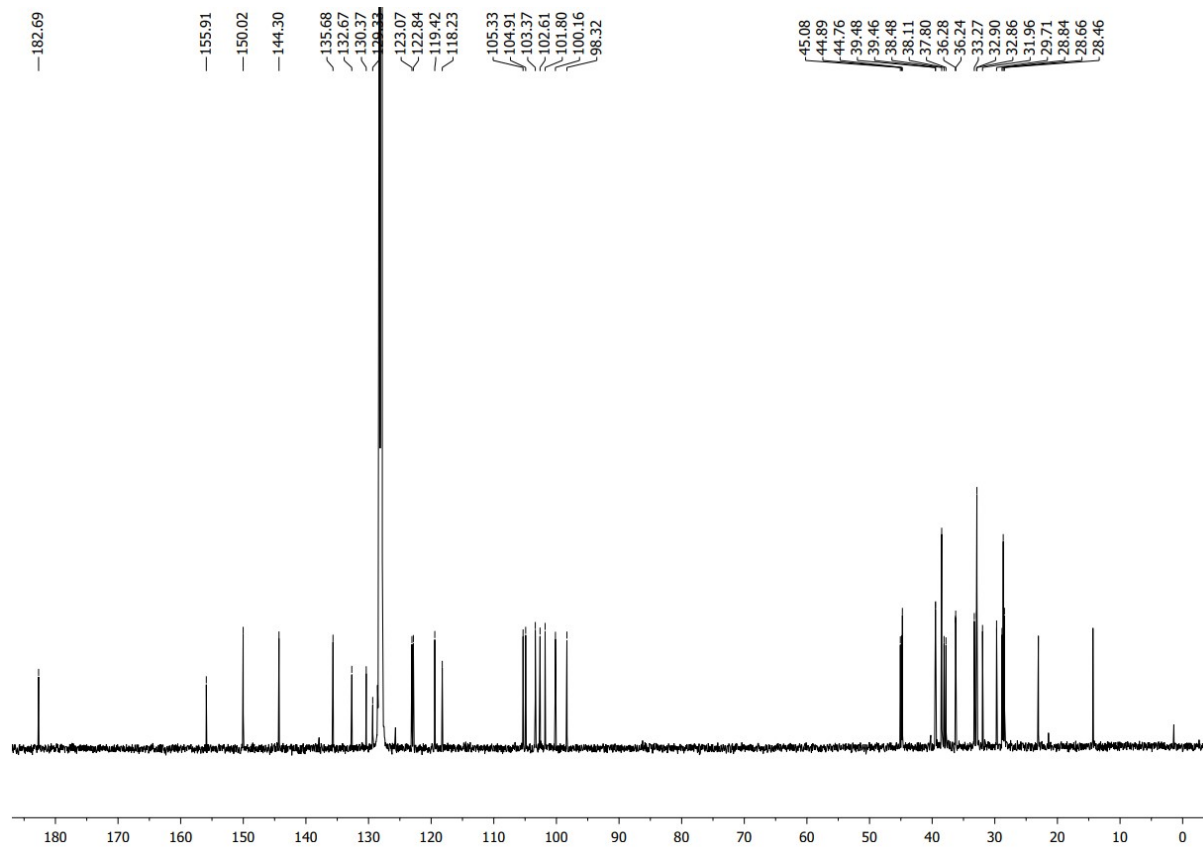


Figure S8: ^{13}C NMR spectrum (125 MHz, C_6D_6 , 305 K) of **Ti1c**.

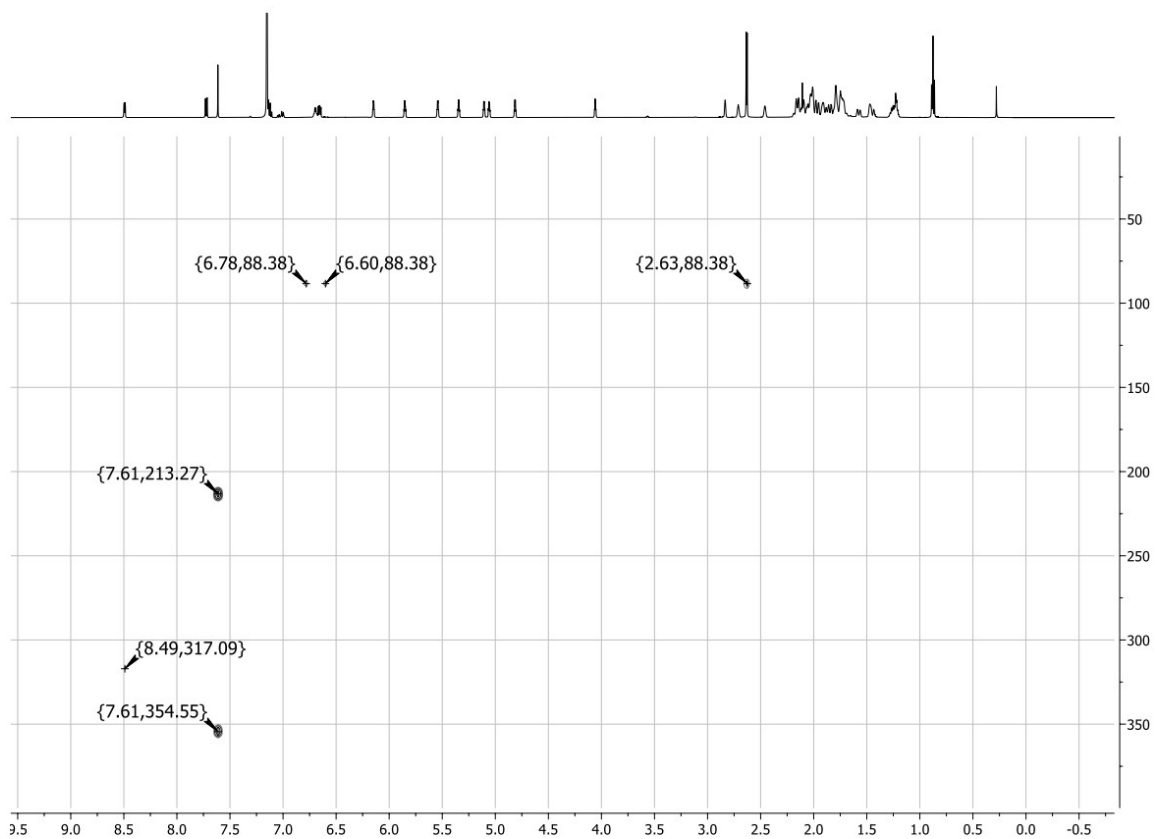


Figure S9: ^1H - ^{15}N -HMBC NMR spectrum (51 MHz, C_6D_6 , 305 K) of **Ti1c**.

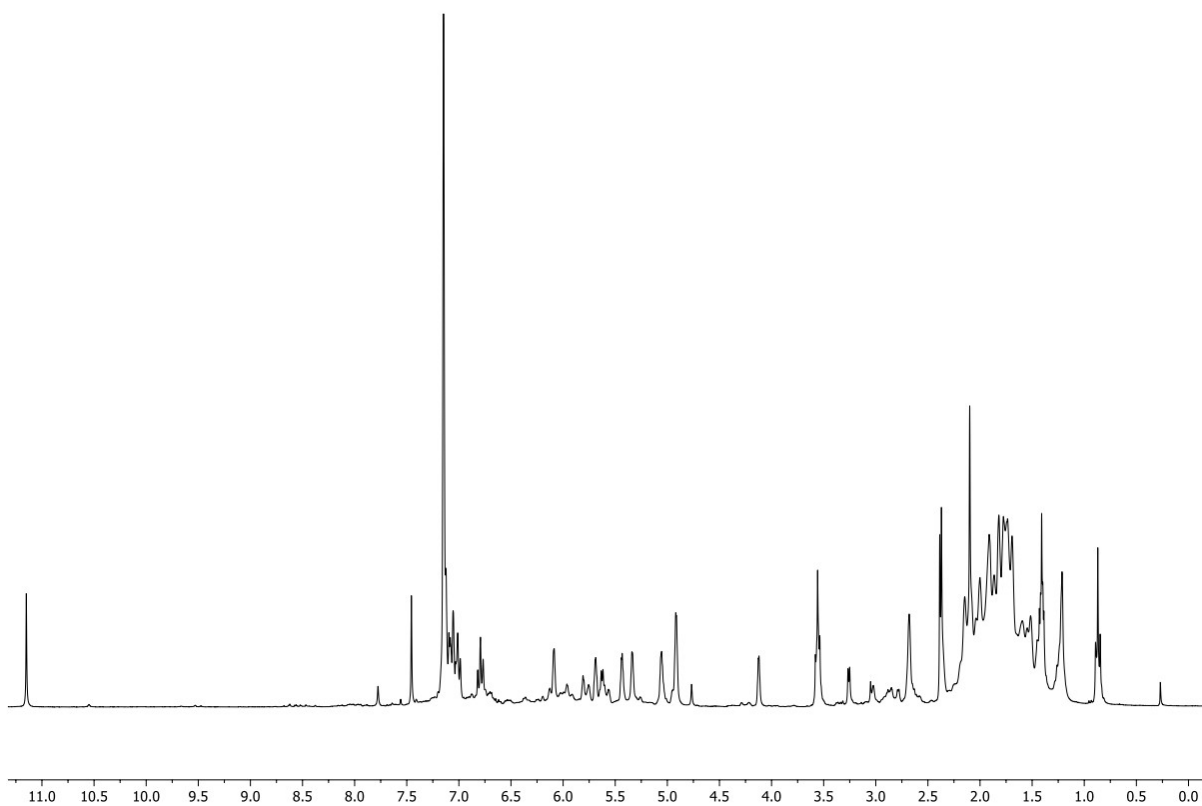


Figure S10: ^1H NMR spectrum (300 MHz, C_6D_6 , 305 K) of product mixture after the reaction of **Ti1** with TSCN **d**.

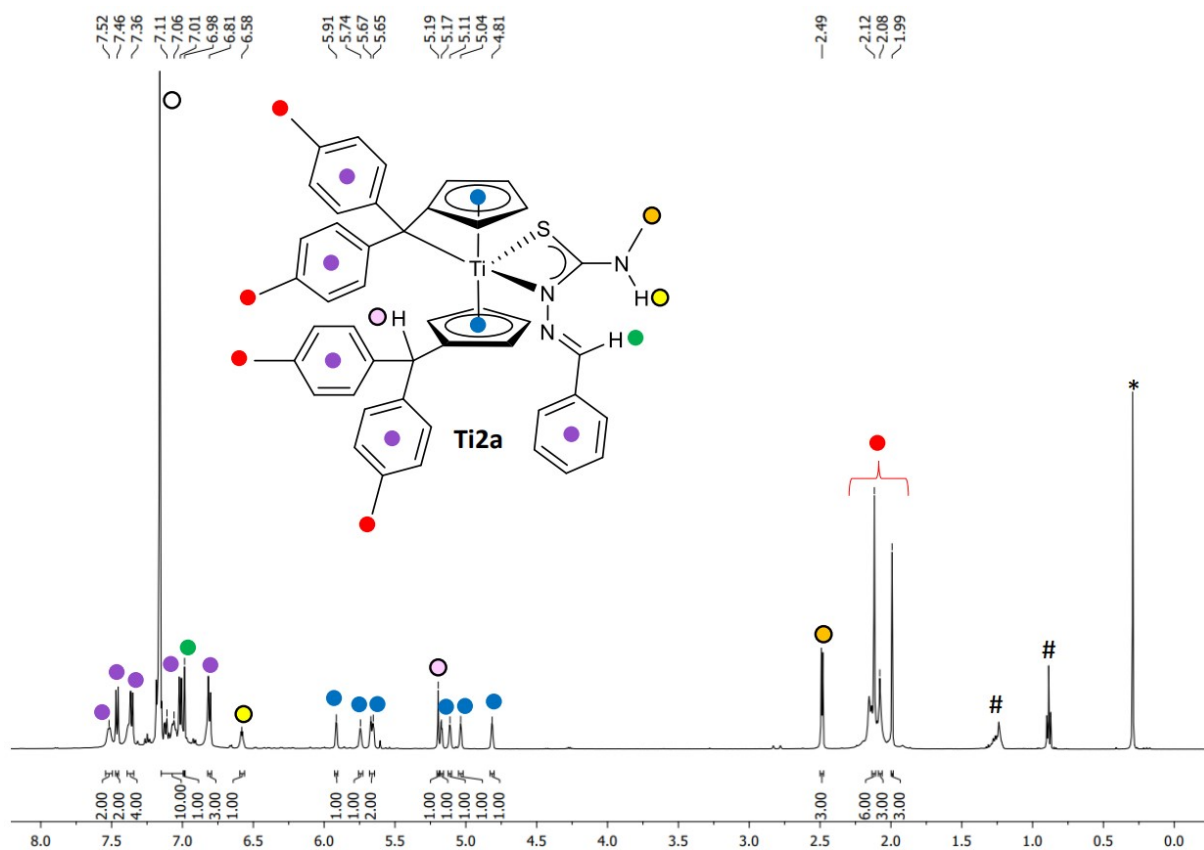


Figure S11: ^1H NMR spectrum (500 MHz, C_6D_6 , 305 K) of **Ti2a**. Product signals given in colours ($^{\circ}$ = $\text{C}_6\text{H}_5\text{D}$, # = n -hexane, * = grease).

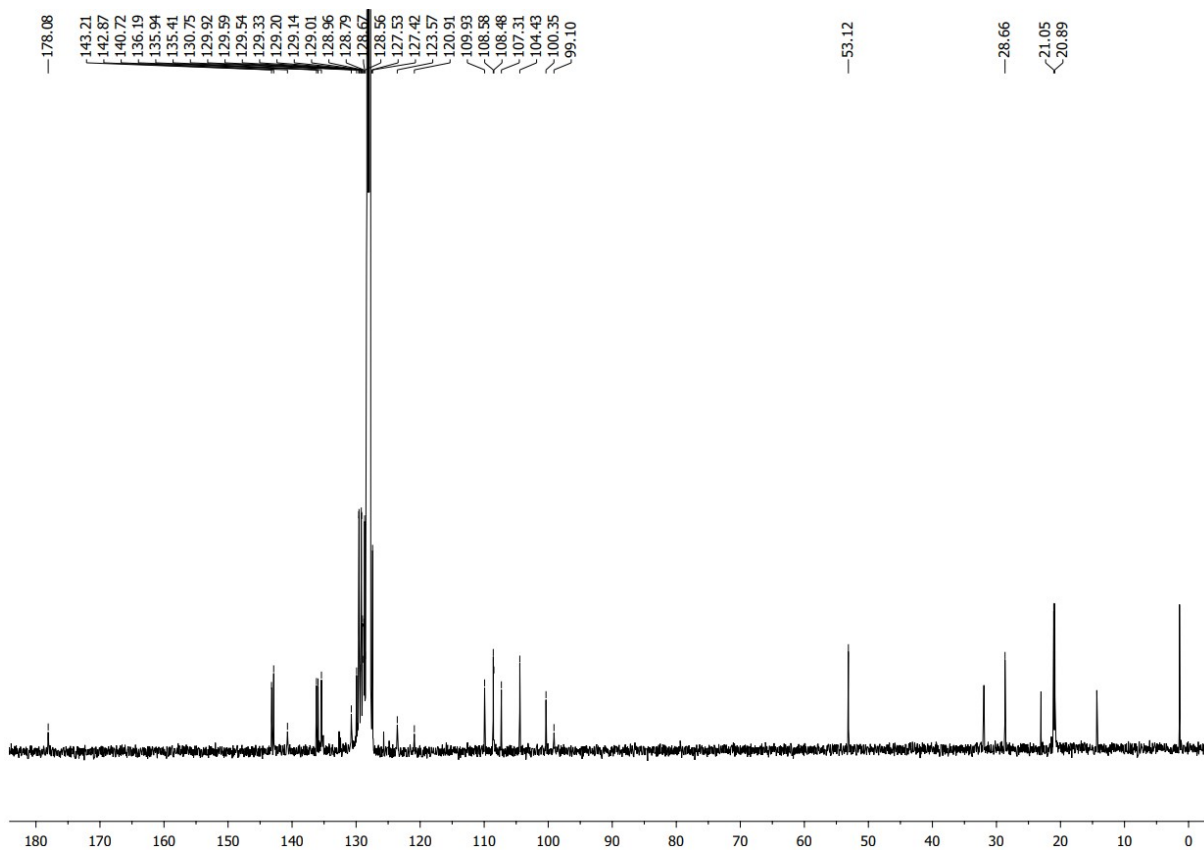


Figure S12: ^{13}C NMR spectrum (125 MHz, C_6D_6 , 305 K) of **Ti2a**.

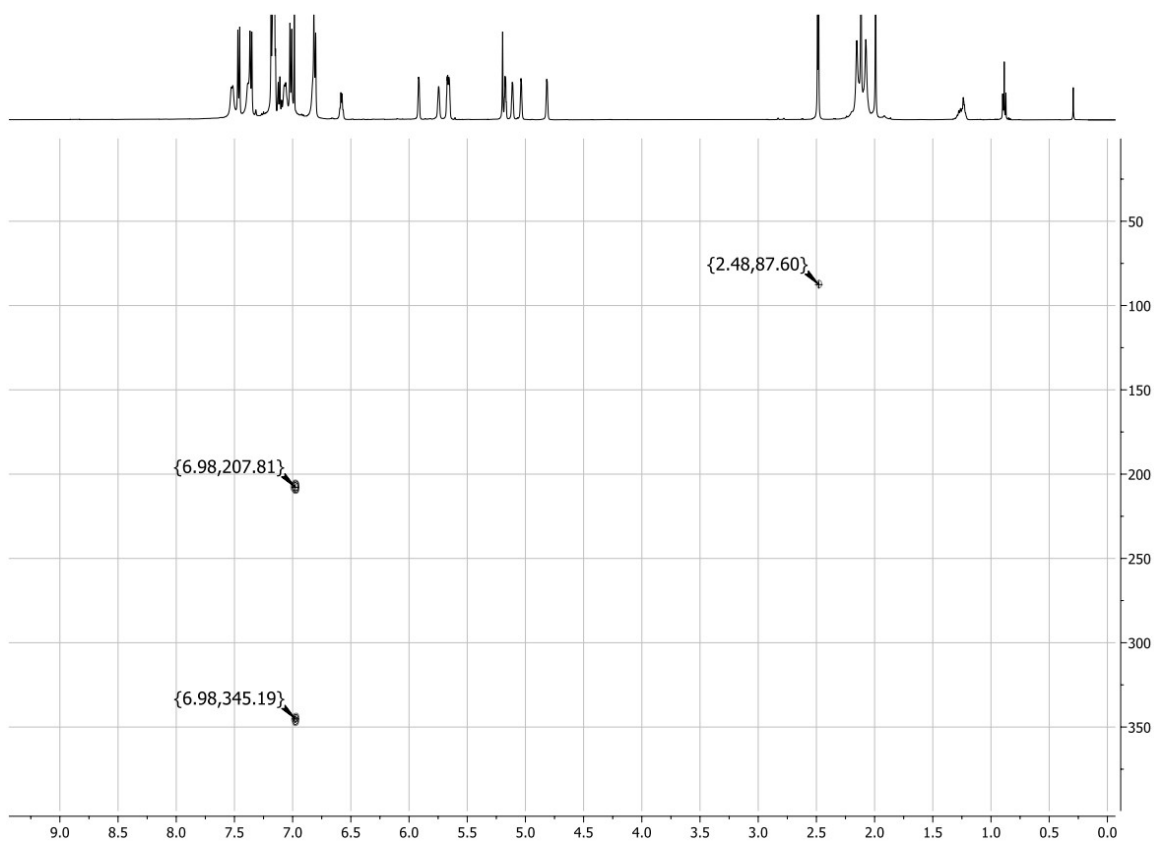


Figure S13: ^1H - ^{15}N -HMBC NMR spectrum (51 MHz, C_6D_6 , 305 K) of **Ti2a**.

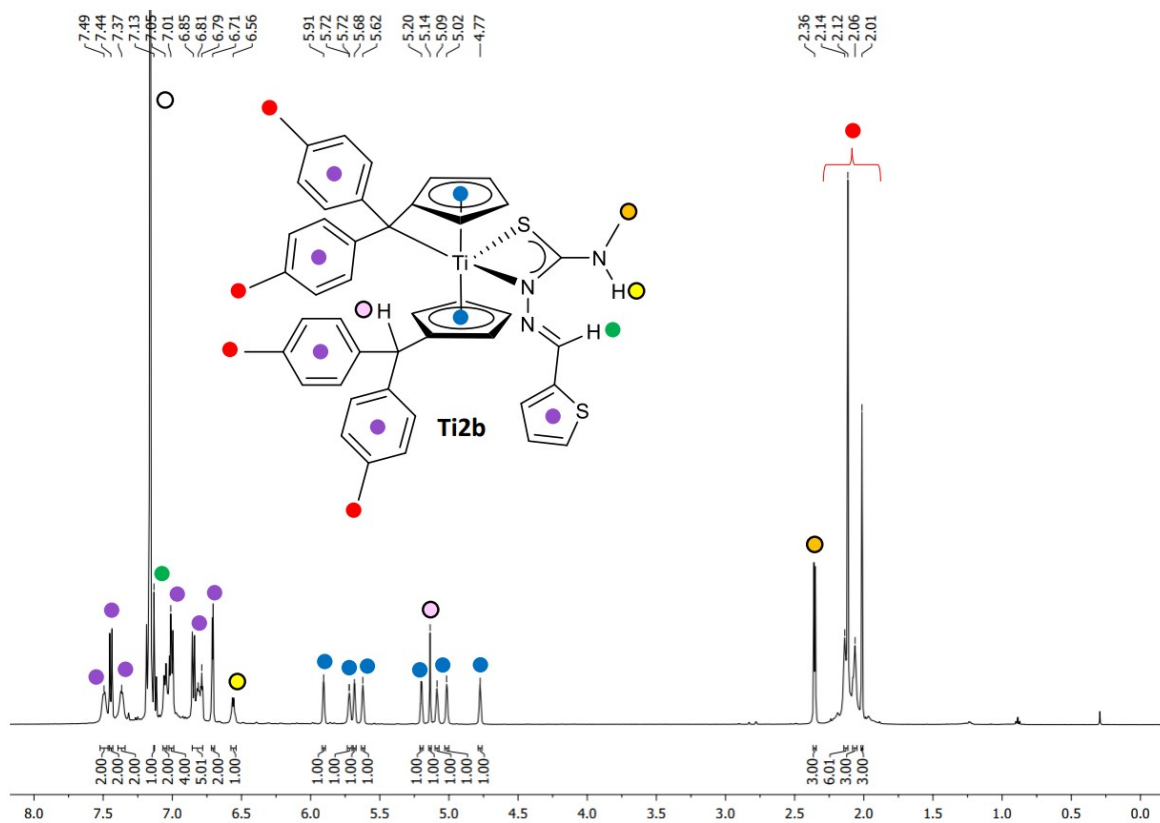


Figure S14: ^1H NMR spectrum (500 MHz, C_6D_6 , 305 K) of **Ti2b**. Product signals given in colours ($^\circ = \text{C}_6\text{H}_5\text{D}$).

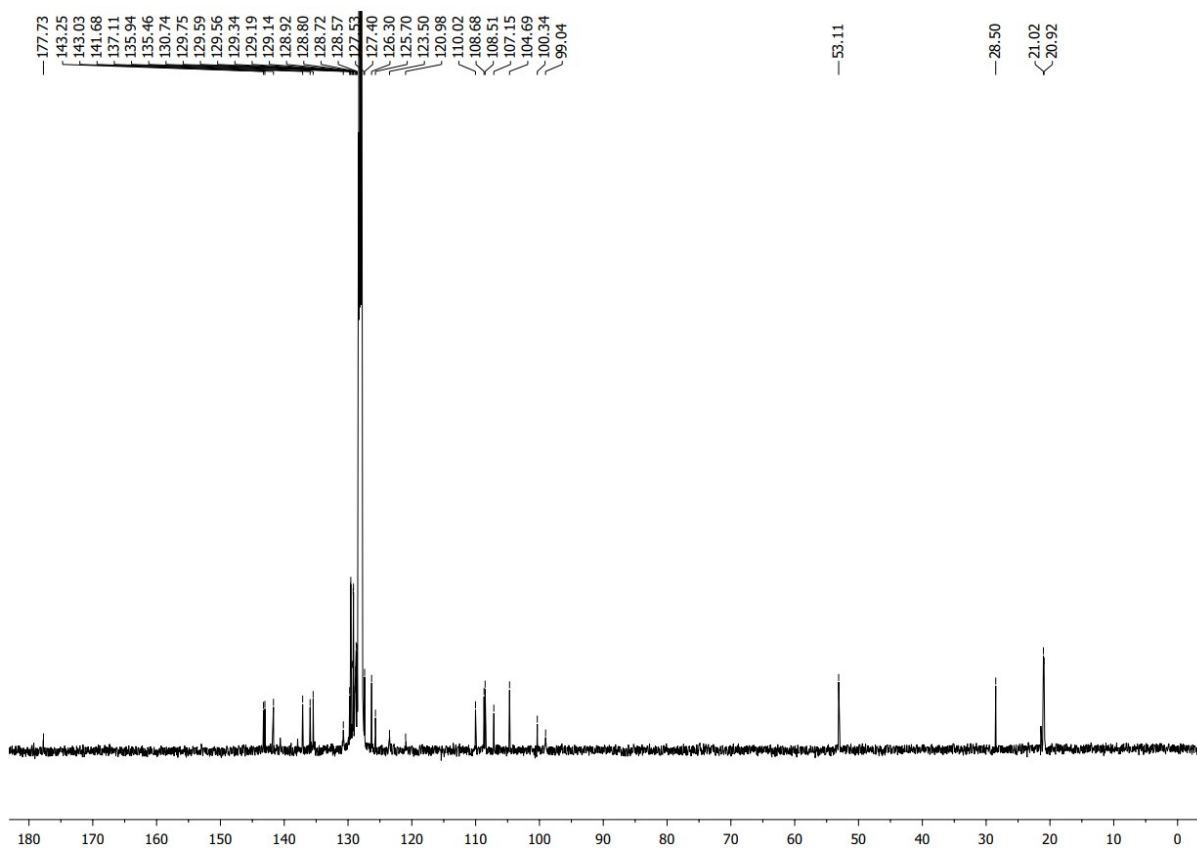


Figure S15: ^{13}C NMR spectrum (125 MHz, C_6D_6 , 305 K) of **Ti2b**.

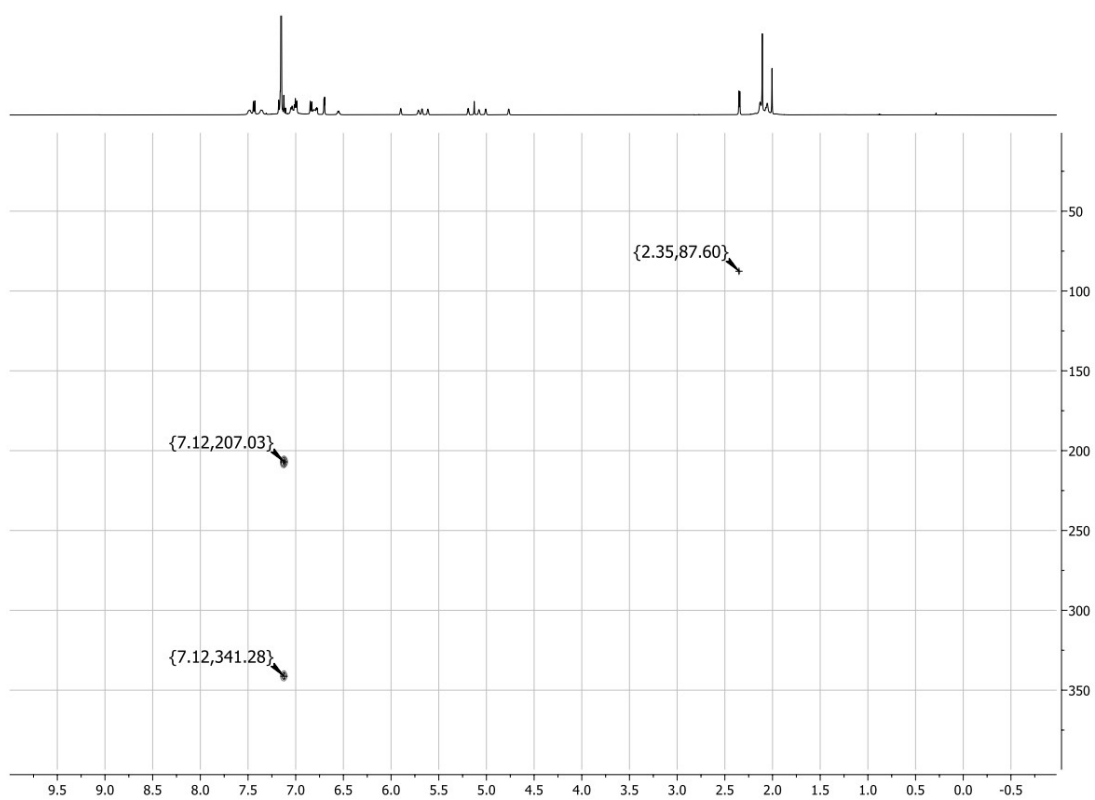


Figure S16: ^1H - ^{15}N -HMBC NMR spectrum (51 MHz, C_6D_6 , 305 K) of **Ti2b**.

Computational methods

The DFT (density functional theory) calculations were performed with the B3LYP/Def2-TZVP level of theory.^[1] The optimized ground state geometry of **Ti3c** was calculated in gas phase.

Cartesian coordinates (Å) of **Ti3c**:

Ti	1.824692	3.439617	1.086387
N	3.276898	4.189097	2.645833
N	0.528687	4.185418	2.948117
C	0.828001	5.392527	0.034905
C	2.236556	1.422539	2.328711
C	3.102956	1.412646	1.206314
C	2.152658	5.722689	0.397554
C	0.880758	4.383560	-0.943802
C	2.302358	1.309022	0.049925
C	2.243807	4.102327	-1.207180
C	0.944483	1.262484	0.452291
C	0.908459	1.318102	1.856826
C	3.032721	4.922102	-0.375287
N	-0.780398	4.185759	3.281096
C	1.285936	4.641002	3.898334
C	4.609209	4.197199	2.541084
C	2.720864	4.661120	3.780724
H	2.534921	1.480529	3.363219
H	4.180623	1.446813	1.231375
H	2.663001	1.252476	-0.963471
H	0.085824	1.204432	-0.195431
H	0.017430	1.311512	2.462108
H	2.442731	6.466566	1.122122
H	4.110396	4.956304	-0.357022
H	2.614655	3.396204	-1.931217
H	0.030114	3.905763	-1.399423
H	-0.073139	5.804868	0.456773
H	0.867764	4.987645	4.841678
C	3.495625	5.144338	4.841312
C	4.873178	5.147344	4.718033
H	2.999201	5.492437	5.738053
C	5.443627	4.666019	3.543069
H	5.494753	5.514593	5.524313
H	6.515319	4.646641	3.401581
H	5.018987	3.810376	1.617712
S	-0.920136	4.581897	7.090213
O	0.405678	5.154871	6.911605
O	-1.709170	4.593893	5.840327
O	-1.650285	4.947888	8.270430
C	-0.567984	2.759470	7.282528
F	0.154770	2.505600	8.377476
F	0.134459	2.309398	6.213890

F	-1.698616	2.044718	7.348062
H	-0.984502	4.435560	4.265324
C	-1.872947	3.774539	2.541484
S	-1.879403	3.366804	0.924999
N	-2.978902	3.766484	3.308069
H	-2.884838	3.989886	4.294172
C	-4.301127	3.444212	2.810480
H	-5.002763	3.555721	3.635085
H	-4.586063	4.113399	1.996917
H	-4.342927	2.420606	2.433808

Crystallographic data

Single crystal X-ray data for **Ti1a** were measured on a Bruker AXS Apex II diffractometer (graphite monochromator, Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$, Kappa 4-circle goniometer, Apex II CCD detector). Single crystal data for **Ti1c**, **Ti1d**, **Ti2b** and **Ti3d** were measured on a Bruker AXS D8 Venture diffractometer (multilayer optics, Mo-K α and Cu-K α radiation with $\lambda = 0.71073 \text{ \AA}$ and 1.54178 \AA respectively, Kappa 4-circle goniometer, Photon III C14 CPAD detector). All crystals were measured at a temperature of 100 K. Absorption corrections using equivalent reflections were performed with the program SADABS.^[2] For **Ti1a** a numerical absorption correction was performed using the same program. All structures were solved with the program SHELXS^[3] and refined with SHELXL^[4] using the OLEX2^[5] GUI.

All non H atoms were refined using anisotropic atomic displacement parameters (ADPs). H atoms bonded to C were located in the difference Fourier maps and placed on idealized geometric positions with idealized atomic displacement parameters using the riding model. H atoms bonded to N were refined freely. The geometry of the disordered solvent tetrahydrofuran in **Ti3d** was restrained to be the same (SAME instruction in SHELXL), and the isotropic ADPs were constrained to be the equal (EADP).

The crystallographic data can be obtained free of charge from <https://www.ccdc.cam.ac.uk/structures/> quoting the CCDC numbers 2377764-2377768.

	Ti1a	Ti1c	Ti1d	Ti2b	Ti3d
CCDC	2377765	2377767	2377764	2377768	2377766
Lab-ID	KESC146	MACL22	MACL25	MACL28	KESC269
empirical formula	C ₃₉ H ₄₇ N ₃ STi	C ₄₄ H ₅₂ N ₄ STi	C ₃₉ H ₄₇ N ₃ OSTi	C ₄₇ H ₄₅ N ₃ S ₂ Ti	C ₄₂ H ₅₄ F ₆ N ₆ O ₁₁ S ₄ Ti ₂
Fw	637.75	716.85	653.75	763.88	1156.95
Colour	red	orange	orange	red	yellow green orange
Habit	block	rod	block	block	block
cryst. dimens. mm	0.40 x 0.35 x 0.25	0.25 x 0.07 x 0.02	0.06 x 0.06 x 0.03	0.12 x 0.09 x 0.05	0.12 x 0.10 x 0.04
cryst. system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	P-1	Pbca	P2 _{1/n}	P2 _{1/n}	C2/c
a, Å	11.6805(6)	23.3583(14)	12.0547(3)	14.4377(5)	13.7863(7)
b, Å	12.0032(6)	10.5011(5)	11.8933(3)	12.5870(5)	22.5048(13)
c, Å	12.9169(7)	30.2781(18)	22.4765(5)	21.9625(8)	17.5439(10)
α, deg	92.218(3)	90	90	90	90
β, deg	107.971(3)	90	101.8642(12)	97.4150(15)	105.069(2)
γ, deg	109.627(2)	90	90	90	90
V, Å ³	1601.95(15)	7426.8(7)	3153.62(13)	3957.8(3)	5256.0(5)
Z	2	8	4	4	4
D _{calc.} g cm ⁻³	1.322	1.282	1.377	1.282	1.462
μ, mm ⁻¹	0.366	0.324	3.200	0.359	0.544
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	1.54178	0.71073	0.71073
θ range, deg	1.679 – 40.248	1.345 – 27.103	3.871 – 74.469	1.598 – 30.033	1.777 – 30.033
reflections collected	100842	134443	54536	235418	95632
Indep. Reflecons R(int)	20177 0.0243	8197 0.0786	6406 0.0440	11566 0.0418	7702 0.0504
Observed reflections (I > 2(I))	17407	7084	5846	10485	6819
Absorption correction	numerical	semi-empirical	semi-empirical	semi-empirical	semi-empirical
max, min transm.	0.9319, 0.8918	1.0000, 0.9099	1.0000, 0.9074	1.0000, 0.9392	1.0000, 0.9135
final R indices [I > 2σ(I)]	R1 = 0.0283, wR2 = 0.0773	R1 = 0.0449, wR2 = 0.0904	R1 = 0.0315, wR2 = 0.0818	R1 = 0.0350, wR2 = 0.0909	R1 = 0.0556, wR2 = 0.1387
R indices (all data)	R1 = 0.0357, wR2 = 0.0812	R1 = 0.0553, wR2 = 0.0954	R1 = 0.0355, wR2 = 0.0847	R1 = 0.0394, wR2 = 0.0939	R1 = 0.0634, wR2 = 0.1434
GOF on F ²	1.045	1.085	1.037	1.068	1.113
largest diff peak / hole (e.Å ⁻³)	0.604 / -0.352	0.331 / -0.407	0.515 / -0.260	0.435 / -0.317	1.629 / -0.638

IR spectra

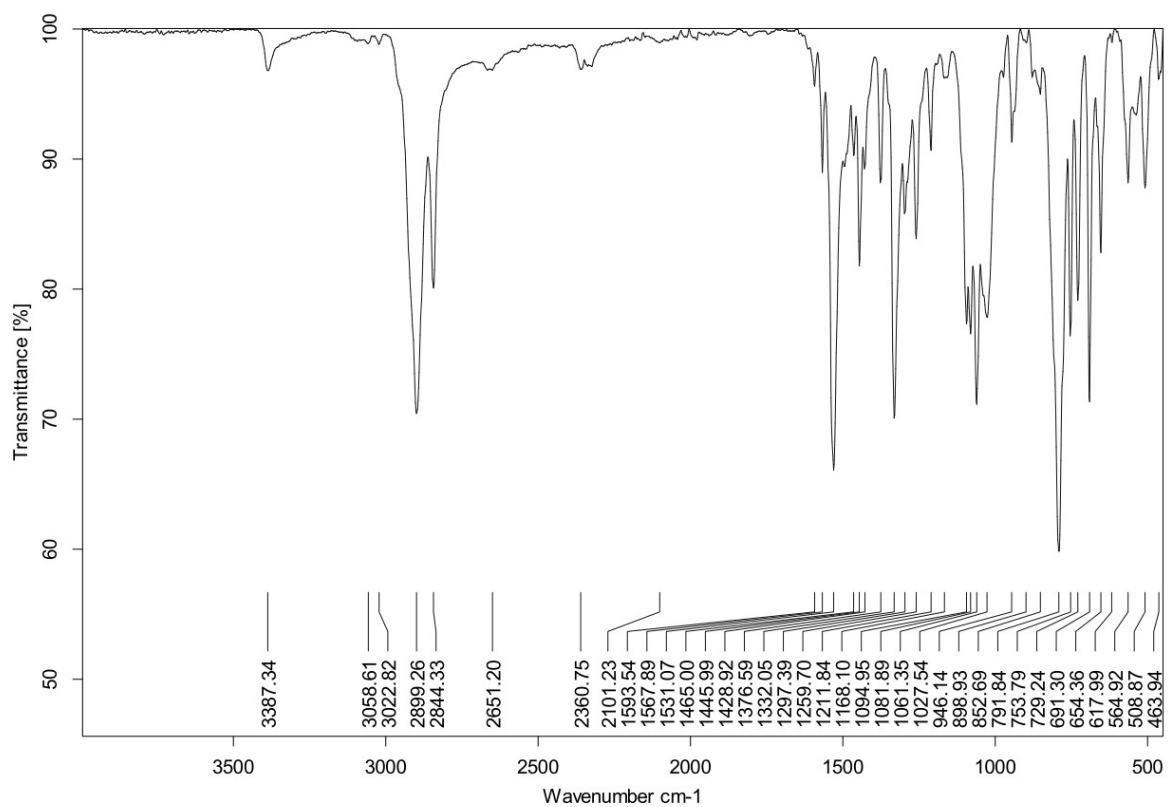


Figure S17: IR Spectrum of Ti1a.

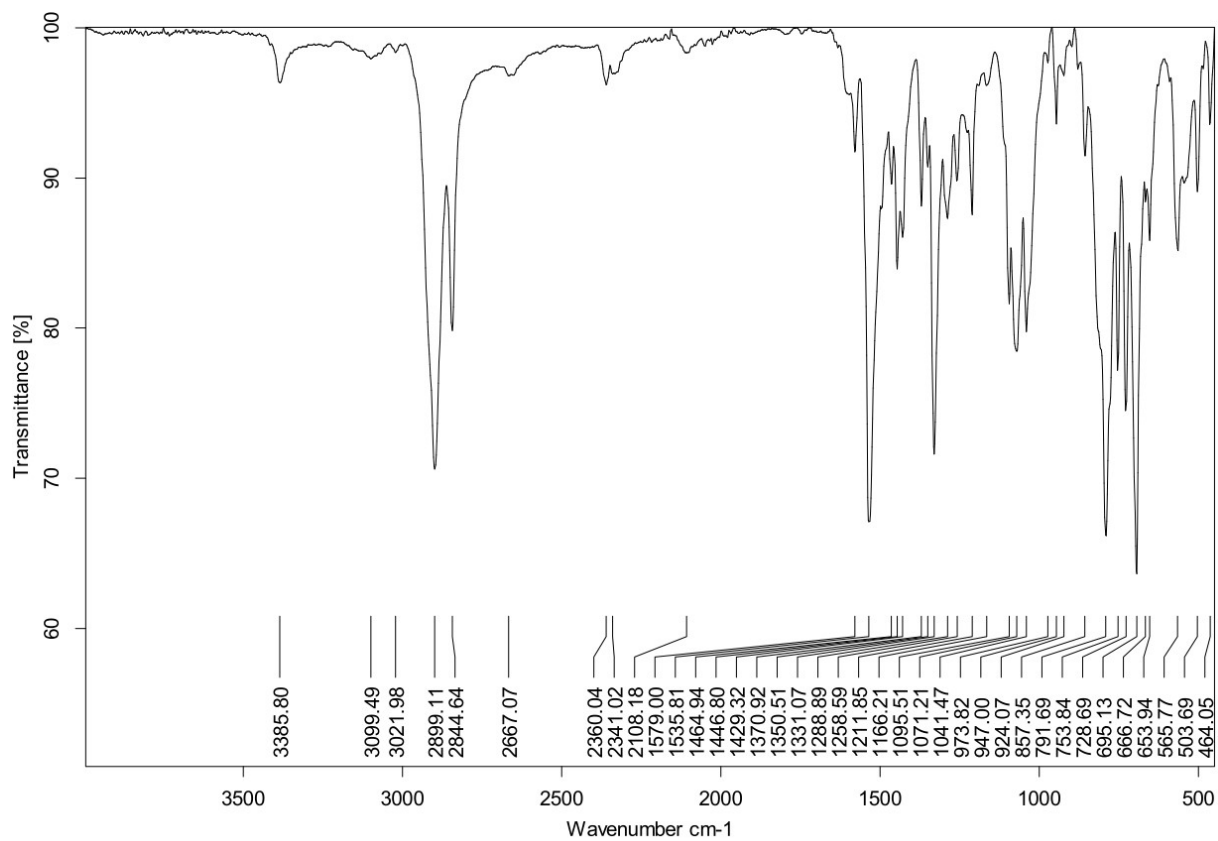


Figure S18: IR Spectrum of Ti1b.

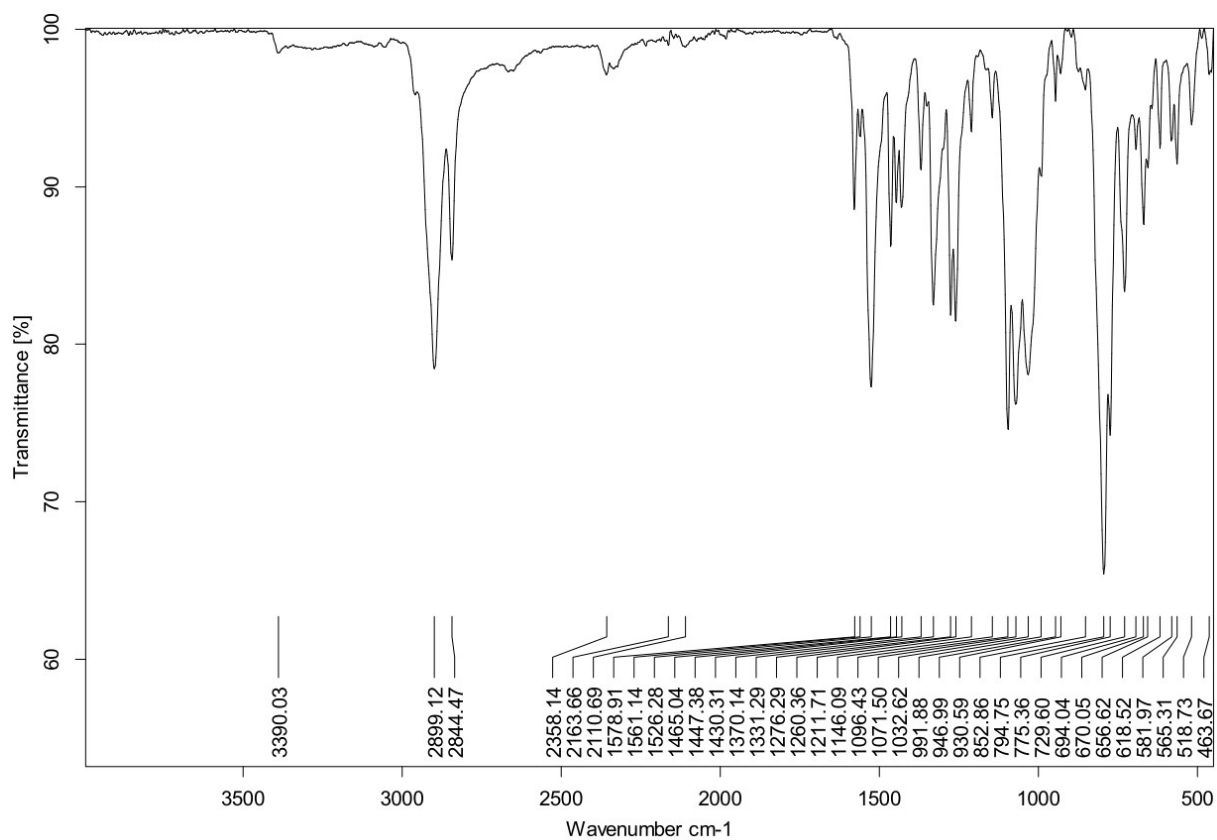


Figure S19: IR Spectrum of Ti1c.

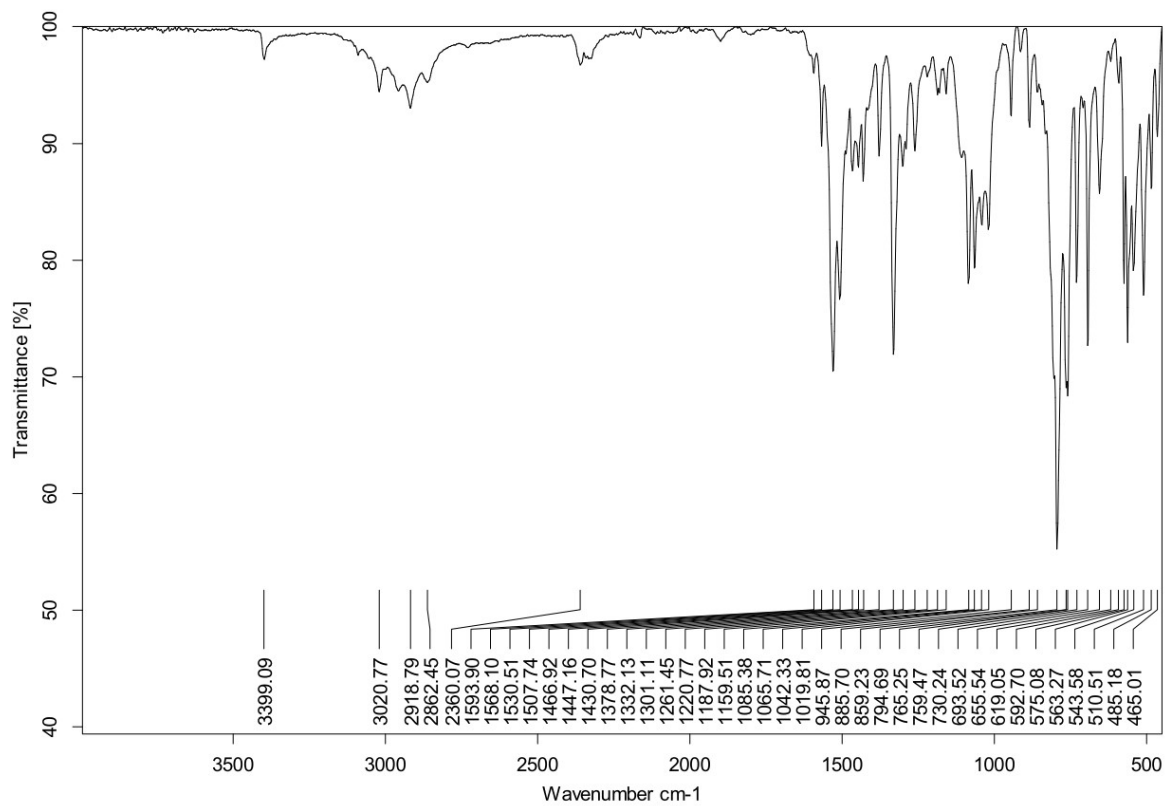


Figure S20: IR Spectrum of Ti2a.

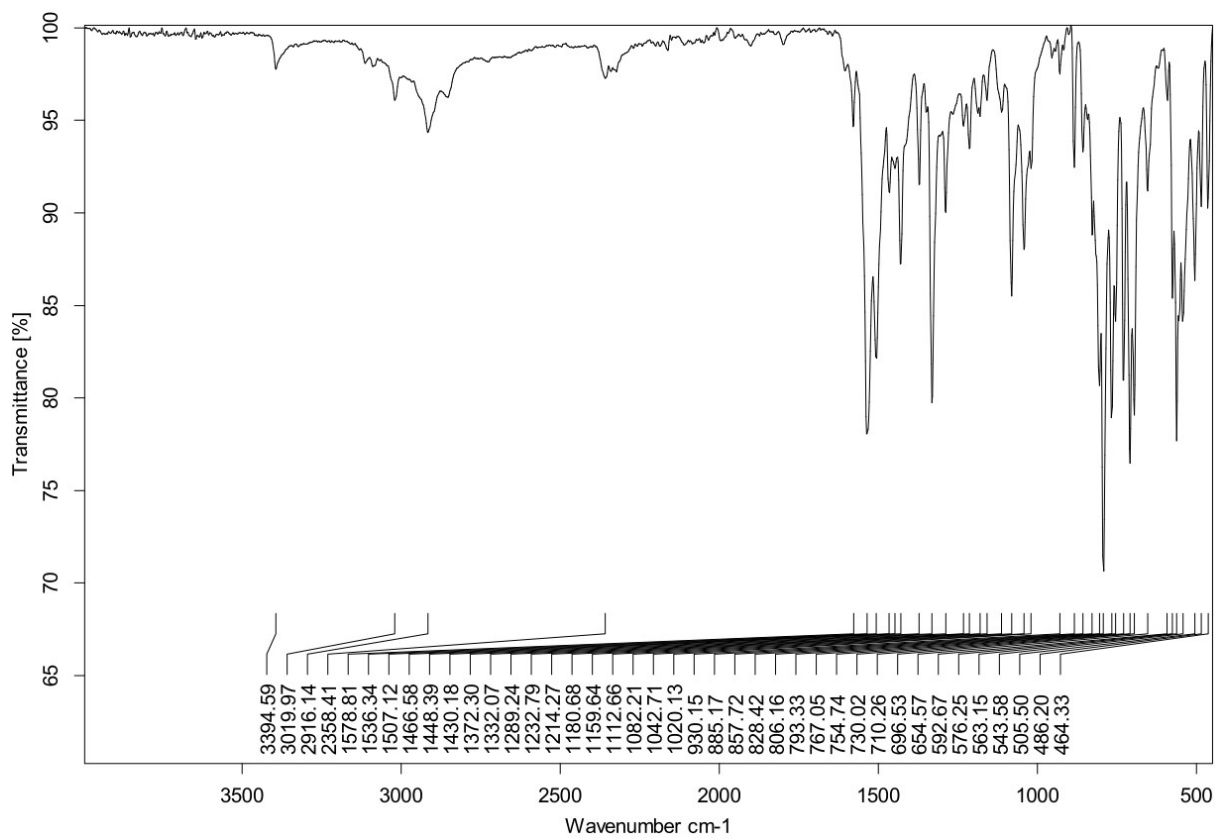


Figure S21: IR Spectrum of Ti2b.

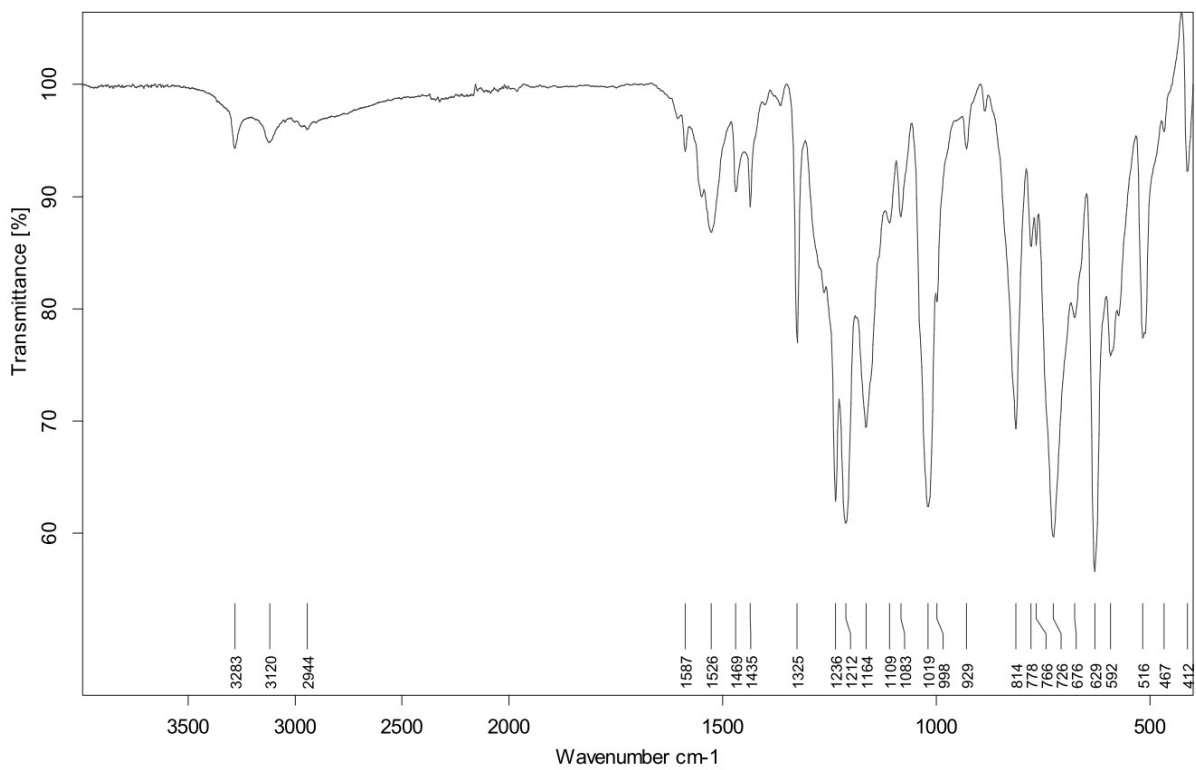


Figure S22: IR Spectrum of Ti3c.

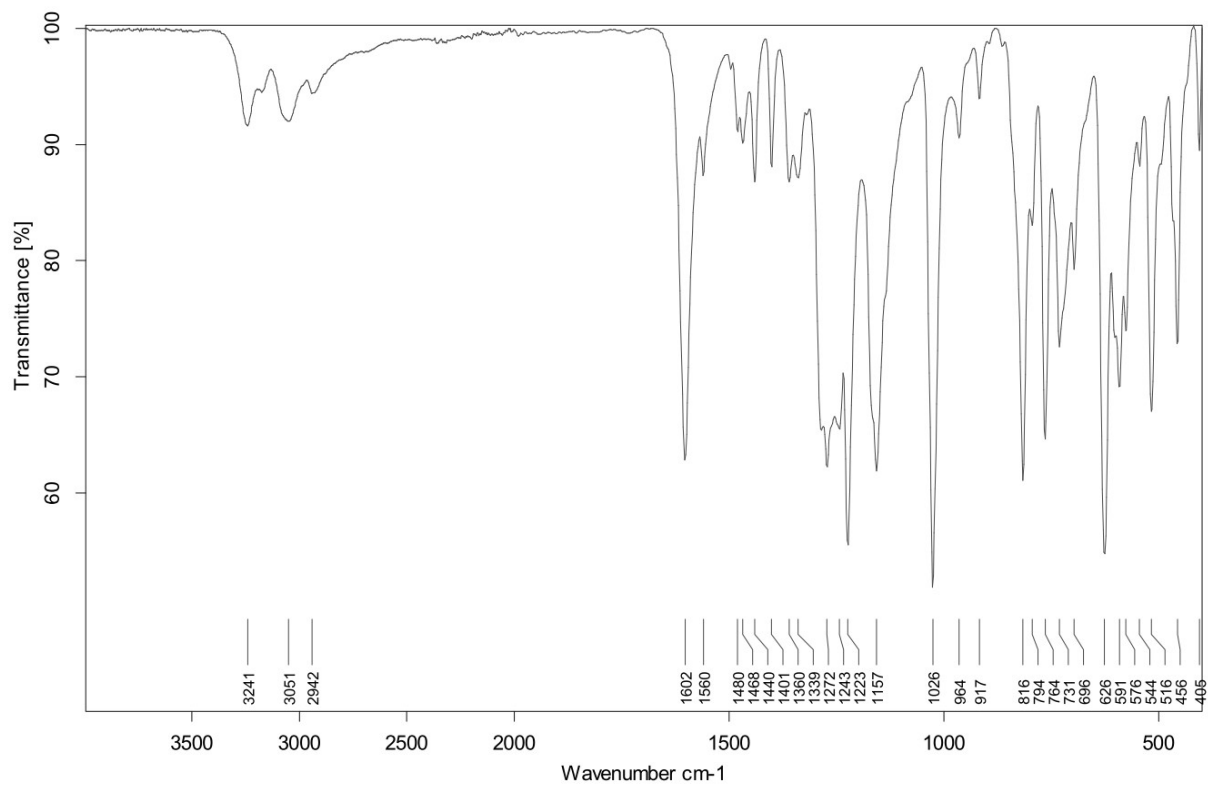


Figure S23: IR Spectrum of **Ti3d**.

EPR Spectra

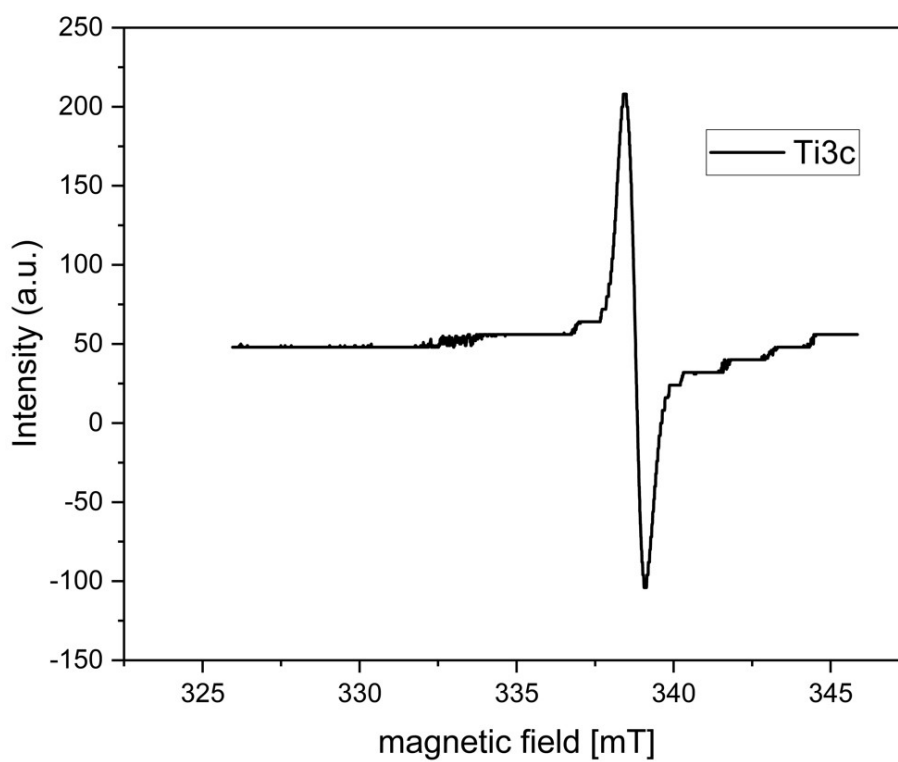


Figure S24: EPR spectrum of complex **Ti3c** in toluene at room temperature ($g = 1.980$).

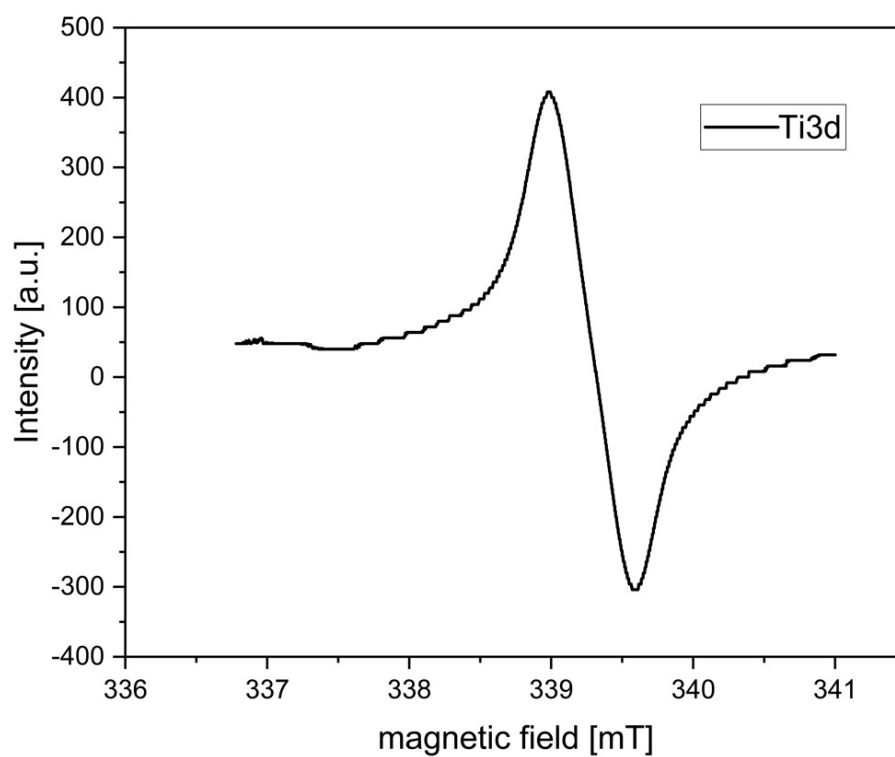


Figure S25: EPR spectrum of complex **Ti3d** in THF at room temperature ($g = 1.977$).

References

- [1] Weigend, F.; Ahlrichs, R., *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
- [2] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2015**, *48*, 3-10.
- [3] G. M. Sheldrick, *Acta Crystallogr. Sec. A* **2008**, *64*, 112-122.
- [4] G. M. Sheldrick, *Acta Crystallogr. Sec. C* **2015**, *71*, 3-8.
- [5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.