

Electronic Supplementary Information for Dalton Transactions
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The reaction of TiF_4 with $\text{Li}(\text{OC}(\text{CF}_3)_2\text{Ph})$ - direct synthetic route to the lithium - titanium heterometallic fluoride bridged complex $\{\text{Li}(\text{THF})_2\text{TiF}_3(\text{OC}(\text{CF}_3)_2\text{Ph})_2\}_2$ and $\text{Ti}(\text{OC}(\text{CF}_3)_2\text{Ph})_4$ alkoxide.

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1. IR 4000-350 cm^{-1} and Raman 4000-120 cm^{-1} spectra of complexes 1 and 2

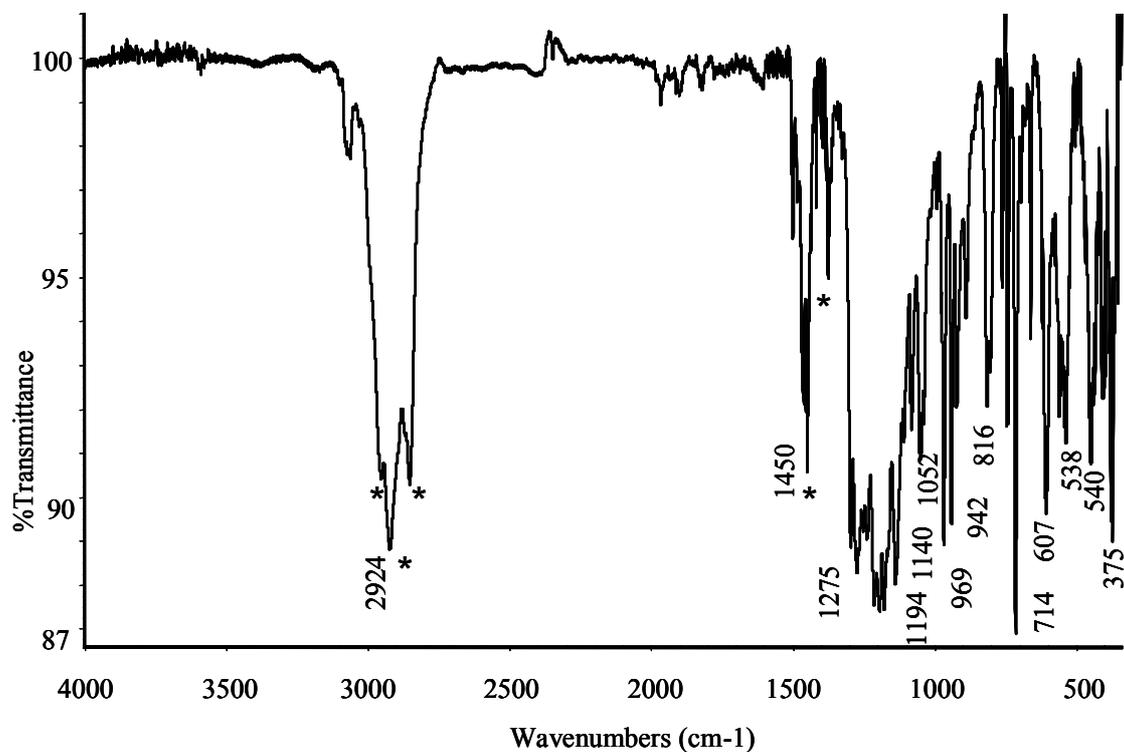


Figure 1

IR spectrum of **1** (4000-350 cm^{-1}), KBr, * Nujol.

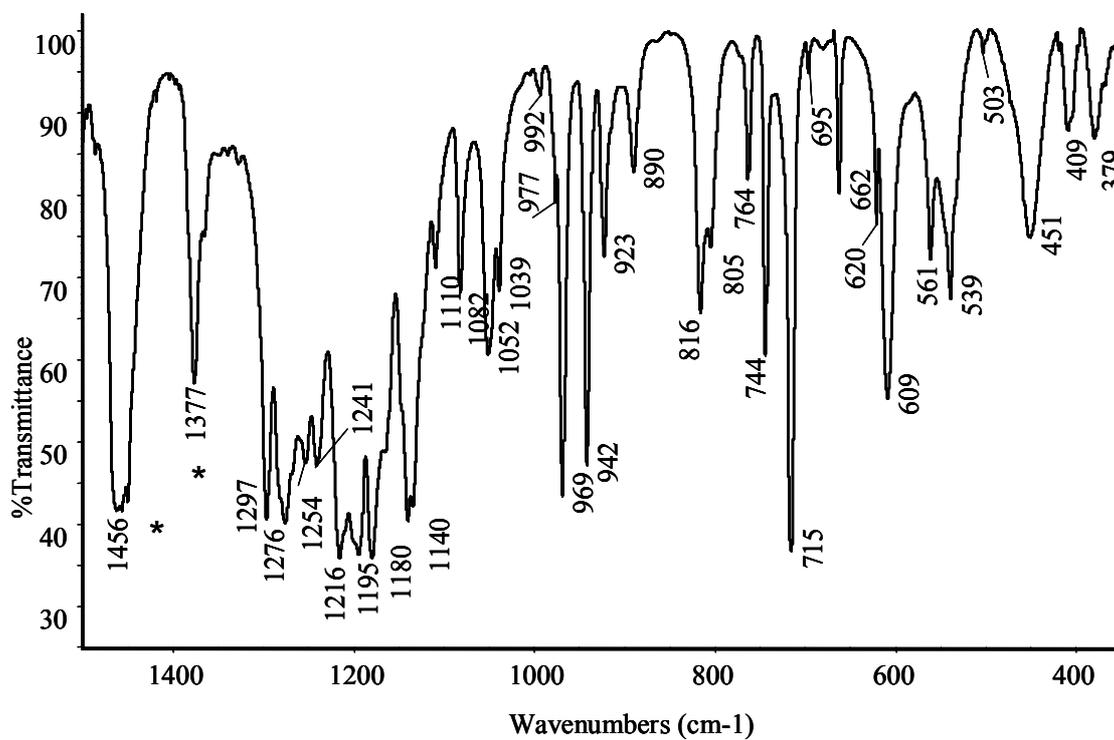


Figure 2

IR spectrum of **1** ($1500\text{-}350\text{cm}^{-1}$), Nujol *, KBr.

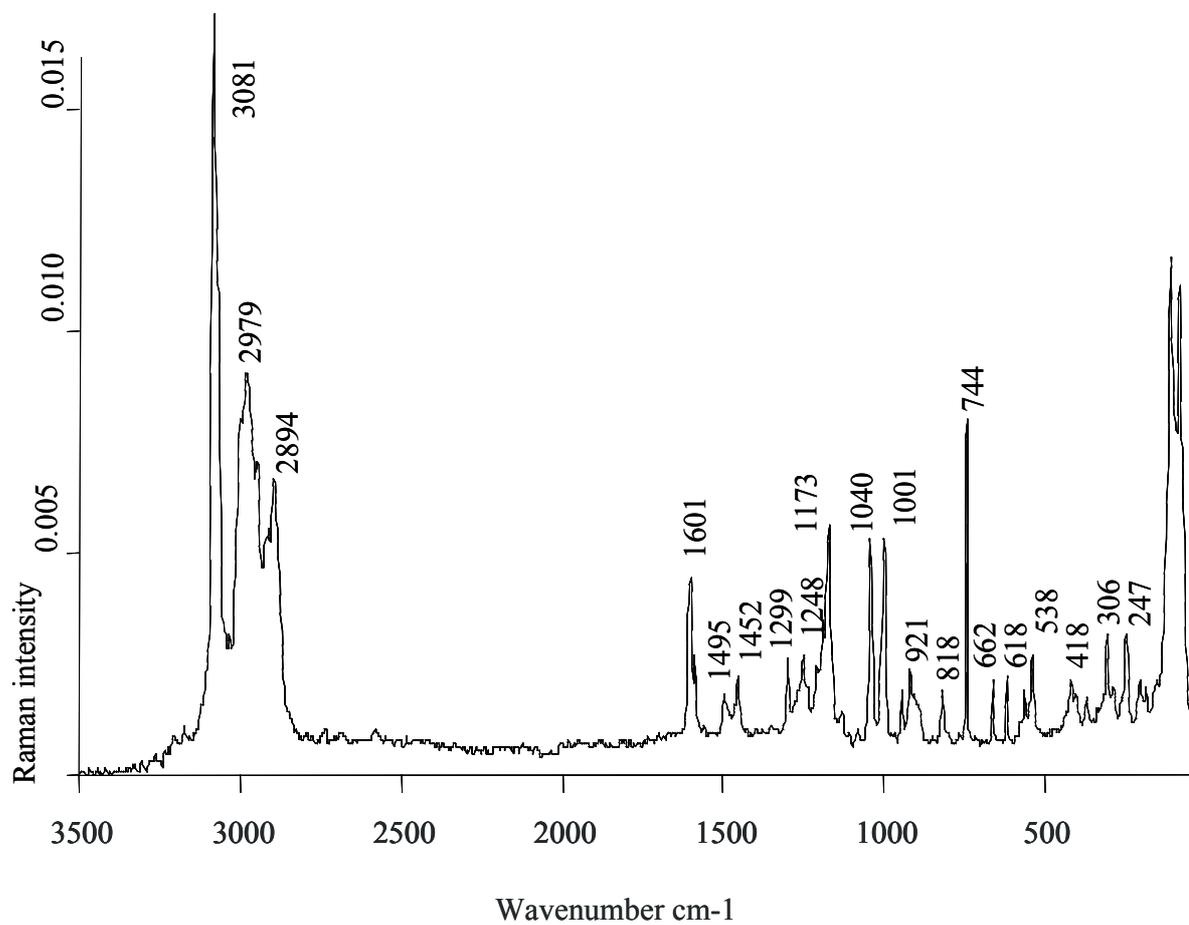


Figure 3

Raman spectrum of **1**, resolution 4, 1000 scans

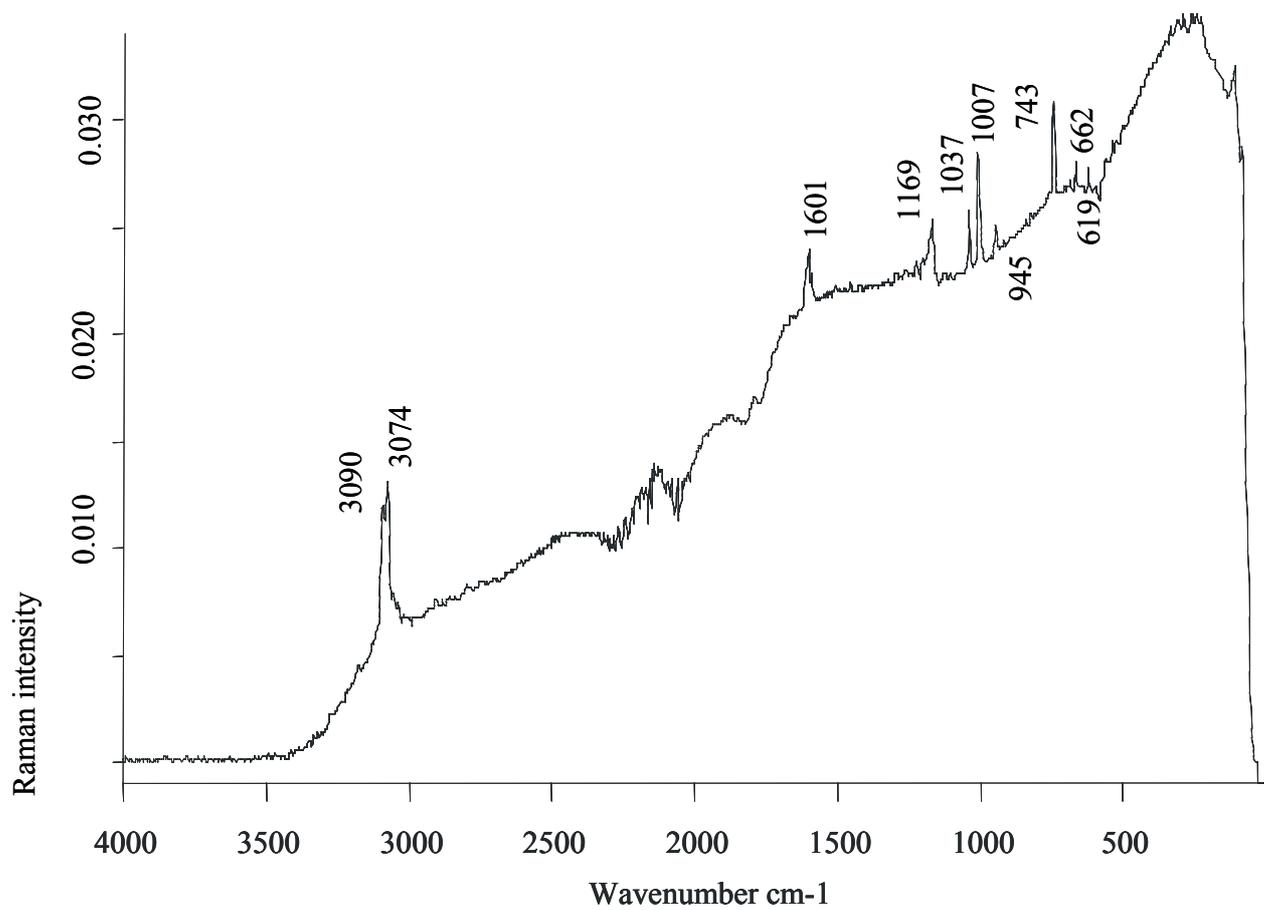


Figure 4

Raman spectrum of **2**, resolution 4, 1000 scans

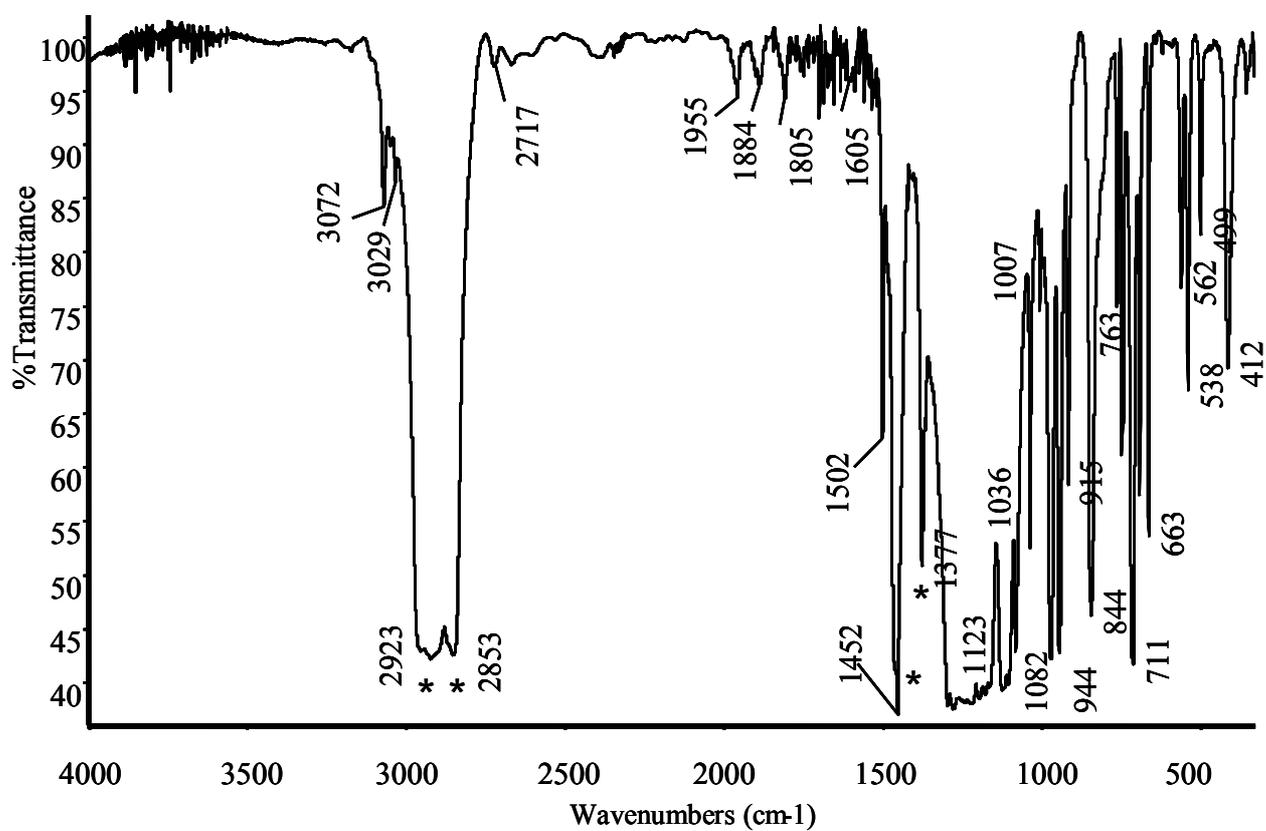


Figure 5

IR spectrum of **2** ($4000\text{-}350\text{cm}^{-1}$), Nujol *, KBr.

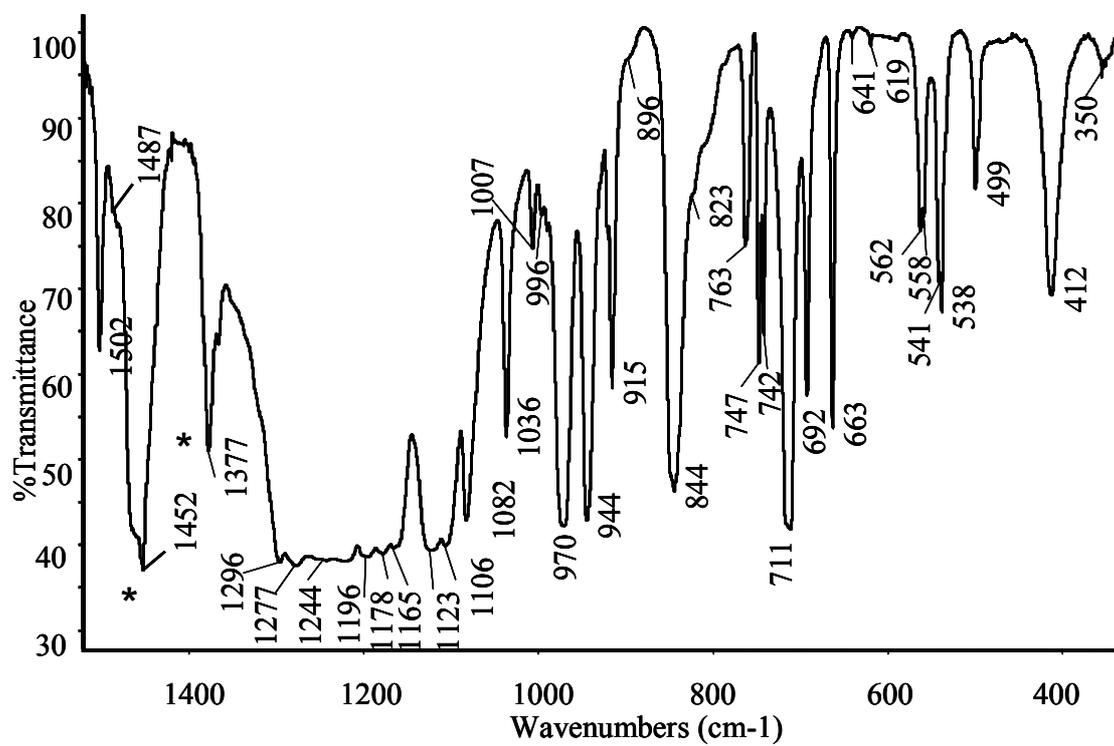


Figure 6

IR spectrum of **2** (1500-350 cm^{-1}), Nujol *, KBr.

2. NMR spectra of 1 and 2

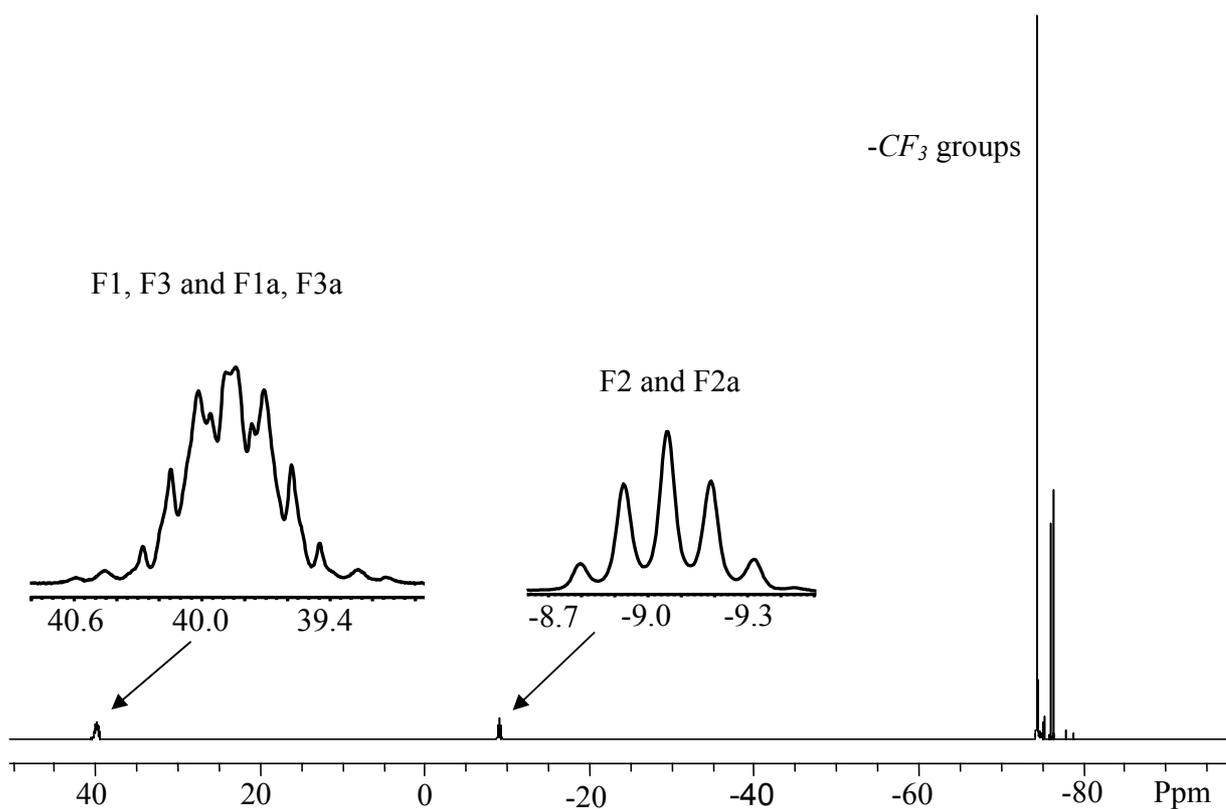
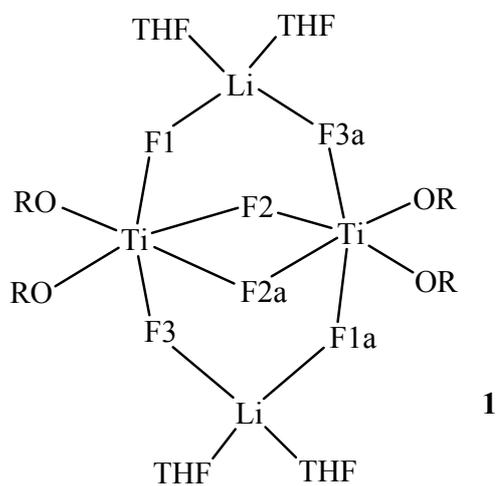


Figure 7.

^{19}F NMR spectrum of **1** in THF showing resonances of F1, F3, F1a, F3a and F2, F2a with the fine structure, as well as resonances of $-\text{CF}_3$ groups.

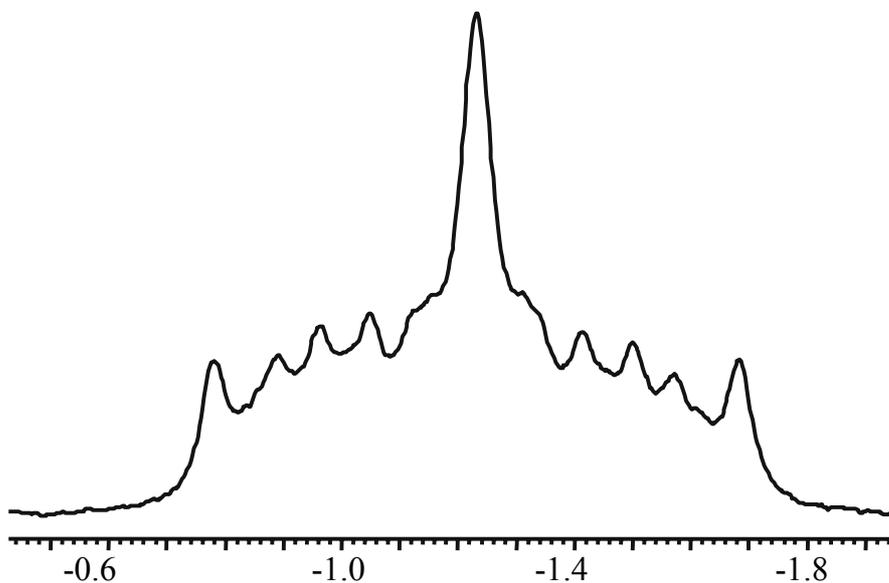


Figure 8

Fine structure of the ^7Li NMR resonance of **1** in THF.

Table 1
 The NMR data for compounds **1** and **2** in THF at r.t.

Compound 1		
Atoms	δ , ppm	multiplicity, J , Hz
F1, F1a, F3, F3a	39.8*	m, J were not assigned
F2, F2a	-9.1*	quintet, 51
F of $-\text{CF}_3$	-74.4	singlet
Li	-1.23**	m, J were not assigned
C of $\text{C}(\text{CF}_3)_2\text{Ph}$	87.6 [†]	br.
C of $-\text{CF}_3$	121.9 [†]	quartet, 290
Compound 2		
F of $-\text{CF}_3$	-75.3*	singlet
C of $\text{C}(\text{CF}_3)_2\text{Ph}$	90.0 [†]	m, 31
C of $-\text{CF}_3$	121.1 [†]	quartet, 288

* relative to CFCl_3 , ** relative to LiClO_4 , [†] relative to SiMe_4 .

The ^{19}F NMR spectrum of **1** consists from the multiplet at 39.8 ppm assigned to the F1, F1a, F3, F3a, quintet at -9.1 assigned to the F2, F2a and singlet at -74.4 assigned to the fluorine atoms of $-\text{CF}_3$ groups. Relative intensity of three resonances are 2 : 1 : 12, supporting assignment. The minor singlet at -75.1 was assigned to **2**, minor singlets at -76.0, -76.4, -77.8 ppm could belong to the titanium alkoxide complexes. Essentially complex **1** could exhibit ^{19}F NMR spectrum of the AA'A''A'''BB'XX' type, where A, B are ^{19}F and X lithium nuclei. The distances between the F2, F2a and F1, F1a, F3, F3a are in the range 2.622 - 2.651 Å, shorter than those between the F2, F2a and Li, Lia 3.196 and 3.201 Å, thus the fine structure of the quintet at -9.1 ppm (due to F2 and F2a, Figure 7.) assigned to the coupling of F2, F2a and F1, F1a, F3, F3a nuclei. This coupling constant is close to the literature data for the dimeric titanium complexes having two (μ -F) atoms between titanium centers $J(\text{F}_{\text{terminal}} - \mu\text{-F})$ 57 Hz in $\text{Ti}_2\text{F}_8(\text{MeCN})_2$ ^[1(c)], 50 Hz in $[\text{Ti}_2\text{F}_8(\text{SO}_3\text{F})]^{2-}$ ^[2], 44 ± 1 , 45 ± 1 Hz in $[\text{Ti}_2\text{F}_{10}]^{2-}$ ^[1(a)]. The multiplet at 39.8 ppm could resulted by coupling of F1, F1a, F3, F3a with the F2, F2a and ^6Li , ^7Li nuclei. However available data did not allow extracting exact coupling constants since exact simulation is unavailable. Available programs do not allow simulating coupling between nuclei of different types.

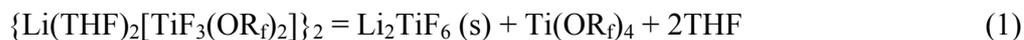
Nonetheless, the simulation of the 6-spin system ABB'X₃, consisting only the fluorine nuclei was attempted. The fine structure of the multiplet was never identical to the observed at 39.8 ppm. However, fine structure of the simulated multiplet resembled that observed at the constants 51 and 75 Hz and at the linewidth 25 Hz. We proposed that the fine structure of the multiplet might resulted the superposition of the multiplets given

on coupling of ^{19}F - ^7Li and ^{19}F - ^6Li precluding accurate estimation of the coupling constants.

The $-\text{CF}_3$ groups of the 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxide ligand of **1** and **2** in THF and toluene exhibited a singlet at r.t. and at lower temperatures in the ^{19}F NMR spectrum due to fast exchange processes much like in the $[\text{Al}(\text{OR}_f)_4]^-$ anions with the similar ligands [3].

The ^7Li NMR spectrum of **1** in THF contained one unresolved multiplet (Figure 8). The lithium nucleus could be coupled with protons of THF and F1, F1a, F3, F3a nuclei. Additionally relaxation time of lithium nucleus, which is unknown, affect on the shape of resonance as well as ^7Li NMR resonance is overlapped with the ^6Li NMR resonance complicating exact simulation.

The ^{19}F NMR spectrum of a toluene solution of **1** over the undissolved solid showed resonances of **1** at 37.6, -12.1, -74.0 ppm assigned to the F1, F1a, F3, F3a; F2, F2a; $-\text{CF}_3$ groups as well as a resonance at -76.1 ppm assigned to **2**, indicating that solid **1** afford complexes **1** and **2** in toluene solution (relative concentrations are 1 : 3) together with an undissolved solid. Transformation of **1** into **2** might be represented by model equation 1.



3. NMR reactions *in situ*

Interaction of TiF_4 and 1 equivalent of $(\text{CF}_3)_2(\text{Ph})\text{COLi}$ in THF

Solution of TiF_4 (0.37 g, 3.0 mmol) and 1 eqv. of $(\text{CF}_3)_2(\text{Ph})\text{COLi}$ (3 mmol) in THF, prepared as described in the main experimental section. Crystalline **1** (0.46 g, yield of **1** 60% eq.a, see page 13, 80% eq. b, see page 13), which formed was removed by filtration, then the remaining solution was evaporated to dryness. The resulting white solid residue given after removal of solvent was also soluble in THF forming a clear solution.

^{19}F NMR (376.3 MHz, THF, $-40\text{ }^\circ\text{C}$), δ_{F} (ppm) = 226.4 (2F *cis* - $\text{TiF}_4(\text{THF})_2$), 163.1 (2F *cis* - $\text{TiF}_4(\text{THF})_2$), 69.0 ($\Delta\omega_{1/2}$ 201 Hz)*, 47.8 ($\Delta\omega_{1/2}$ 121 Hz)*, 46.4 ($\Delta\omega_{1/2}$ 112 Hz)*, 45.3 ($\Delta\omega_{1/2}$ 169 Hz)*, 44.6 ($\Delta\omega_{1/2}$ 145 Hz)*, 42.2 ($\Delta\omega_{1/2}$ 200 Hz)*, 40.1 ($\Delta\omega_{1/2}$ 169 Hz)*, 38.8 (qt, 4F, $J(^{19}\text{F}-^{19}\text{F})$ 51 Hz, $J(^{19}\text{F}-^7\text{Li})$ 70 Hz, F1, F1a and F3, F3a of **1**), 37.5 ($\Delta\omega_{1/2}$ 210 Hz)*, 35.7 ($\Delta\omega_{1/2}$ 230 Hz)*, 12.2, 11.2, -11.3 (q, 2F, $J(^{19}\text{F}-^{19}\text{F})$ 51 Hz, F2, F2a of **1**)[†], -15.2 (m, 9 lines, $J(^{19}\text{F}-^{19}\text{F})$ 40 Hz)[†], (octet, $J(^{19}\text{F}-^{19}\text{F})$ 46 Hz)[†], -20.4 (m, $J(^{19}\text{F}-^{19}\text{F})$ 40 Hz)[†], -21.9[†], -22.7 (m, $J(^{19}\text{F}-^{19}\text{F})$ 36 Hz)[†], -25.0[†], -26.5[†], -28.3[†], -74.5 (s)[‡], -74.7 (s)[‡], -

* resonances due to fluorine of the $\text{Ti}(\mu\text{-F})\text{Li}$ moiety, assignment is made by analogy to **1** and (a) A. Pevec, F. Perdih, J. Kosmrlj, B. Modec, H. W. Roesky, A. Demsar, *Dalton Trans.*, 2003, 420; (b) A. Demsar, A. Pevec, L. Golic, S. Petricek, A. Petric, H. W. Roesky, *Chem. Comm.*, 1998, 1029.

[†] resonances due to fluorine in the $\text{Ti}(\mu\text{-F})\text{Ti}$ moiety, assignment is made according to the endnote [1].

[‡] resonances due to fluorine in the $-\text{CF}_3$ groups of $[(\text{CF}_3)_2(\text{Ph})\text{CO}]$, chemical shift is close to the reported in ref. A. Decken, H. D. B. Jenkins, G. B. Nikiforov, J. Passmore,

74.8 (s)[‡], -74.9 (s)[‡], -75.0 (s)[‡], -75.1 (s)[‡], -75.2 (s)[‡], -75.3 (s)[‡], -76.5 (s)[‡], -79.0 (s)[‡], -79.07 (s)[‡], -79.11 (s)[‡], -79.20 (s)[‡], -79.24 (s)[‡], ⁷Li NMR (155.4 MHz, THF, -40 °C), δ_{Li} (ppm) = -1.35 ($\Delta\omega_{1/2}$ 39 Hz)[§]. Actual ¹⁹F NMR spectrum is shown in Figure 9, page 9.

Notes: 1) $\Delta\omega_{1/2}$ was measured for the resonances having large signal to noise ratio. 2) Since resonances with the close chemical shift are overlapped, integration was applied for the resonances in the ranges 69 ppm to 35 ppm, -11 ppm to -29 ppm, -74 ppm to -79 ppm. Integrated intensities were 1.8 : 1 : 20.9 correspondingly.

Dalton Trans., 2004, 2496 and in A. Decken, G. B. Nikiforov, J. Passmore, *Polyhedron*, 2005, **24**, 2994.

[§] Line width of the ⁷Li resonances was minimal at -40 °C and increased by lowering and increasing of the temperature. $\Delta\omega_{1/2}$ 33 Hz at r.t.; at -90 °C resonance has steps 23 and 12 Hz, however fine structure was not resolved.

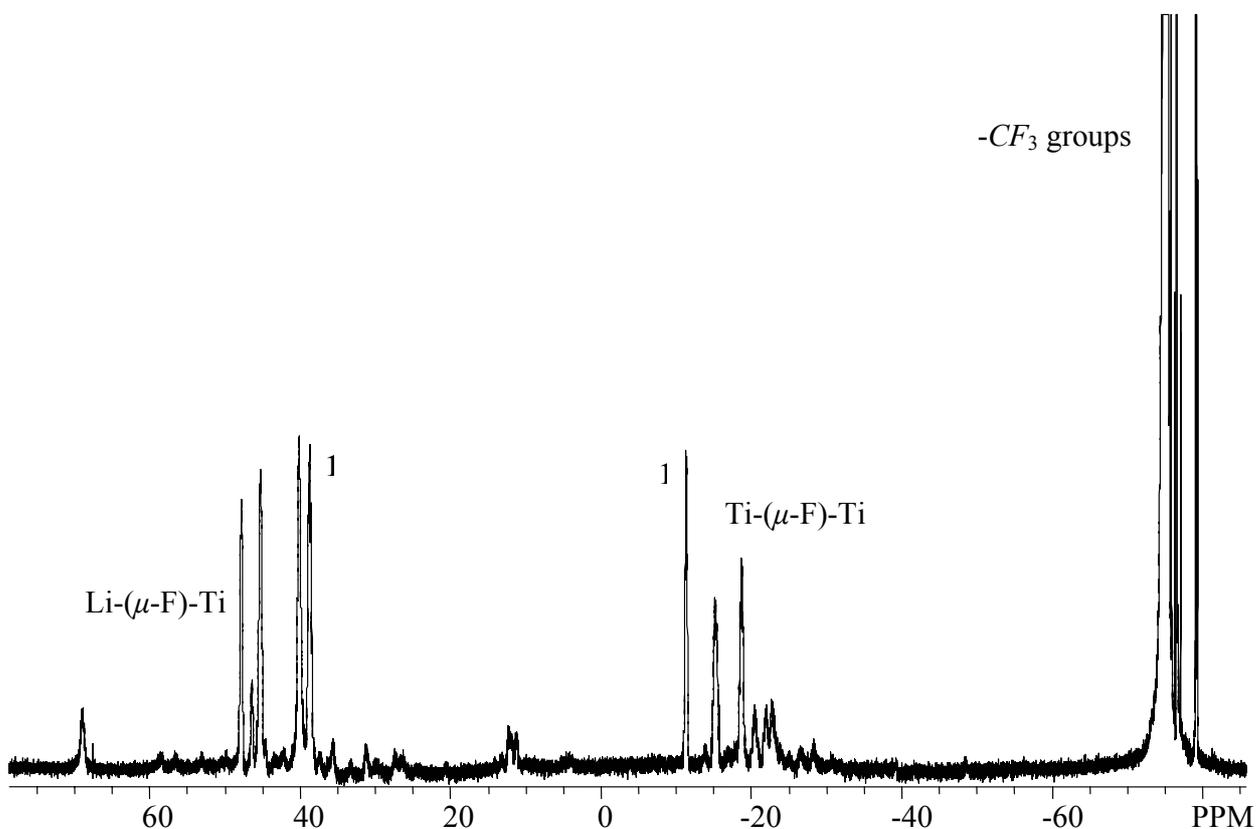


Figure 9

^{19}F NMR spectrum of TiF_4 and 1 eqv. of $(\text{CF}_3)_2(\text{Ph})\text{COLi}$ in THF measured at -40°C .

Interaction of the TiF_4 and LiOR_f can be interpreted by equations (a - c) and the reaction products might have structures drawn in the Figure 10.



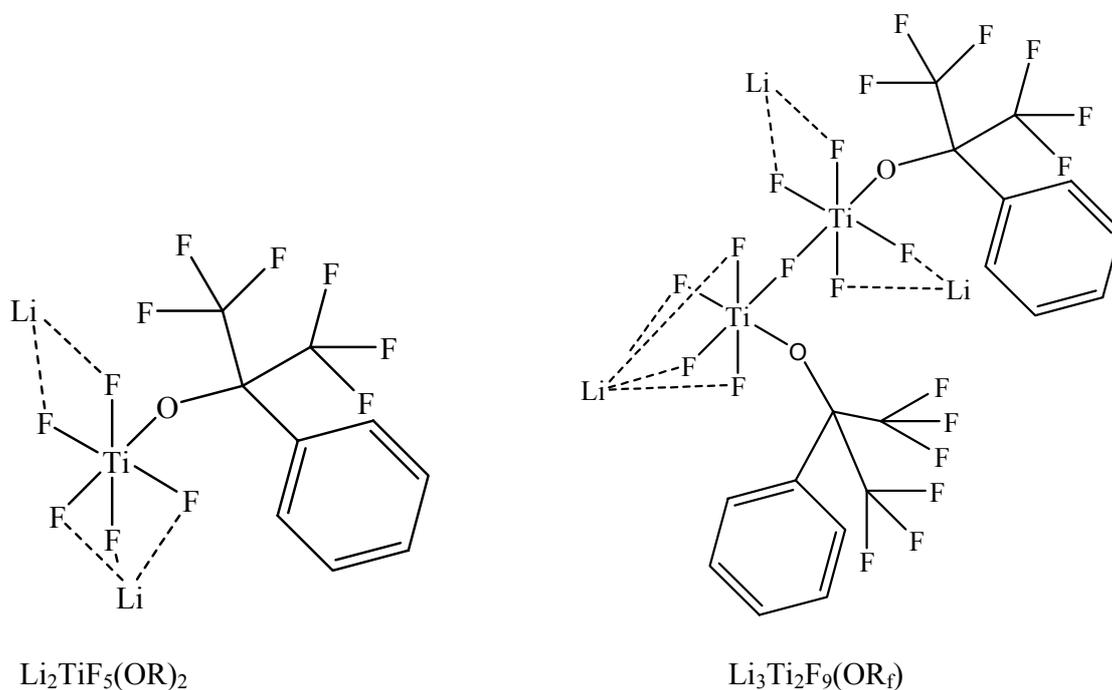


Figure 10

Possible simplest models of the heterometallic complexes obtained by interaction of $\{\text{LiF}\}$ *in situ* and titanium complexes. Solvation of the lithium center by THF is omitted.

We assume that complexes without alkoxide ligand (e.g. Li_2TiF_6) are not soluble in THF and thus did not proposed its. Formation of cationic and anionic complexes in THF ($\epsilon = 7.6$) seems less feasible than molecular aggregates. Lithium center could also be bounded with oxygen atom of the alkoxide ligand.

Interaction of TiF_4 and 3 equivalents of $(\text{CF}_3)_2(\text{Ph})\text{COLi}$ in THF

Solution of TiF_4 (0.74 g, 6.0 mmol) and 3 eqv. of $(\text{CF}_3)_2(\text{Ph})\text{COLi}$ (18 mmol) in THF, prepared as described in the main experimental section. All volatilities are then removed under dynamic vacuum and toluene added to the resulting oily solid. Crystalline **1** (1.2 g, yield of **1** 30%, eq.1 main text) was separated by filtration. The resulting clear toluene solution was evaporated to dryness. The obtained white solid was soluble in THF and toluene with formation of a clear colourless solution.

^{19}F NMR (376.3 MHz, toluene, r.t.), δ_{F} (ppm) = -74.9 (s, **2**), -75.0 (s), -76.2 (s), -78.8 (s), -122.0 (q, $J_{\text{F-Li}} = 277$ Hz, $-\text{CF}_3$), -204.5 ($\Delta\omega_{1/2}$ 587 Hz, Li-F), resonance of **2** has relative intensity 88% of total. Singlet resonances in the area -74.9 to -78.8 ppm assigned to the $-\text{CF}_3$ groups of the Ti(IV) alkoxide complexes. Presence of several resonances reflect presence of the magnetically non equivalent $[\text{OC}(\text{CF}_3)_2\text{Ph}]$ ligands in one complex and/or formation of different alkoxide complexes in solution, probably $[\text{Ti}(\text{OC}(\text{CF}_3)_2\text{Ph})_5]$ and $[\text{Ti}(\text{OC}(\text{CF}_3)_2\text{Ph})_6]^{2-}$, however present data are non sufficient to make the exact assignment.

^{19}F NMR (376.3 MHz, toluene, -70 °C), δ_{F} (ppm) = -75.1 (s), -75.4 (s, **2**), -75.9 (s), -76.1 (s), -78.9 (s), -122.9 (m) -205.4 ($\Delta\omega_{1/2}$ 557 Hz, Li-F), resonance of **2** has relative intensity 93% of total, ^{19}F NMR (376.3 MHz, THF, r.t.), δ_{F} (ppm) = -75.2 (s, **2**), -75.4 (s), -76.0 (s), -76.4 (s), -79.2 (s), -122.5 (m), -204.7 ($\Delta\omega_{1/2}$ 720 Hz, Li-F), resonance of **2** has relative intensity 73% of total**, ^{19}F NMR (376.3 MHz, toluene, -90 °C), δ_{F} (ppm) = -75.7 (s), -76.0 (s, **2**), -76.1 (s), -76.3 (s), -76.6 (s), -79.4 (s), -123.3 (br), -205.0 ($\Delta\omega_{1/2}$

** $w(\text{resonance}) = (^{19}\text{F NMR integrated intensity for (resonance)}) / (\text{Intensities of all lines in the } ^{19}\text{F NMR spectrum})$

1042 Hz, LiF), resonance of **2** has relative intensity 71% of total, the relative intensities of resonances at -76.0 and -76.4 changed by lowering of the temperature from 0.86 : 1 at r.t. to 0.67 : 1 at -90 °C; ^7Li NMR (155.4 MHz, toluene, r.t.), δ_{Li} (ppm) = -1.19 ($\Delta\omega_{1/2}$ 109 Hz), ^7Li NMR (155.4 MHz, toluene, -70 °C), δ_{Li} (ppm) = -1.44 ($\Delta\omega_{1/2}$ 141 Hz), ^7Li NMR (155.4 MHz, THF, r.t.), δ_{Li} (ppm) = -1.28 ($\Delta\omega_{1/2}$ 104 Hz, relative intensity 92%), -3.43 ($\Delta\omega_{1/2}$ 17 Hz, relative intensity 8%), ^7Li NMR (155.4 MHz, THF, -90 °C), δ_{Li} (ppm) = -1.45, -1.50 (two overlapped resonances, relative intensity 75%), -3.81 ($\Delta\omega_{1/2}$ 15 Hz, relative intensity 25%), relative intensity of the lower frequency ^7Li resonance at -3.81 ppm increased by lowering of the temperature, however resonance at -1.45 ppm is superposition of at least 2 resonances, maxima at -1.45 and -1.50 ppm appeared at -90 °C and thermodynamic parameters of the process can not be extracted. The lower frequency ^7Li NMR resonance could be assigned to the lithium cationic complex and/or lithium - titanium complex with extra molecule of THF. Actual ^{19}F NMR spectrum of the reaction product in toluene solution is given in Figure 11, ^7Li NMR spectrum of the reaction product in THF solution is given in Figure 12.

IR (KBr, Nujol mull) and Raman (solid) spectra of the investigated solid containing lithium fluoride are identical to that of **2**.

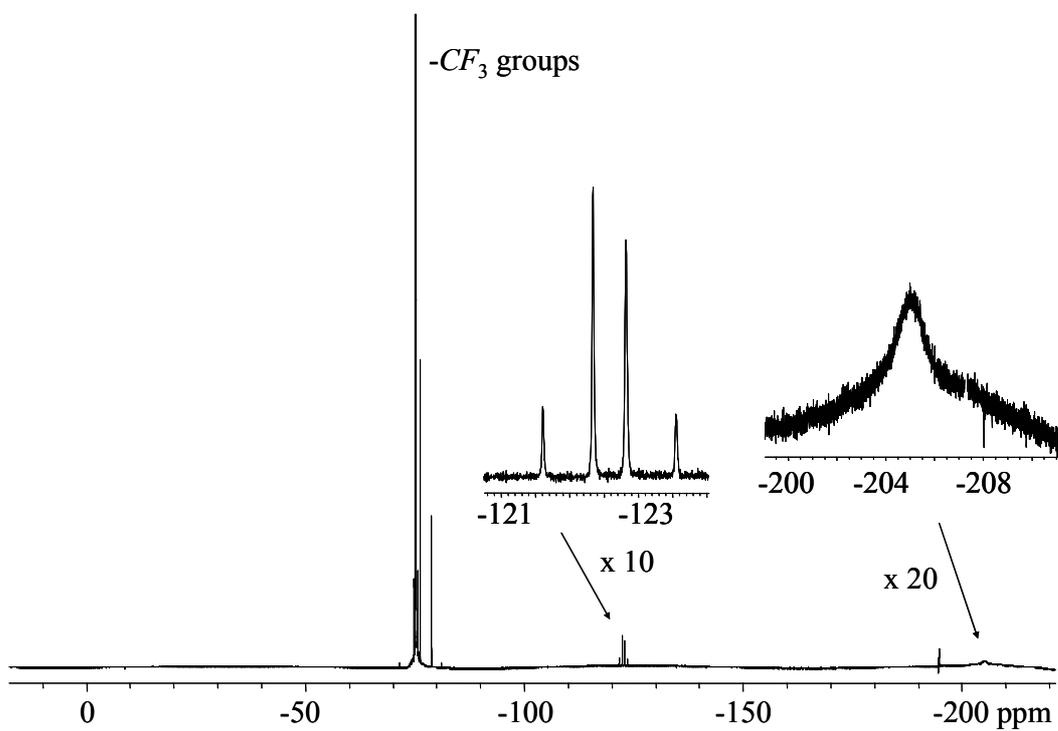


Figure 11

^{19}F NMR spectrum of reaction product TiF_4 and 3 eq. of $(\text{CF}_3)_2(\text{Ph})\text{COLi}$ in THF, after removal of **1**. Resulted solid dissolved in toluene and measured at $-40\text{ }^\circ\text{C}$.

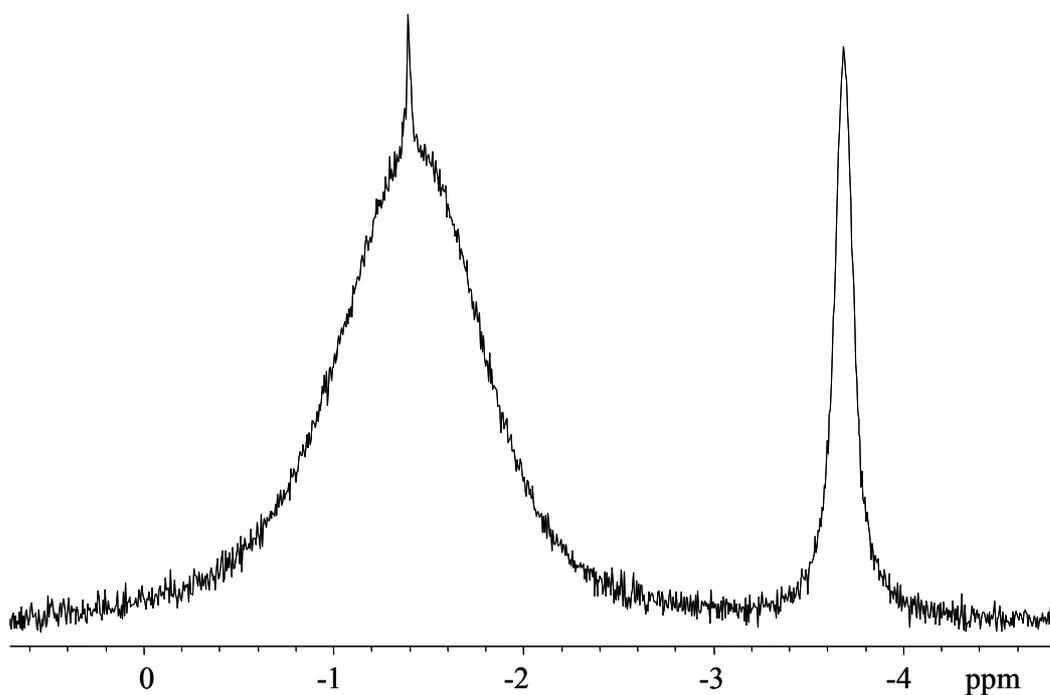


Figure 12

¹⁹F NMR spectrum of reaction product TiF₄ and 3 eqv. of (CF₃)₂(Ph)COLi in THF, after removal of **1**. Resulted solid dissolved in THF and measured at -90 °C.

The ⁷Li NMR spectrum of toluene solution contained one broad line at -1.44 ppm ($\Delta\omega_{1/2}$ 141 Hz at -70 °C) and that in THF solution showed two broad major overlapped resonances at -1.45, -1.50 ppm ($\Delta\omega_{1/2}$ > 100 Hz at -90 °C), and a weak broad resonance at -3.81 ppm in accordance with the presence of at least three lithium containing complexes in solution.

References

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