# Metallomimetic C–F activation catalysis by simple phosphines

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## Supporting Information

Contents

# 1. Experimental Details

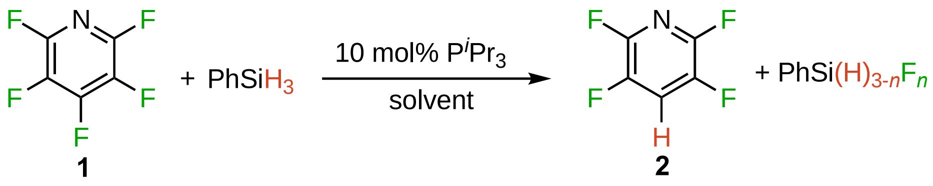
## 1.1. General methods

All reactions were performed in flame- or oven-dried glassware with rigorous exclusion of air and moisture, using a nitrogen-filled *MBraun* glove box ($O_2$ < 1 ppm, $H_2O$ < 1 ppm) or regular Schlenk techniques.[1] Liquids were transferred using either plastic syringes, Teflon canulae with or without filtering tip, or Hamilton™ microsyringes. Unless otherwise indicated, the fluorinated aromatics and the silanes ($Ph_3SiH$, $Ph_2SiH_2$ and $PhSiH_3$) were purchased from Sigma Aldrich, Fluorochem or Apollo Scientific, dried over molecular sieves and degassed by freeze-pump-thaw cycles prior to use. $CD_2Cl_2$, $CD_3CN$, *o*-difluorobenzene (purchased from Merck), $CH_3CN$ (pre-dried by passing through a Puresolv MD 7 solvent purification machine) were degassed by freeze-pump-thaw cycles, dried over $CaH_2$ and distilled. $Et_2O$ was pre-dried by passing through a Puresolv MD 7 solvent purification machine. The phosphines, $Ph_2SiCl_2$, $Et_2NH$, $Et_3N$, $SOCl_2$ and *L*-proline were purchased from Sigma Aldrich and used without further purification. Tetramethylammonium fluoride was purchased from Sigma-Aldrich and dried at 100 °C for 48 h under hi-vac in a round bottom flask prior to its use. MeOH was purchased from Honeywell and dried over molecular sieves prior to use.

$^1H$, $^{31}P$, $^{19}F$ and $^{13}C$ NMR spectra were recorded in $CD_3CN$, $CD_2Cl_2$ or $C_6D_6$ solution by using NMR tubes equipped with J. Young valves on a *Bruker* Avance III 500 (500 MHz for $^1H$, 202 MHz for $^{31}P$, 471 MHz for $^{19}F$) or Avance NEO 600 (600 MHz for $^1H$, 243 MHz for $^{31}P$, 565 MHz for $^{19}F$, 119 MHz for $^{29}Si$) spectrometer at 25 °C. Chemical shifts are in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonances as the internal standard ($CHD_2CN$: $\delta$ reported = 1.94 ppm; $C_6HD_5$: $\delta$ reported = 7.16 ppm; $CHDCl_2$: $\delta$ reported = 5.32 ppm for $^1H$ NMR). $^{13}C$ NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of tetramethylsilane as primary reference.[2,3] Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, mc = multiplet center), coupling constant (Hz), and integration.

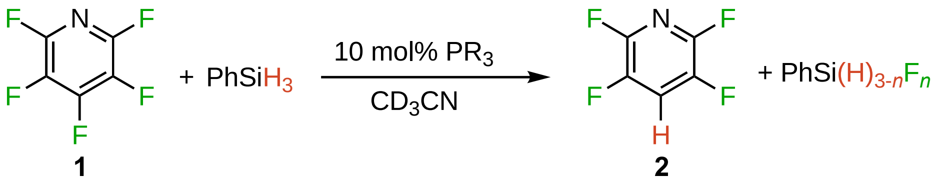
MS spectra were measured using a Bruker Daltronics micrOTOF MS, Agilent series 1200LC with electrospray ionization (ESI and APCI) or on a Thermo LCQ using electrospray ionization, with <5 ppm error recorded for all HRMS samples. Mass spectral data are quoted as the m/z ratio along with the relative peak height in brackets (base peak = 100). Mass to charge ratios (m/z) are reported in Daltons. High-resolution mass spectra are reported with <5 ppm error.

## 1.2. Procedure for solvent optimisation



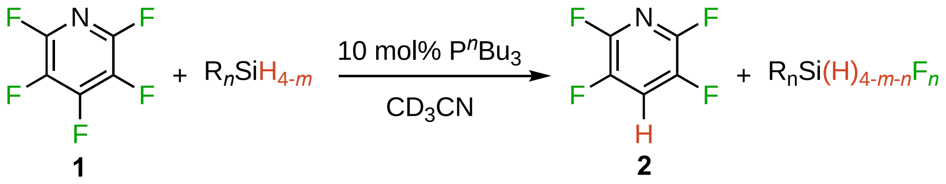
Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and $PhSiH_3$ (50 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of the tested solvent and placed into a J-Young NMR tube. $P^iPr_3$ (7.6 µL, 0.040 mmol, 0.10 equivalent) was added and the tube was heated to monitor the progress of reaction (conditions specified in Table 1 of the manuscript). The reaction mixture was analyzed by quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

## 1.3. Procedure for catalyst optimisation



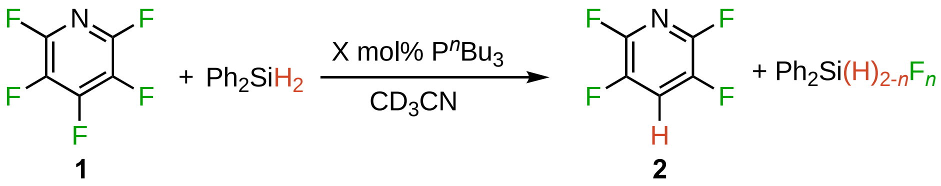
Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and $PhSiH_3$ (50 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. The tested phosphine (0.040 mmol, 0.10 equivalent) was added and the tube was heated to monitor the progress of reaction (conditions specified in Table 1 of the manuscript). The reaction mixture was analyzed by quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

## 1.4. Procedure for silane optimisation



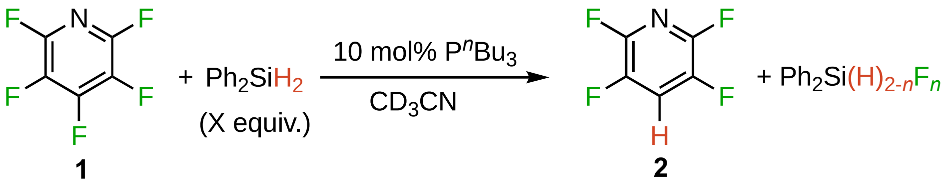
Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and the tested silane (0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. $P^nBu_3$ (10 µL, 0.040 mmol, 0.10 equivalent) or $P^iPr_3$ (7.6 µL, 0.040 mmol, 0.10 equivalent) was added and the tube was heated to monitor the progress of reaction (conditions specified in Table 1 of the manuscript). The reaction mixture was analyzed by quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

### 1.5. Procedure for optimisation of the catalyst loading



Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and $Ph_2SiH_2$ (74 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. Different amounts of $P^nBu_3$ were added (10 mol%, 5 mol% or 1 mol%) and the progress of reaction was monitored (conditions specified in Table 1 of the manuscript). The reaction mixture was analyzed by quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

### 1.6. Procedure for optimisation of the silane loading



Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and different amounts of $Ph_2SiH_2$ (1.0 equivalent and 0.55 equivalents) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. $P^nBu_3$ (10 µL, 0.040 mmol, 0.1 equivalent) was added and the progress of reaction was monitored (conditions specified in Table 1 of the manuscript). The reaction mixture was analyzed by quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

## 1.7. General procedure for the catalytic hydrodefluorination

$$\mathrm{Ar^F\text{-}F} + \mathrm{Ph_2SiH_2} \xrightarrow[\mathrm{CD_3CN}]{\text{10 mol\% } \mathrm{P}^n\mathrm{Bu_3}} \mathrm{Ar^F\text{-}H} + \mathrm{Ph_2Si(H)}_{2\text{-}n}\mathrm{F}_n$$

The Ar–F (0.40 mmol, 1.0 equivalent) and $Ph_2SiH_2$ (74 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. $P^nBu_3$ (10 µL, 0.10 equivalent) was added and the progress of the reaction was monitored by $^{19}$F NMR spectroscopy. If the hydrodefluorination product was volatile, rather than isolating it the reaction mixture was analyzed by quantitative $^{19}$F NMR with trifluorotoluene used as an internal standard. Inversion recovery experiments were performed on **1** to determine appropriate parameters for these experiments. The *meta*-F signal at –162.70 ppm was on resonance throughout the experiment. The D1 was set at 10 seconds and a total of seven values ranging from 1 millisecond to 30 seconds were used for the inversion recovery delay (T1). It was observed that the *meta*-F exhibited the longest T1 value, measuring 7.8 seconds. Thus, the D1 parameter was set to 39 seconds for all the $^{19}$F NMR experiments involving fluorinated pyridines. The product conversion was calculated from the ratio of the integrals of the trifluorotoluene and Ar–F signals before the reaction (blank sample) and the ratio of the trifluorotoluene and Ar–H signals at the end of the reaction. In the case of decafluorobiphenyl hydrodefluorination, after completion of the reaction the solution was evaporated and the crude product fully dried. The residue was dissolved in *n*-hexane and the resulting mixture was purified by chromatography column. The hexane was then evaporated and the residue was thoroughly dried to give an isolated yield of product (**11**).

**Spectroscopic data for the products:**

**2,3,5,6-tetrafluoropyridine (2):**[4] Yield of 93%. $^1$H NMR (600 MHz, $CD_3CN$): 7.88 (tt, $^3J_{HF}$ = 7.9 Hz, $^4J_{HF}$ = 7.1 Hz, 1H). $^{19}$F NMR (565 MHz, $CD_3CN$): δ –93.63 (mc, 2F, *ortho*-F), –141.55 (mc, 2F, *meta*-F).

**3,5,6-trifluoropyridine (4):**[5] Yield of 13%. $^1$H NMR peaks have not been identified due to the low conversion and the overlapping of $Ph_2SiH_2$, 2,3,5,6-tetrafluoropyridine and trifluorotoluene signals in the $^1$H NMR spectrum. $^{19}$F NMR (565 MHz, $CD_3CN$): δ –92.34 (t, $^3J_{FF}$ = 27.9 Hz, 1F, 6-C*F*), –128.98 (ddd, $^5J_{FF}$ = 29.1 Hz, $^3J_{FH}$ = 7.6 Hz, $^3J_{FF}$ = 3.6 Hz, 1F, 5-CF), –136.47 (ddd, $^3J_{FH}$ = 26.3 Hz, $^3J_{FH}$ = 9.2 Hz, $^3J_{FF}$ = 3.7 Hz, 1F, 3-C*F*).

**2,6-difuoropyridine (5):**[6] Yield of 79%. $^1$H NMR (600 MHz, $CD_3CN$): δ 7.99 (m, 1H, *para*-H), 6.93 (d, $J$ = 8.0 Hz, 2H, *meta*-H). $^{19}$F NMR (565 MHz, $CD_3CN$): δ –70.33 (bs, 2F).

**2,3,5,6-tetrafluorobenzonitrile (6):**[4] Yield of 86%. $^1$H NMR (600 MHz, $CD_3CN$): δ 7.67 (m, 1H). $^{19}$F NMR (471 MHz, $CD_3CN$): –134.81 (mc, 2F), –137.58 (mc, 2F).

**1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene (7):**[4] Yield of 89%. $^1$H NMR (600 MHz, CD$_3$CN): δ 7.63 (m, 1H). $^{19}$F NMR (565 MHz, CD$_3$CN): δ –57.35 (t, $^4J_{FF}$ = 22.3 Hz, 3F, CF$_3$), –138.41 (mc, 2F), –142.65 (mc, 2F).

**1,2,4,5-tetrafluorobenzene (8):**[7] Yield of 84% when Ar–F is C$_6$F$_6$, 93% when Ar–F is C$_6$F$_5$H. $^1$H NMR (500 MHz, CD$_3$CN): δ 7.26 (p, *J* = 8.9 Hz, 2H). $^{19}$F NMR (471 MHz, CD$_3$CN): δ –141.03 (t, *J* = 8.9 Hz, 4F).

**2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (11):**[4] Isolated yield of 86%. $^1$H NMR (600 MHz, CD$_2$Cl$_2$): δ 7.37 – 7.27 (m, 2H). $^{19}$F NMR (565 MHz, CD$_3$CN): δ –138.65 – –138.78 (m, 2F), –139.12 – –139.25 (m, 2F).

**[16]Br:** $^1$H NMR (500 MHz, CD$_3$CN): δ 2.93 (td, *J* = 12.9, 8.6 Hz, 6H), 1.65 (dq, *J* = 16.6, 8.6 Hz, 6H), 1.59 – 1.49 (m, 6H), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 9H). {$^1$H}$^{31}$P NMR (202 MHz, CD$_3$CN): δ 36.79 – 36.50 (m, 1P). $^{19}$F NMR (471 MHz, CD$_3$CN): δ –128.37 (mc, 2F), –143.48 (mc, 1F), –158.54 (mc, 2F).

## 1.8. Key Spectroscopic Data

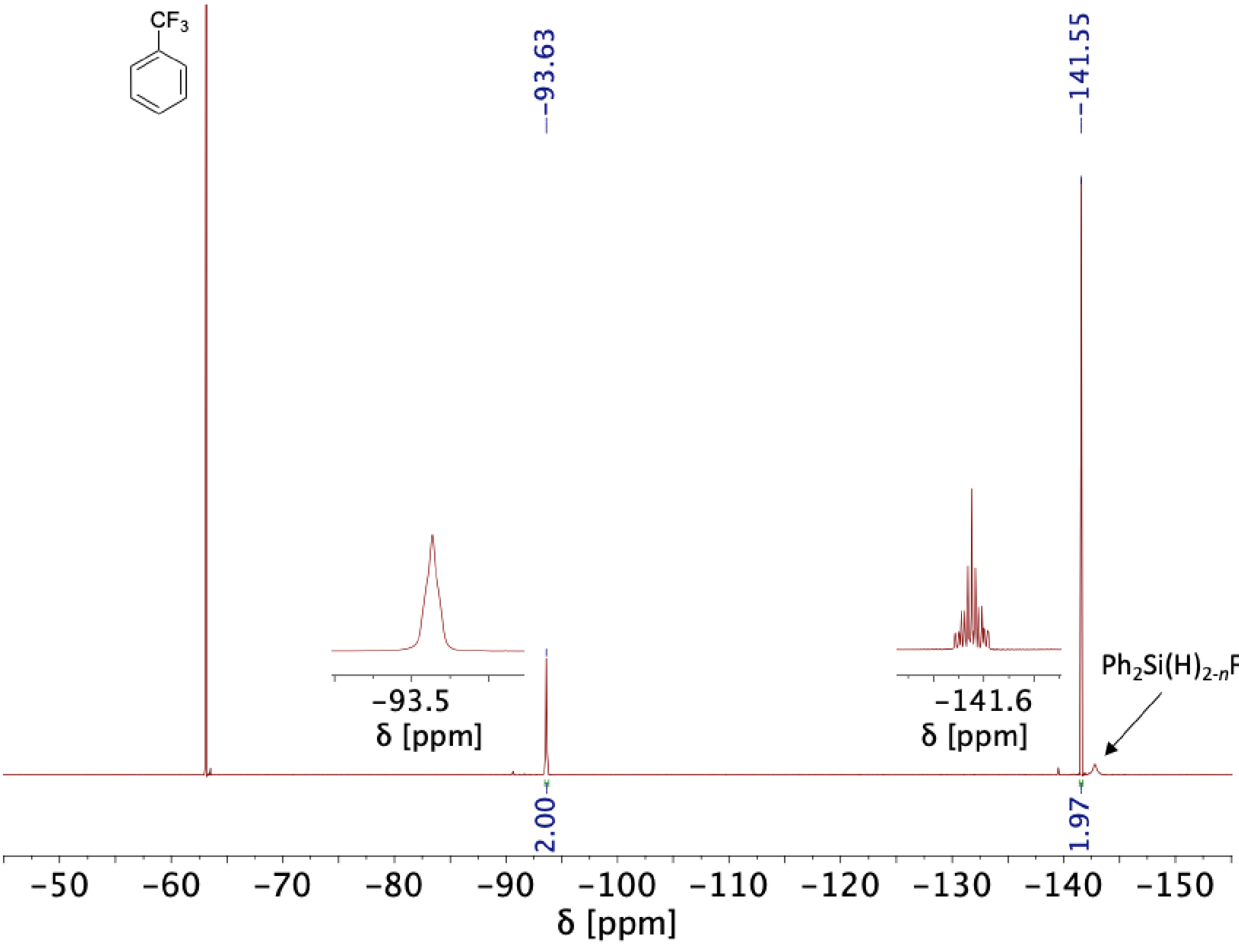


**Figure S1:** $^{19}$F NMR spectrum (565 MHz, CD$_3$CN) of 2,3,5,6-tetrafluoropyridine (**2**) obtained after 20 minutes at 20 °C, using the general procedure in section 1.7.

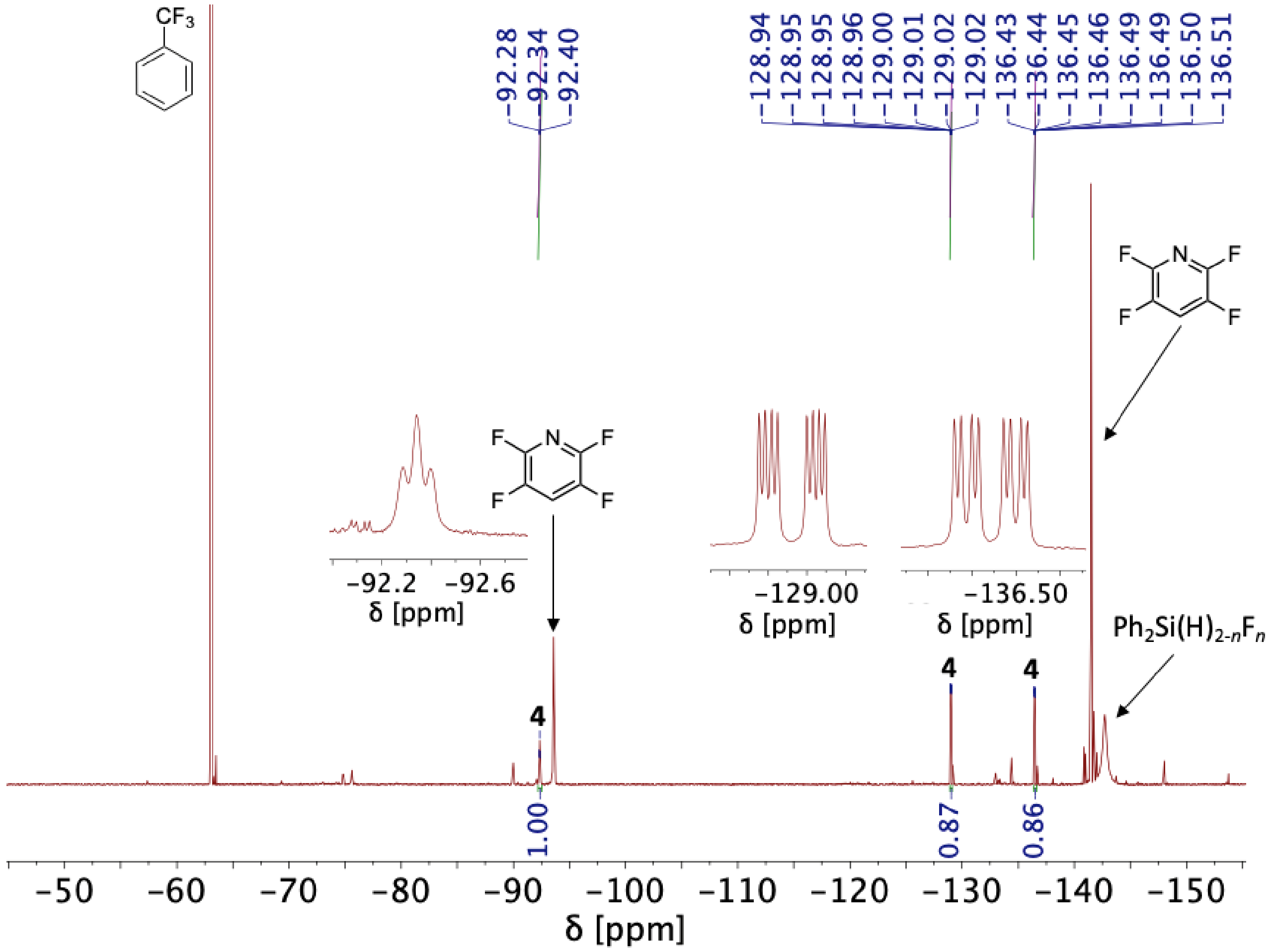


**Figure S2:** $^{19}$F NMR spectrum (565 MHz, $CD_3CN$) of 3,5,6-trifluoropyridine (**4**) obtained after 5 days at 70 °C, using the general procedure in section 1.7.

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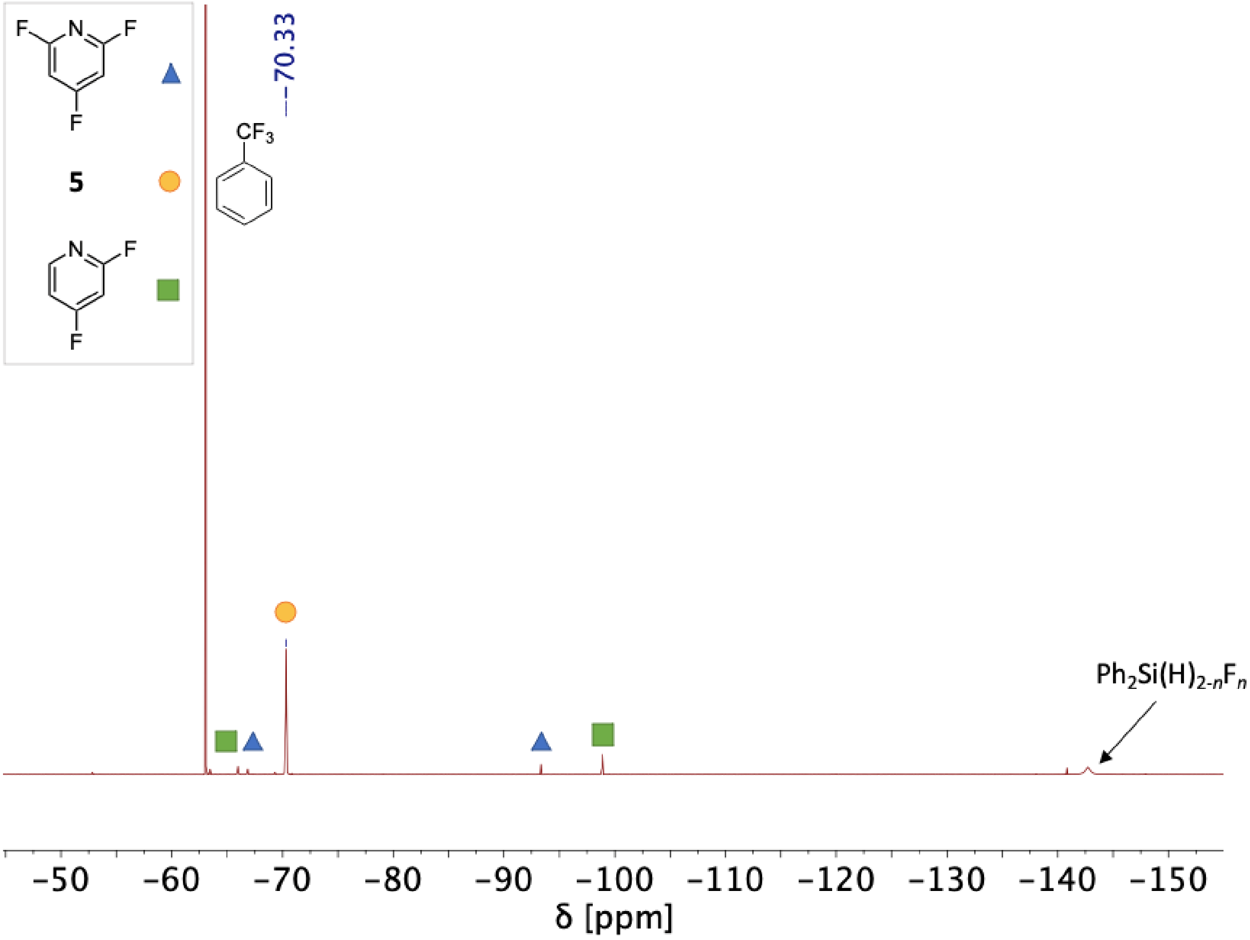

**Figure S3:** $^{19}$F NMR spectrum (565 MHz, $CD_3CN$) of 2,6-difluoropyridine (**5**) obtained after 6 days at 60 °C, using the general procedure in section 1.7.

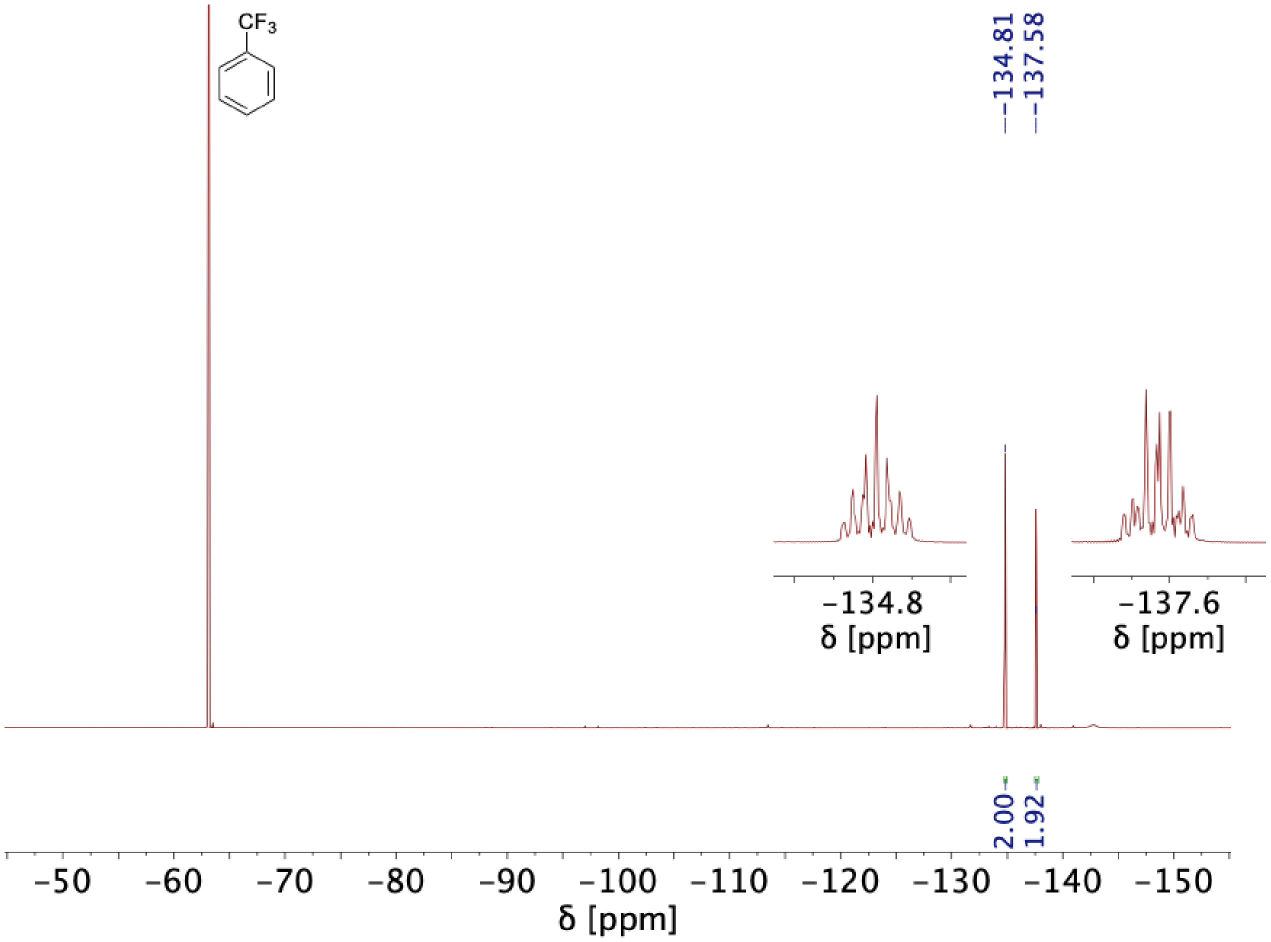

**Figure S4:** $^{19}$F NMR spectrum (565 MHz, $CD_3CN$) of 2,3,5,6-tetrafluorobenzonitrile (**6**) obtained after 10 minutes at 20 °C, using the general procedure in section 1.7.

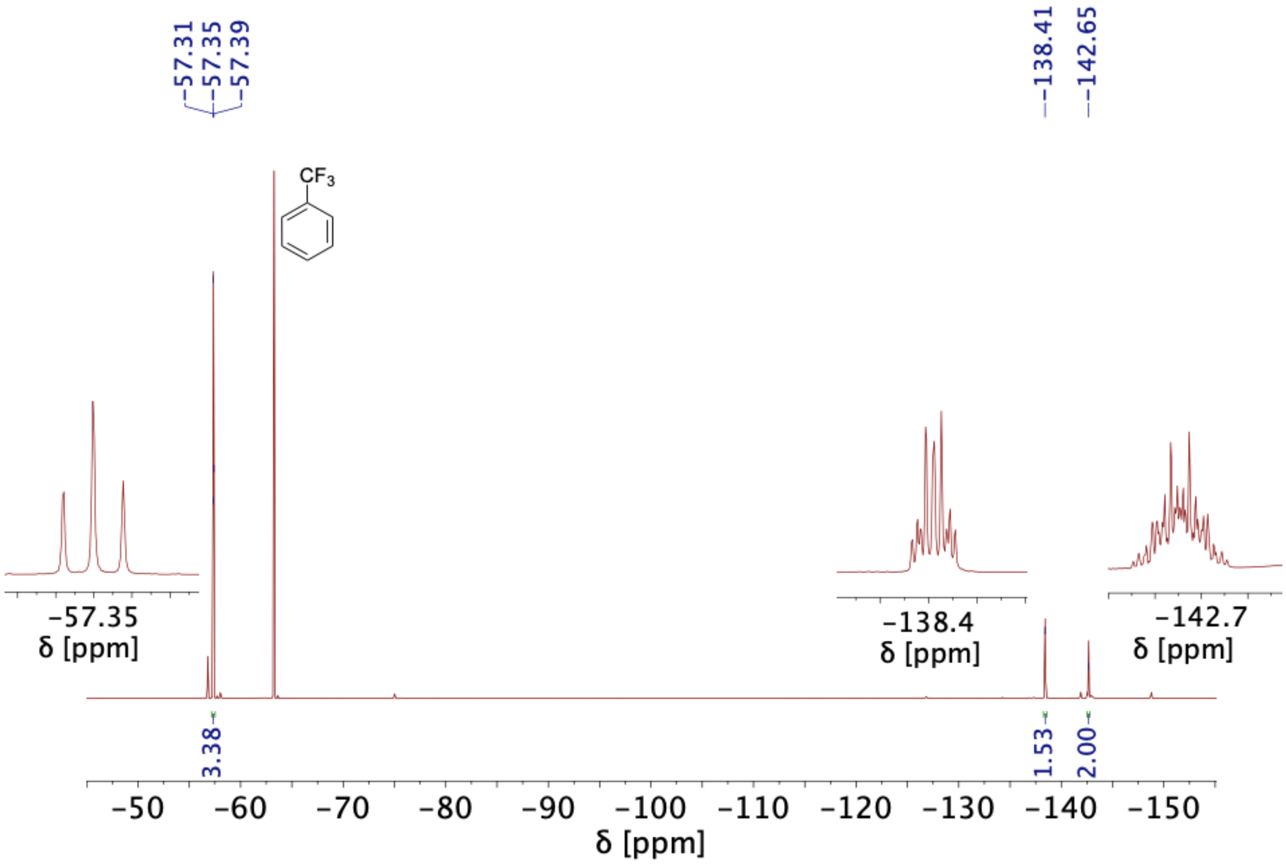

**Figure S5:** $^{19}$F NMR spectrum (565 MHz, $CD_3CN$) of 1,2,4,5-tetrafluoro-3-(trifluoromethyl)benzene (**7**) obtained after 3 hours at 20 °C, using the general procedure in section 1.7.

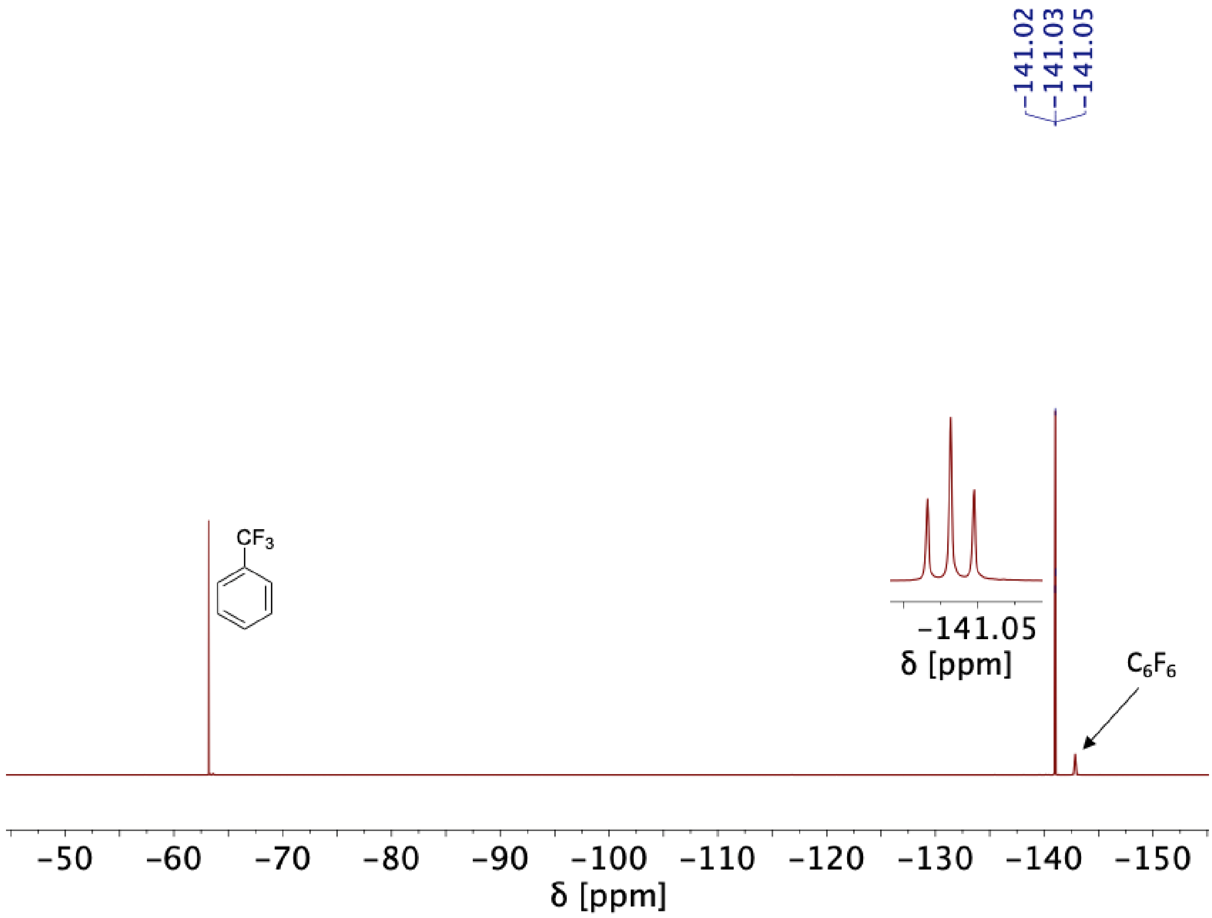

**Figure S6:** $^{19}$F NMR spectrum (565 MHz, $CD_3CN$) of 1,2,4,5-tetrafluorobenzene (**8a**) obtained after 9 days at 60 °C, using the general procedure in section 1.7.

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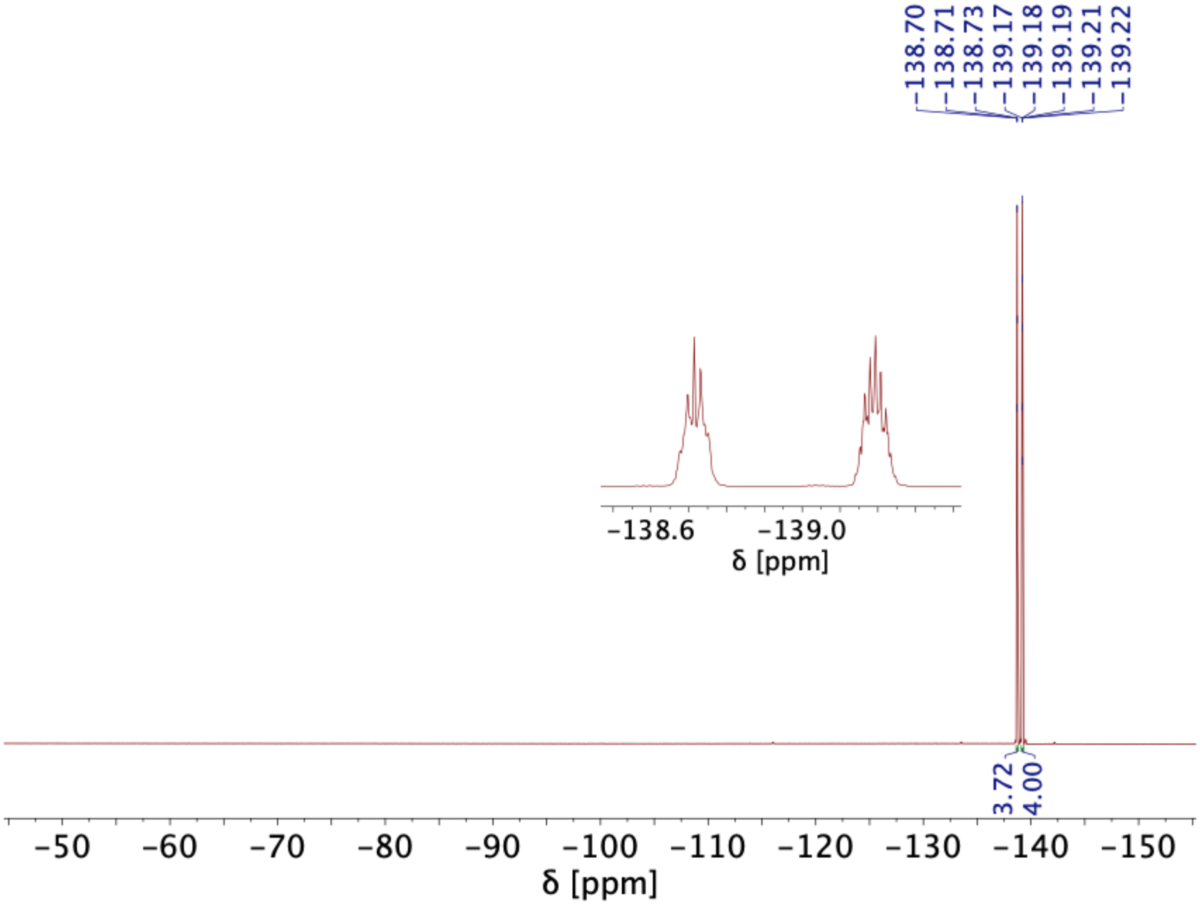


**Figure S8:** $^{19}$F NMR spectrum (565 MHz, $CD_3CN$) of 2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (**11**) isolated and purified according to the general procedure in section 1.7.

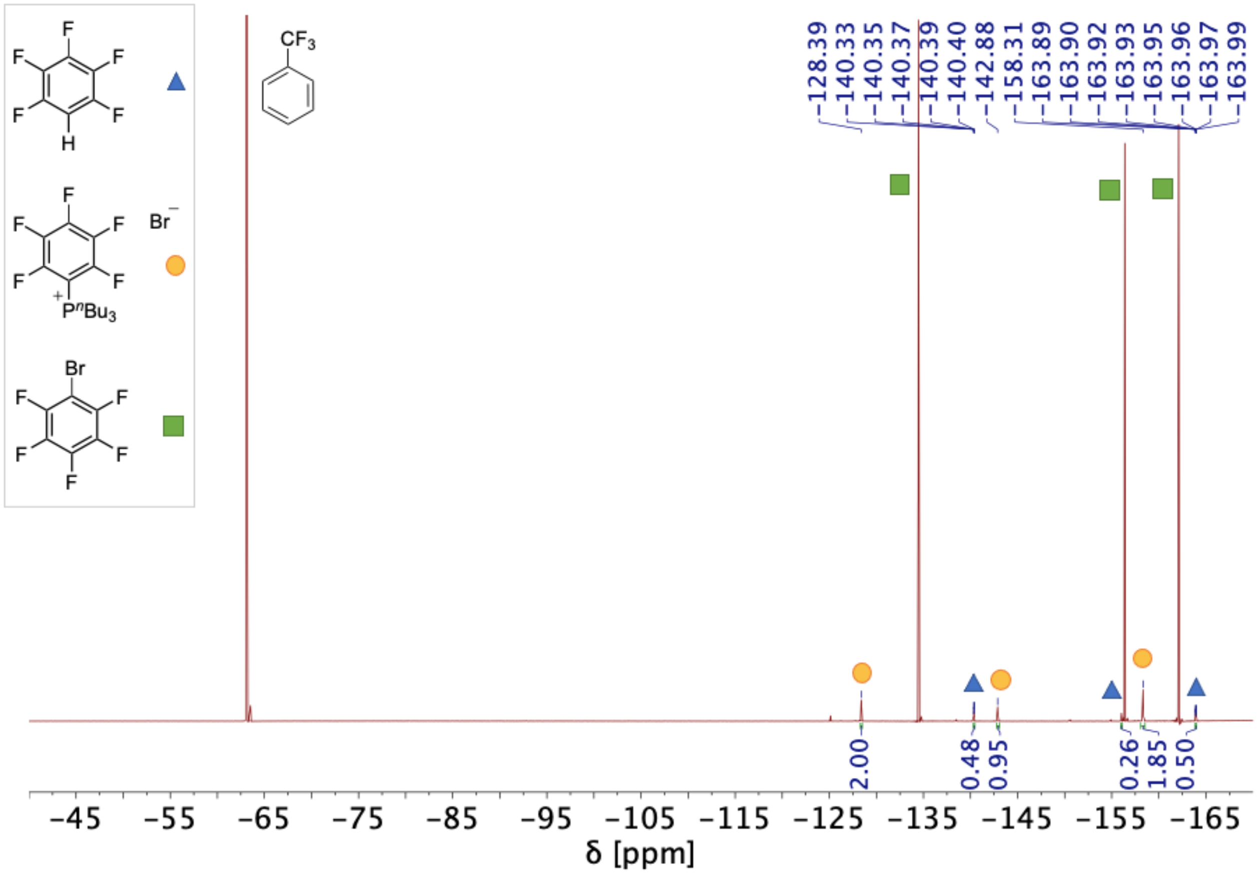


**Figure S7:** $^{19}F$ NMR spectrum (565 MHz, $CD_3CN$) of the mixture resulting from the catalytic HDF attempt of bromopentafluorobenzene and the assigned phosphonium salt **[16]Br** obtained after 20 minutes 20 °C, using the general procedure in section 1.7.

### 1.9. Preparation of $Ph_2Si(Cl)(NEt_2)$

$$Ph_2SiCl_2 + 2\ Et_2NH \xrightarrow{Et_2O} \underset{\textbf{S1}}{Ph_2Si(Cl)(NEt_2)} + [Et_2NH_2]Cl$$

This product was prepared according to a literature method.[8] In a Schlenk tube were placed 1.2 mL (5.9 mmol, 1.0 equiv.) of diphenyldichlorosilane and 13 ml of ether. The solution was cooled to –78°C in a dry-ice/acetone bath and treated with a solution of 2.4 mL (24 mmol, 4.0 equiv.) of diethylamine in 4.4 mL of ether over a 30 min period, causing formation of a voluminous precipitate of diethylamine hydrochloride. The mixture was filtered under a positive pressure of nitrogen with a filter-stick, the solid was washed with diethylether (3 x 7 mL), the ether layers were combined and the product dried under vacuum. A yellow oil was obtained in 78% yield. N.B. The product may fume in contact with air.

$^1H$ NMR ($C_6D_6$, 600 MHz): δ 7.88 – 7.84 (m, 4H), 7.17 – 7.13 (m, 6H), 2.86 (q, $^3J_{HH}$ = 7 Hz, 4H), 0.92 (t, $^3J_{HH}$ = 7 Hz, 6H). $^{29}Si$ NMR ($C_6D_6$, 119 MHz): –6.56 (s, 1Si). MS-APCI: $[C_{16}H_{21}ClNSi]^+$ 290.113336 *m/z* (2.4 ppm deviation from theoretical mass).

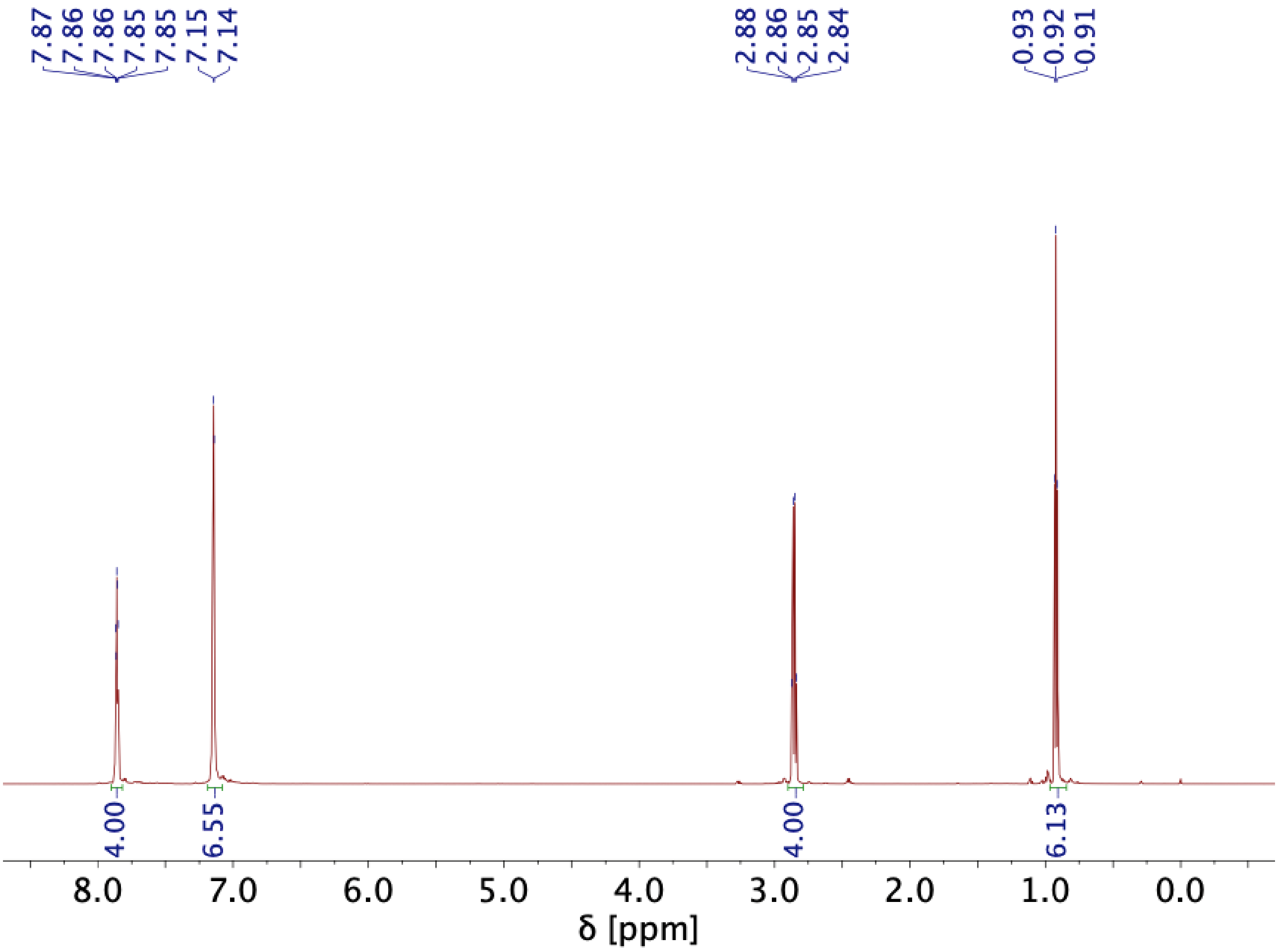


**Figure S9:** $^1H$ NMR spectrum ($C_6D_6$, 600 MHz) of $Ph_2Si(Cl)(NEt_2)$.

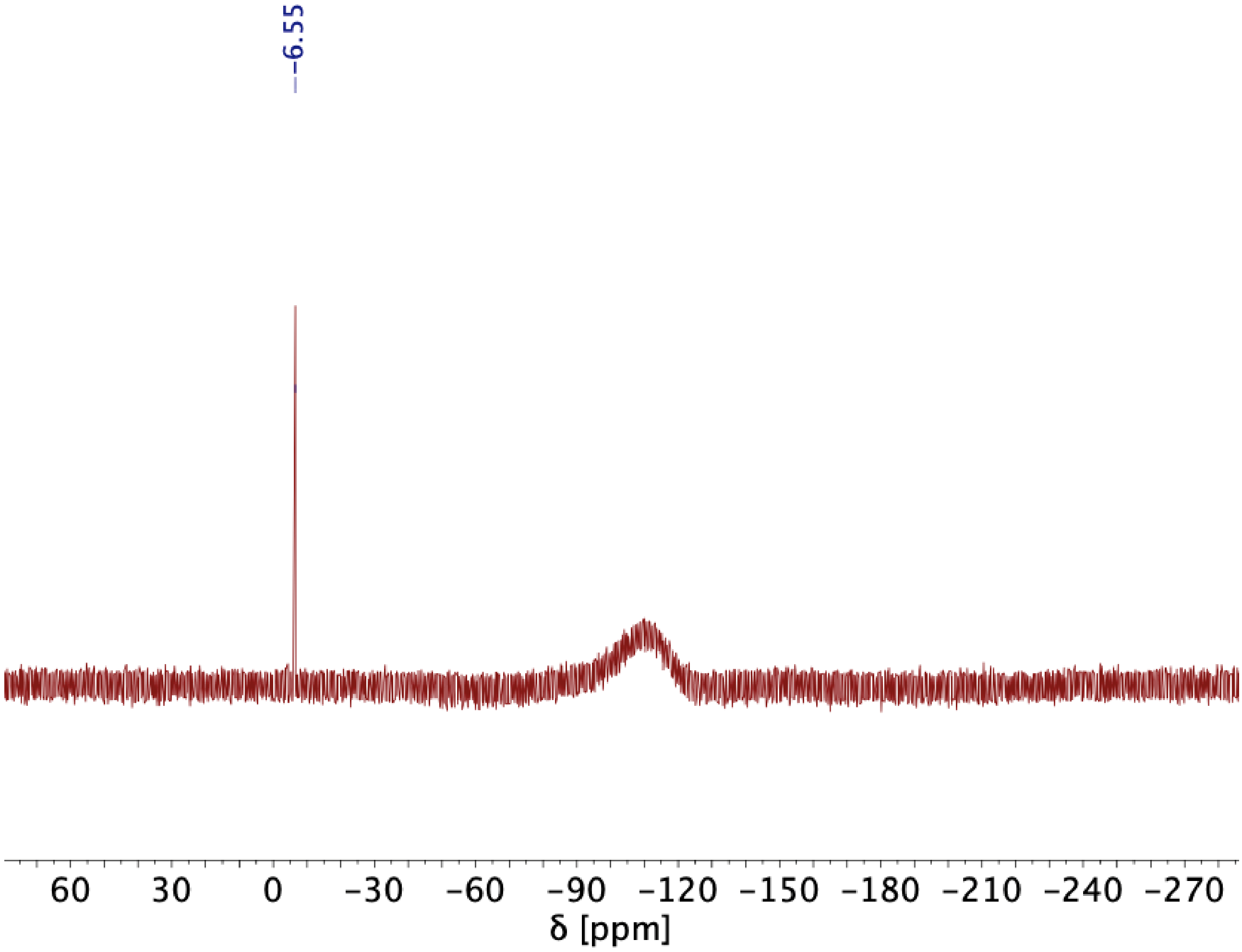
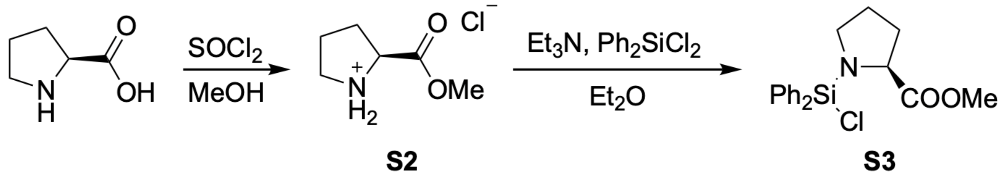


**Figure S10:** $^{29}$Si NMR spectrum ($C_6D_6$, 119 MHz) of $Ph_2Si(Cl)(NEt_2)$. The broad signal corresponds to Si in the glass NMR tube.

### 1.10. Preparation of $Ph_2Si(Cl)(pro)$



*L*-Proline methyl ester hydrochloride (**S2**) was prepared according to a literature method.[9] Thionyl chloride (0.72 mL, 10 mmol, 1.2 equivalent) was added dropwise to anhydrous methanol (42 mL) at 0 °C. The solution was stirred at 0 °C for 30 min and *L*-Proline (0.95 g, 8.3 mmol, 1 equivalent) was added. The reaction mixture was refluxed for 5 h and TLC ($CH_3Cl$/MeOH, 9/1) indicated complete disappearance of *L*-Proline. The reaction mixture was evaporated under reduced pressure and a yellow oil was obtained.

Silane **S3** was then prepared following a modified literature procedure.[8] The obtained hydrochloride salt, **S2**, (1.6 g, 10 mmol, 1.2 equivalent) was dissolved in 11 mL of ether and $Et_3N$ (2.8 mL, 20 mmol, 2.4 equivalents) was added in the solution to obtain the *L*-Proline methyl ester. 1.0 mL (5.0 mmol, 0.60 equivalent) of diphenyldichlorosilane and 3.8 mL of ether were placed in another Schlenck tube. The solution was cooled to –78°C in a dry-ice/acetone bath and treated with the solution of *L*-Proline methyl ester over a 30 min period, causing formation of a voluminous precipitate. Filtration under a positive pressure of nitrogen with a filter-stick, washing the solid with ether, combination of the ether layers and drying the product under vacuum followed. The desired product was extracted with pentane (2 × 10 mL). A yellow oil was obtained in 43% yield.

$^1$H NMR (500 MHz, DCM-$d_2$): δ 7.91 – 7.85 (m, 2H), 7.56 – 7.42 (m, 8H), 3.94 (dd, $^3J_{HH}$ = 8.6, $^3J_{HH}$ = 3.3 Hz, 1H), 3.47 (s, 3H), 2.23 – 2.09 (m, 2H), 2.02 – 1.88 (m, 4H). $^{29}$Si NMR ($C_6D_6$, 119 MHz): –8.90 (s, 1Si). $^{13}$C NMR (151 MHz, DCM-$d_2$): δ 175.62, 135.02, 130.71, 128.08, 60.63, 51.36, 47.65, 31.67, 25.93. MS-APCI: $[C_{18}H_{20}NO_2Si]^+$ 310.126372 *m/z* (1.9 ppm deviation from theoretical mass); $[C_{18}H_{21}ClO_2Si]^+$ 346.102908 *m/z* (1.3 ppm deviation from theoretical mass). $[\alpha]_D^{20}$ –25° (*c* 0.5, MeOH).

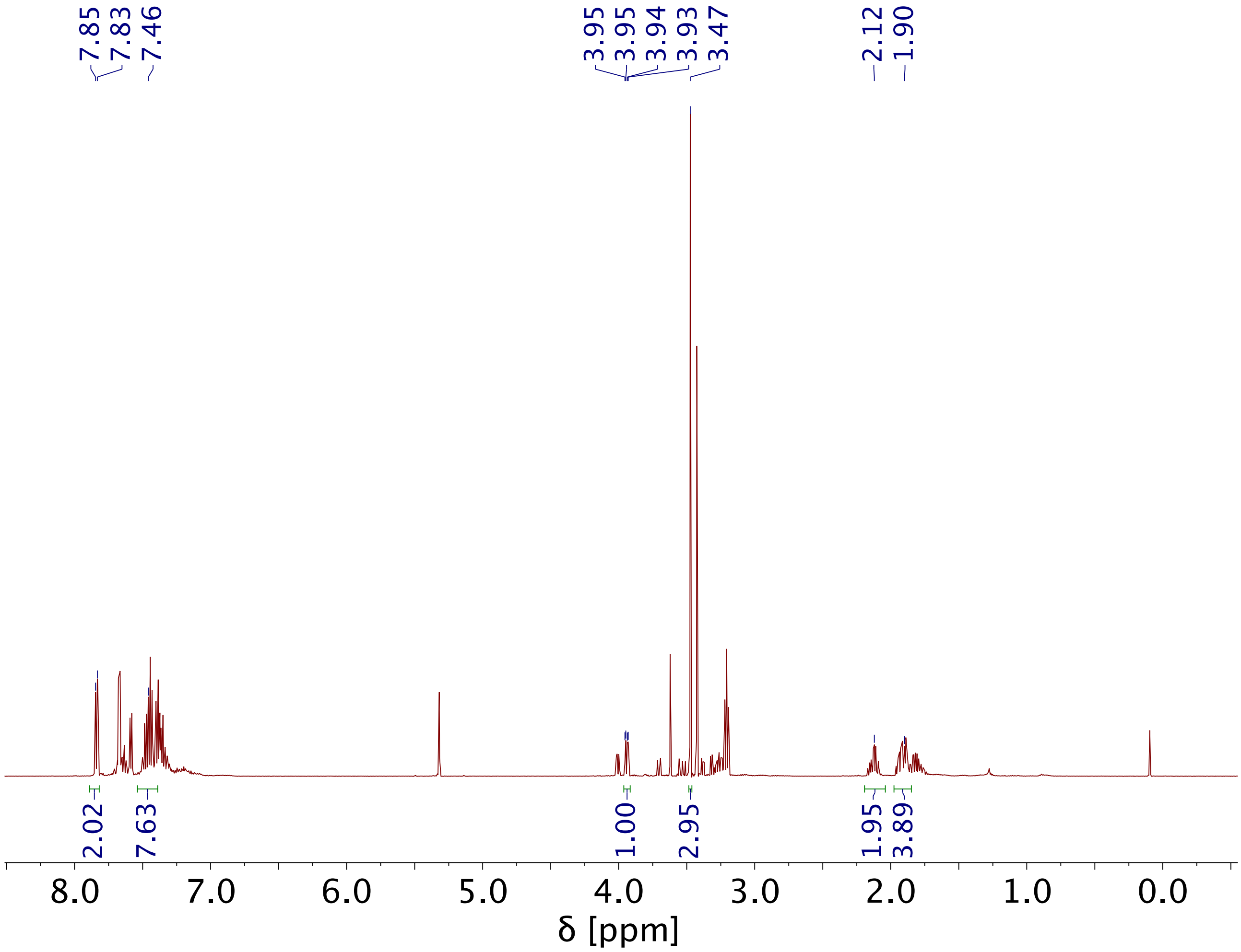


**Figure S11:** $^1$H NMR spectrum ($CD_2Cl_2$, 600 MHz) of $Ph_2Si(Cl)(pro)$.

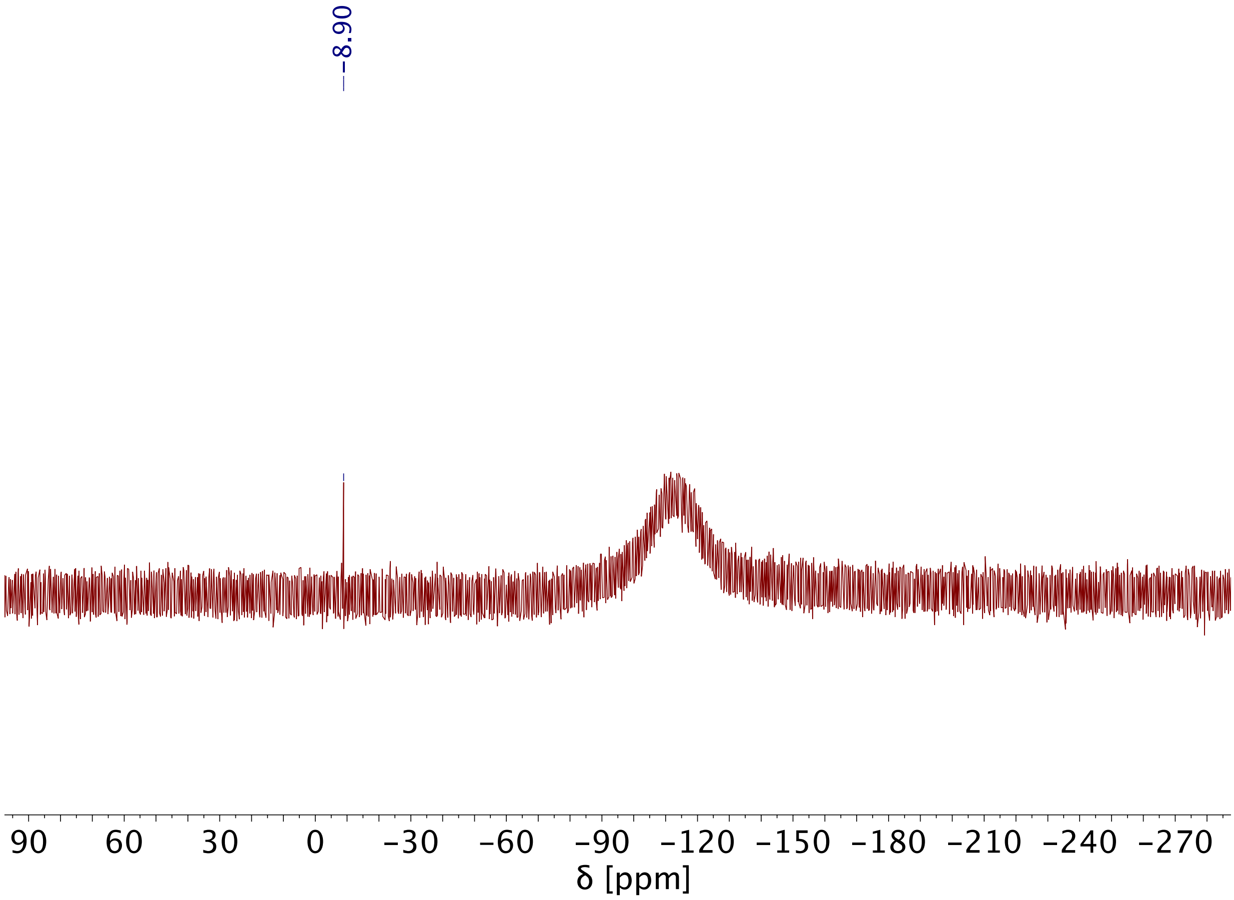


**Figure S12:** $^{29}$Si NMR spectrum ($CD_2Cl_2$, 119 MHz) of $Ph_2Si(Cl)(pro)$. The broad signal corresponds to Si in the glass NMR tube.

## 1.11. Procedure for the catalytic aminodefluorination reaction

$$\mathrm{Ar^F\text{-}F} + \mathrm{Ph_2Si(Cl)(NR_2)} \xrightarrow[\mathrm{CD_3CN}]{10\ \mathrm{mol\%}\ \mathrm{P}^n\mathrm{Bu_3}} \mathrm{Ar^F\text{-}NR_2} + \mathrm{Ph_2Si(Cl)F} + \mathrm{Ph_2SiF_2}$$

**S1,** $NR_2 = NEt_2$
**S3,** $NR_2$ = L-proline ester

The Ar–F (0.40 mmol, 1.0 equivalent) and $Ph_2Si(Cl)(NR_2)$ (0.44 mmol, 1.1 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. $P^nBu_3$ (10 µL, 0.10 equivalent) was added and the system was heated at 60 °C for the synthesis of **12** and **13**, 80 °C for **14** and **15**. The reaction mixture was analyzed by quantitative $^{19}$F NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

**N,N-diethyl-2,3,5,6-tetrafluoropyridin-4-amine (12):**[10] Yield of 75%. $^1$H NMR (600 MHz, $CD_3CN$): δ 3.43 (qt, $^3J_{HH}$ = 7.1 Hz, $^5J_{HF}$ = 1.6 Hz, 4H), 1.22 (t, $^3J_{HH}$ = 7.1 Hz, 6H). $^{19}$F NMR (565 MHz, $CD_3CN$): δ –96.66 (mc, 2F), –157.05 (mc, 2F). GC-MS(EI) $[C_9H_{10}N_2F_4]^{+\circ}$ 222.07810 *m/z* (2.85 ppm deviation from theoretical mass); $[C_8H_7F_4N_2]^{+\circ}$ 207.05472 *m/z*; $[C_7H_5F_4N_2]^{+\circ}$ 193.03912 *m/z*.

**Methyl 2,3,5,6-tetrafluoropyrid-4-ylpyrrolidine-2-carboxylate (13):** Yield of 88%. $^1$H NMR (500 MHz, $CD_3CN$): δ 4.83 (dq, *J* = 8.2, 3.5 Hz, 1H), 3.92 (dtt, *J* = 10.1, 6.7, 3.3 Hz, 1H), 3.88 – 3.84 (m, 1H), 3.73 (s, 3H), 2.32 (dq, *J* = 12.9, 7.6 Hz, 1H), 2.06 (dq, *J* = 12.2, 6.1 Hz, 1H), 1.95 (p, *J* = 6.8 Hz, 2H). $^{19}$F NMR (565 MHz, $CD_3CN$): δ –97.03 (mc, 2F), –160.09 (mc, 2F). $^{13}$C (151 MHz, $CD_3CN$): δ 62.88 (t, *J* = 5.4 Hz, *C*H), 52.25 (t, *J* = 6.6 Hz, *C*H$_2$), 52.06 (s, *C*H$_3$), 30.28 (bs, *C*H$_2$), 23.58 (t, *J* = 2.0 Hz, *C*H$_2$). GC-MS(EI) $[C_{11}H_{10}N_2O_2F_4]^{+\circ}$ 278.06880 *m/z* (5.41 ppm deviation from theoretical mass); $[C_9H_7N_2F_4]^{+\circ}$ 219.05493 *m/z*; ; $[C_6HN_2F_4]^{+\circ}$ 177.00778 *m/z*. $[\alpha]_D^{20}$ –65 (*c* 2.5, $CH_2Cl_2$).

**4-(diethylamino)-2,3,5,6-tetrafluorobenzonitrile (14):**[10] Yield of 82%. $^1$H NMR (600 MHz, $CD_3CN$): δ 3.37 (qt, $^3J_{HH}$ = 7.1 Hz, $^5J_{HF}$ = 1.4 Hz, 4H), 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 6H). $^{19}$F NMR (565 MHz, $CD_3CN$): δ –137.99 (mc, 2F), –151.34 (mc, 2F).

**N,N-diethyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)aniline (15):**[10] Yield of 50%. $^1$H NMR (600 MHz, $CD_3CN$): δ 3.33 (qt, $^3J_{HH}$ = 7.1 Hz, $^5J_{HF}$ = 1.1 Hz, 4H), 1.13 (t, $^3J_{HH}$ = 7.1 Hz, 6H). $^{19}$F NMR (565 MHz, $CD_3CN$): δ –56.05 (t, *J* = 21.1 Hz), –145.49 (mc, 2F), –151.27 (mc, 2F).

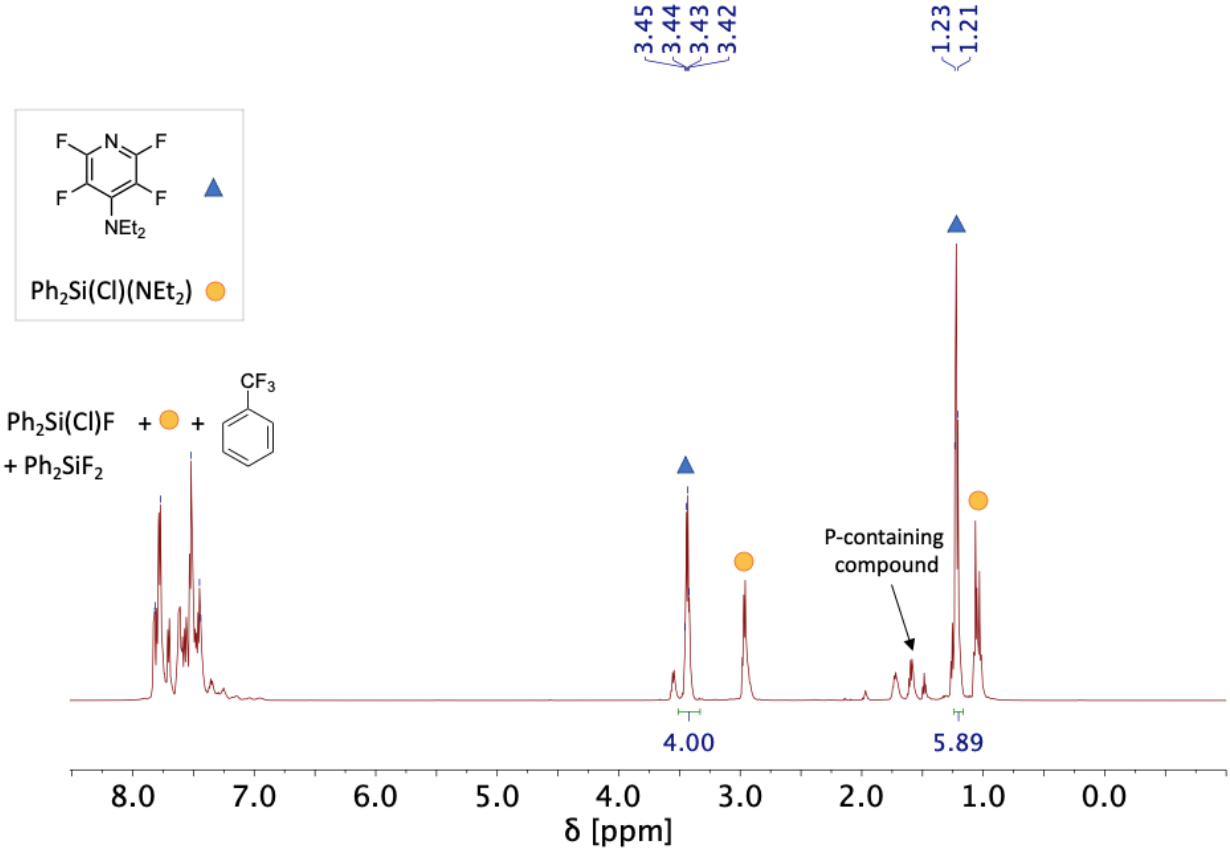


**Figure S13:** $^1$H NMR spectrum (600 MHz, CD$_3$CN) of N,N-diethyl-2,3,5,6-tetrafluoropyridin-4-amine (**12**) obtained after 18 hours at 60 °C, using the general procedure in section 1.11.

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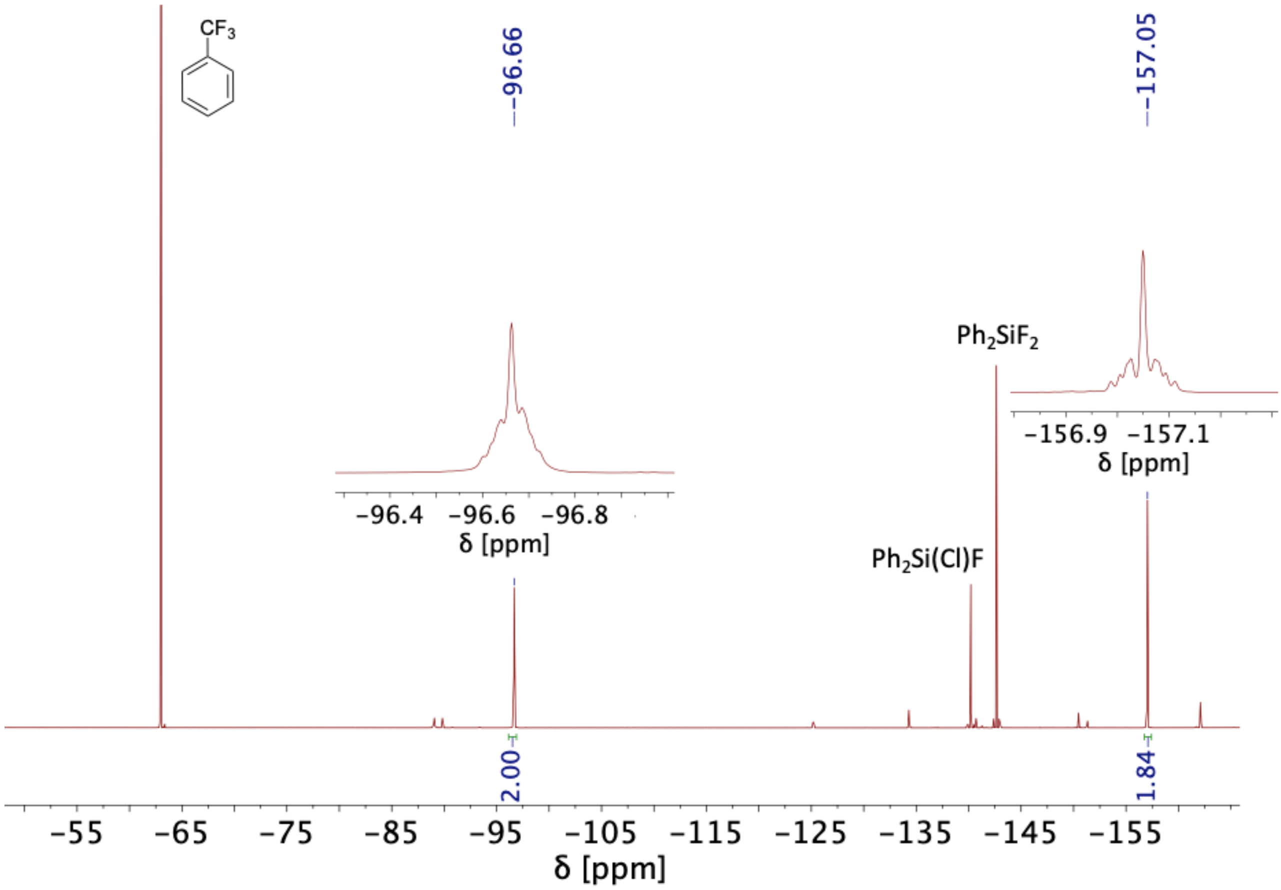


**Figure S14:** $^{19}$F NMR spectrum (565 MHz, $CD_3CN$) of N,N-diethyl-2,3,5,6-tetrafluoropyridin-4-amine (**12**) obtained after 18 hours at 60 °C, using the general procedure in section 1.11.

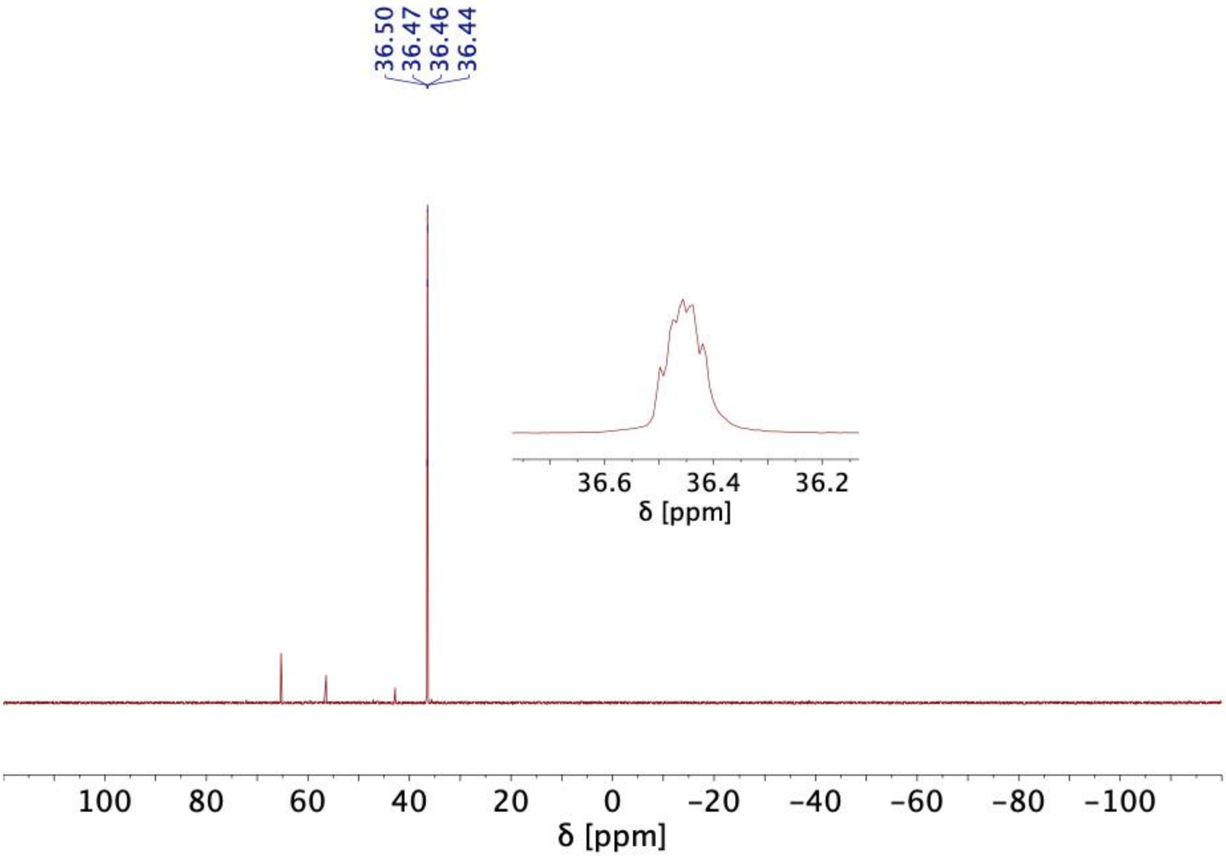


**Figure S15:** {$^1$H}$^{31}$P NMR spectrum (243 MHz, $CD_3CN$) of the reaction mixture obtained after 18 hours at 60 °C for the synthesis of N,N-diethyl-2,3,5,6-tetrafluoropyridin-4-amine (**12**), using the general procedure in section 1.11.

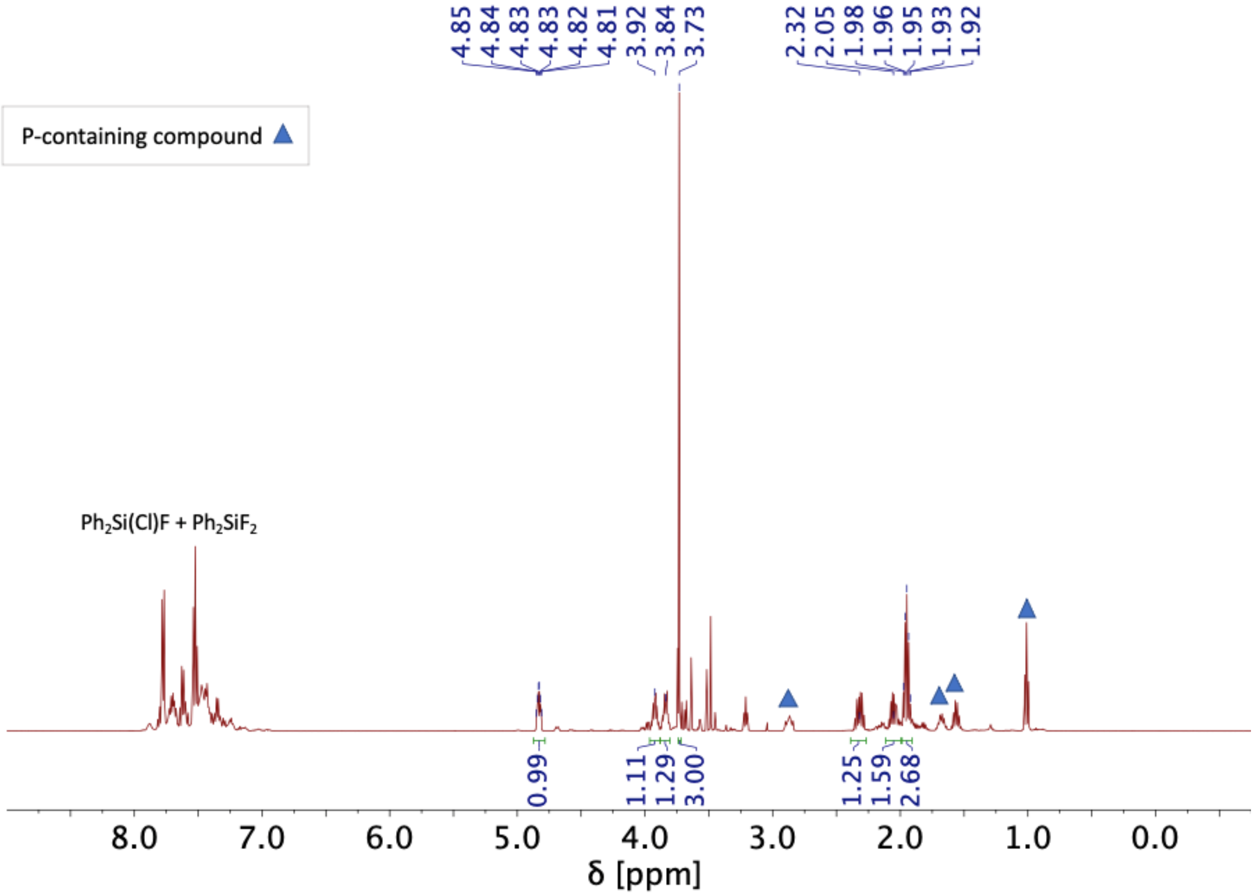


**Figure S16:** $^1$H NMR spectrum (600 MHz, $CD_3CN$) of **13** obtained after 18 hours at 60 °C, using the general procedure in section 1.11.

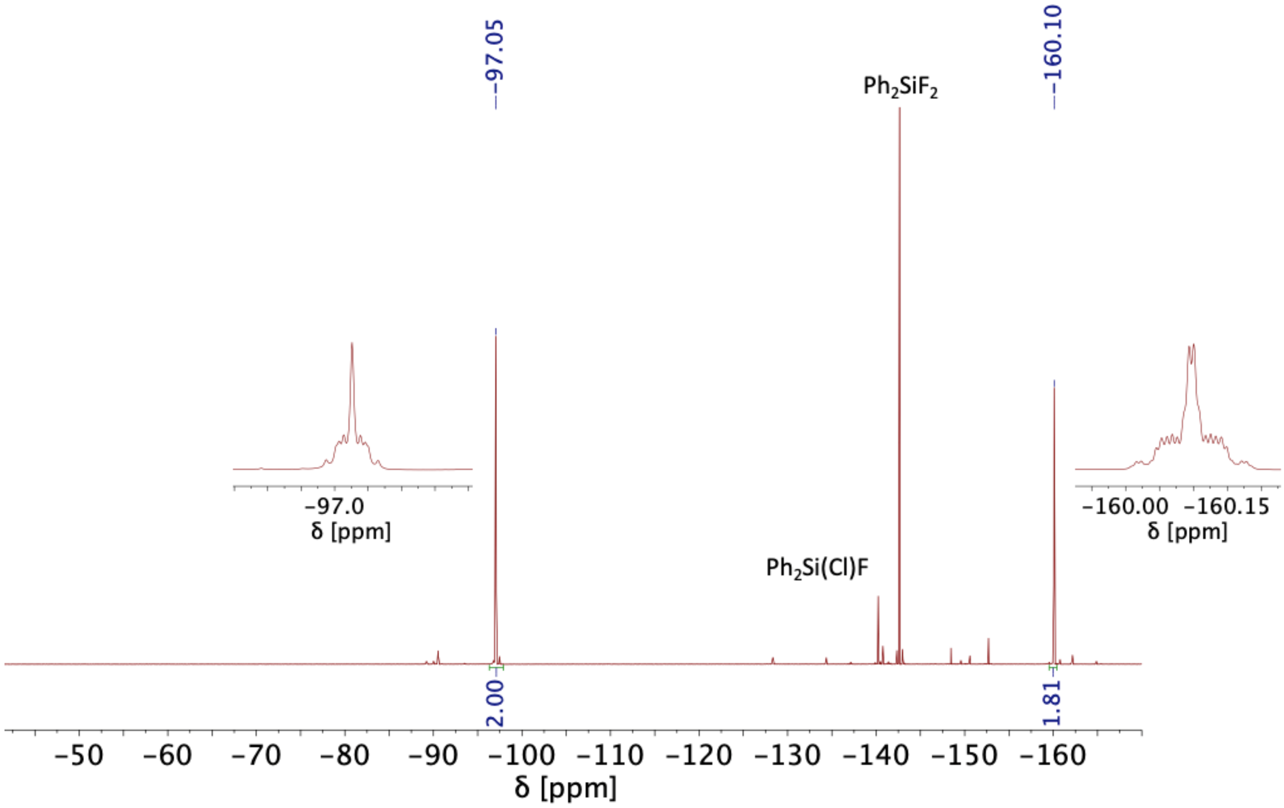


**Figure S17:** $^{19}$F NMR spectrum (471 MHz, $CD_3CN$) of **13** obtained after 18 hours at 60 °C, using the general procedure in section 1.11.

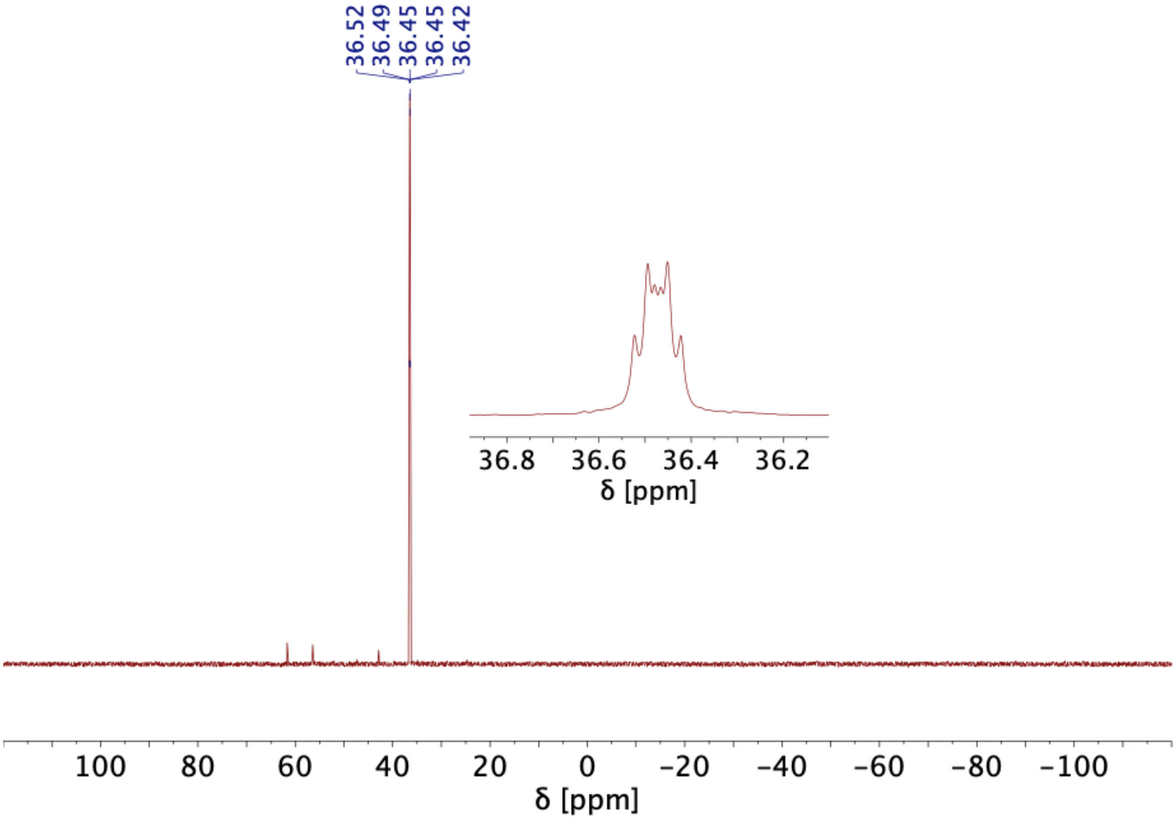


**Figure S18:** {$^1$H}$^{31}$P NMR spectrum (202 MHz, $CD_3CN$) of the reaction mixture obtained after 18 hours at 60 °C for the synthesis of **13**, using the general procedure in section 1.11.

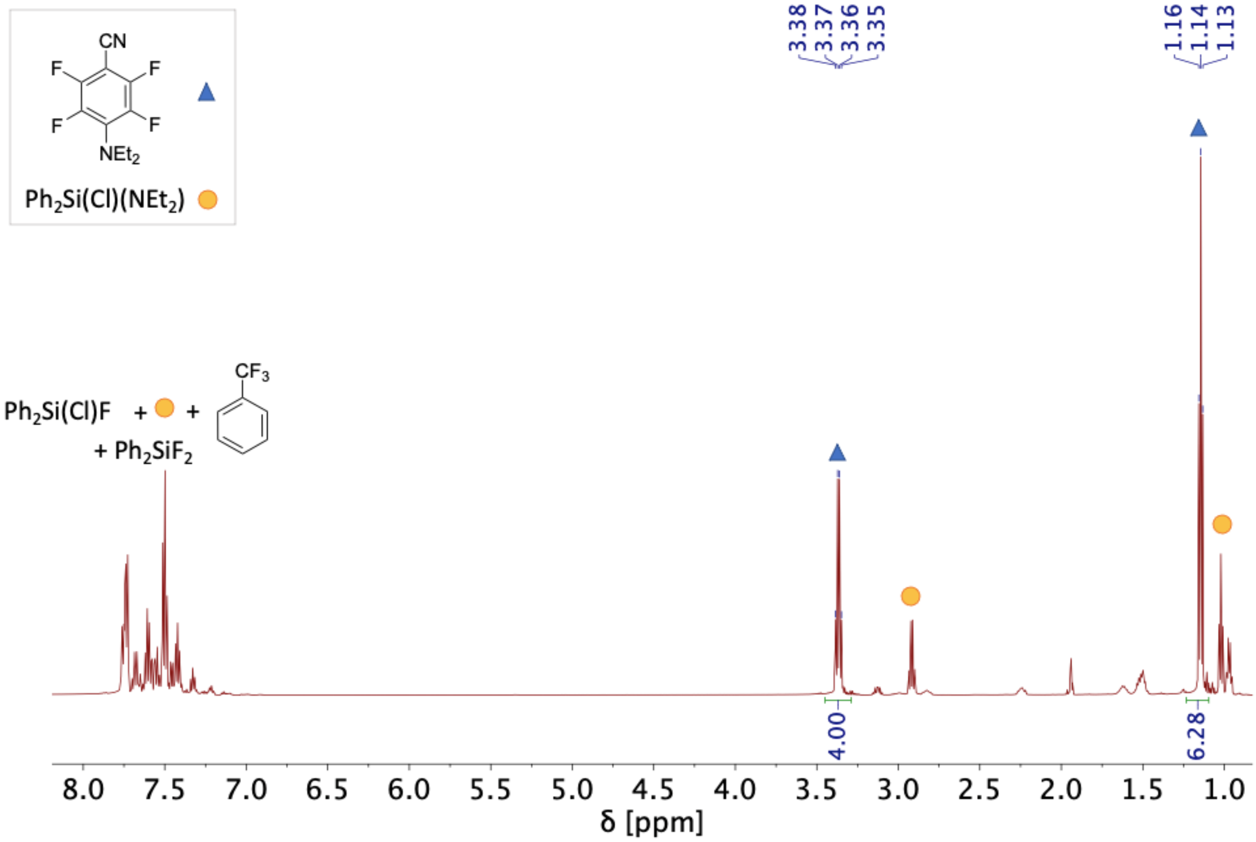


**Figure S19:** $^1$H NMR spectrum (600 MHz, $CD_3CN$) of **14** obtained after 4 days at 60 °C followed by 1 day at 80 °C, using the general procedure in section 1.11.

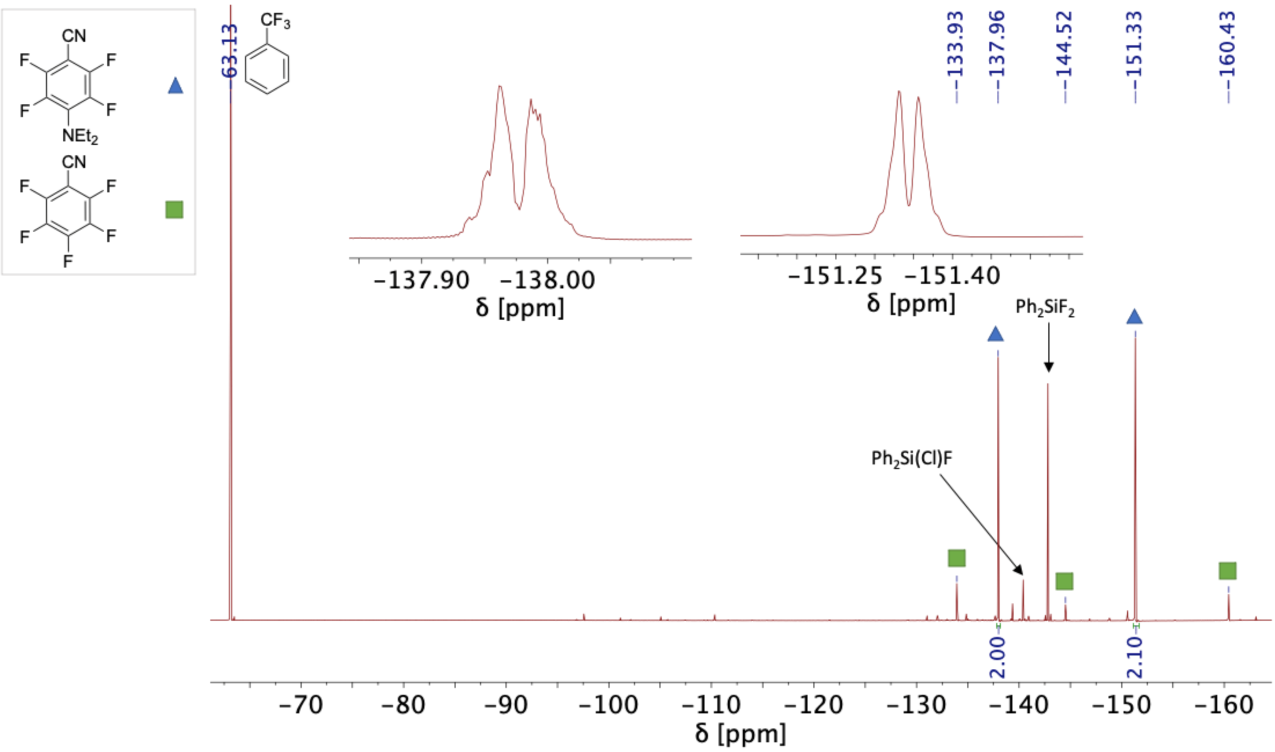


**Figure S20:** $^{19}$F NMR spectrum (471 MHz, CD$_3$CN) of **14** obtained after 4 days at 60 °C followed by 1 day at 80 °C, using the general procedure in section 1.11.

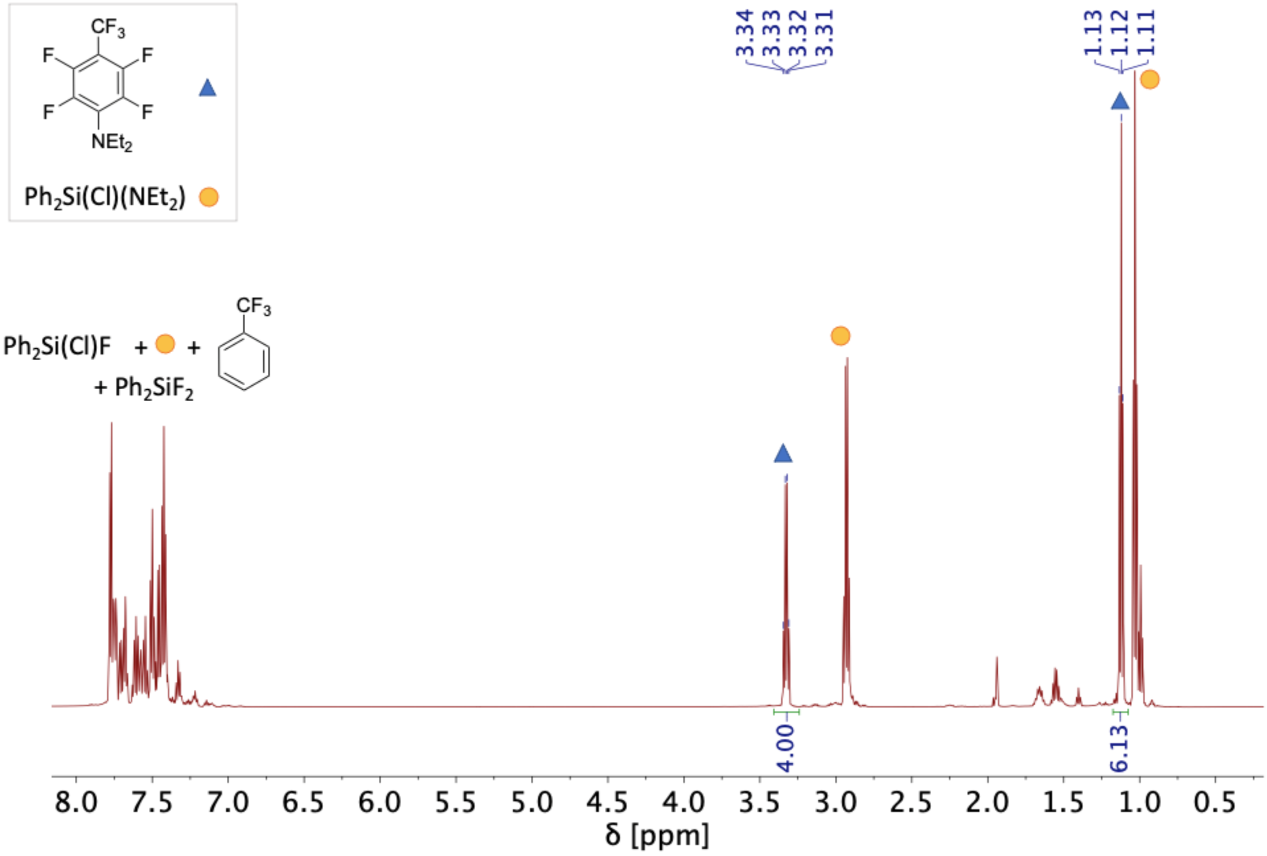


**Figure S21:** $^1$H NMR spectrum (600 MHz, $CD_3CN$) of **15** obtained after 4 days at 60 °C followed by 6 days at 80 °C, using the general procedure in section 1.11.

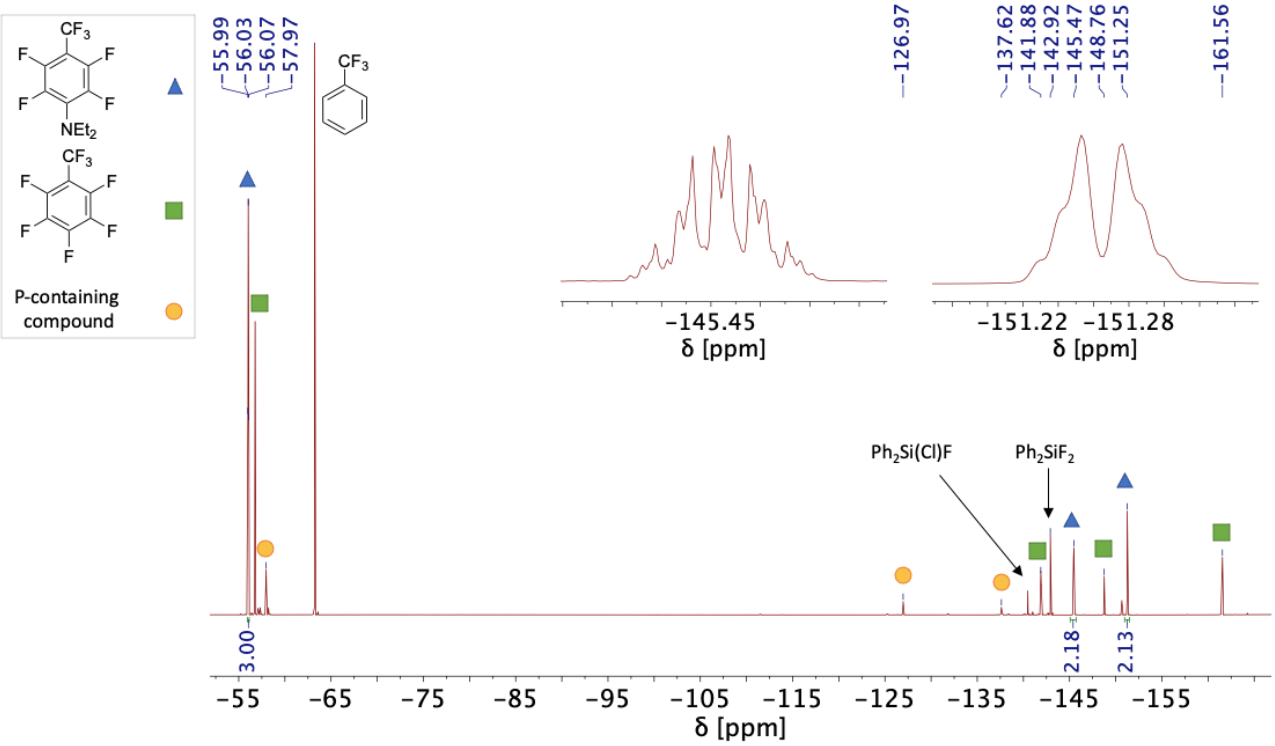
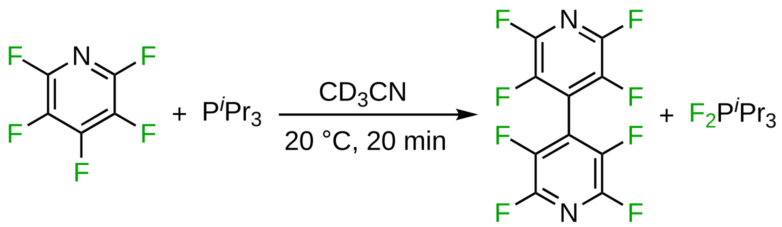


**Figure S22:** $^{19}$F NMR spectrum (471 MHz, $CD_3CN$) of **15** obtained after 4 days at 60 °C followed by 6 days at 80 °C, using the general procedure in section 1.11.

### 1.12. Procedure for the stoichiometric synthesis of 3



**1** **3**

Pentafluoropyridine (33 µL, 0.30 mmol, 3.0 equivalents) and P$^i$Pr$_3$ (19 µL, 0.10 mmol, 1.0 equivalent) were dissolved in 0.4 mL of CD$_3$CN and placed into a J-Young NMR tube. The progress of reaction was monitored by $^{19}$F NMR spectroscopy.

**Perfluoro 4,4'-bipyridine (3):**[11] Yield of 84%. $^{19}$F NMR (565 MHz, CD$_3$CN): δ –91.04 (mc, 4F), –139.84 (mc, 4F). GC-MS(EI) $[C_{10}N_2F_8]^{+\cdot}$ 299.99075 *m/z* (6.92 ppm deviation from theoretical mass).

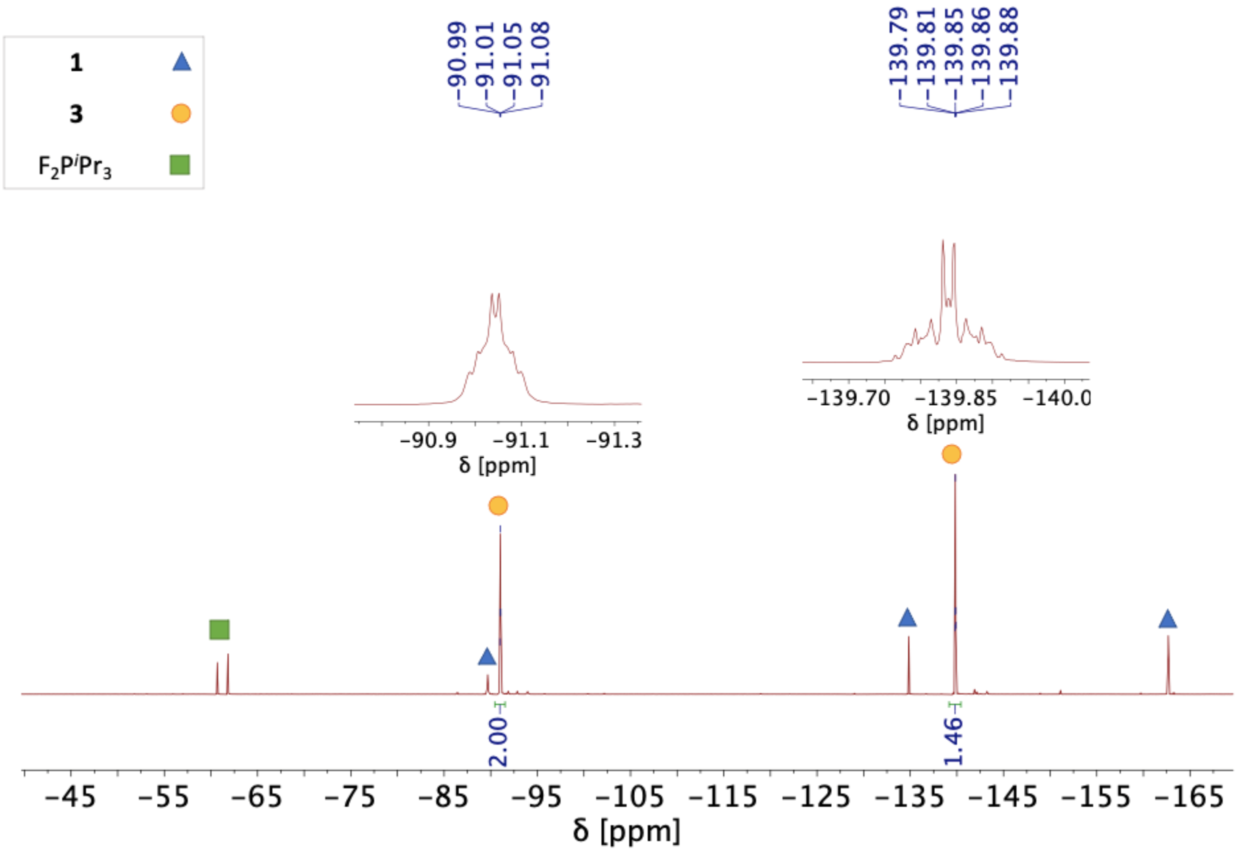
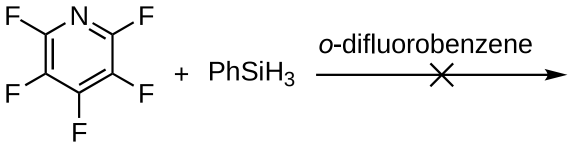


**Figure S23:** $^{19}$F NMR spectrum (565 MHz, CD$_3$CN) of **3** obtained after 30 minutes at 20 °C.

## 2. Mechanistic Studies

### 2.1. Reactivity test of $PhSiH_3$ and pentafluoropyridine (1)



**1**

Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and $PhSiH_3$ (49 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of *o*-difluorobenzene and placed into a J-Young NMR tube. The mixture was heated at 60 °C for 18 hours and monitored by $^{19}F$ NMR spectroscopy, which demonstrated that no reaction occurred.

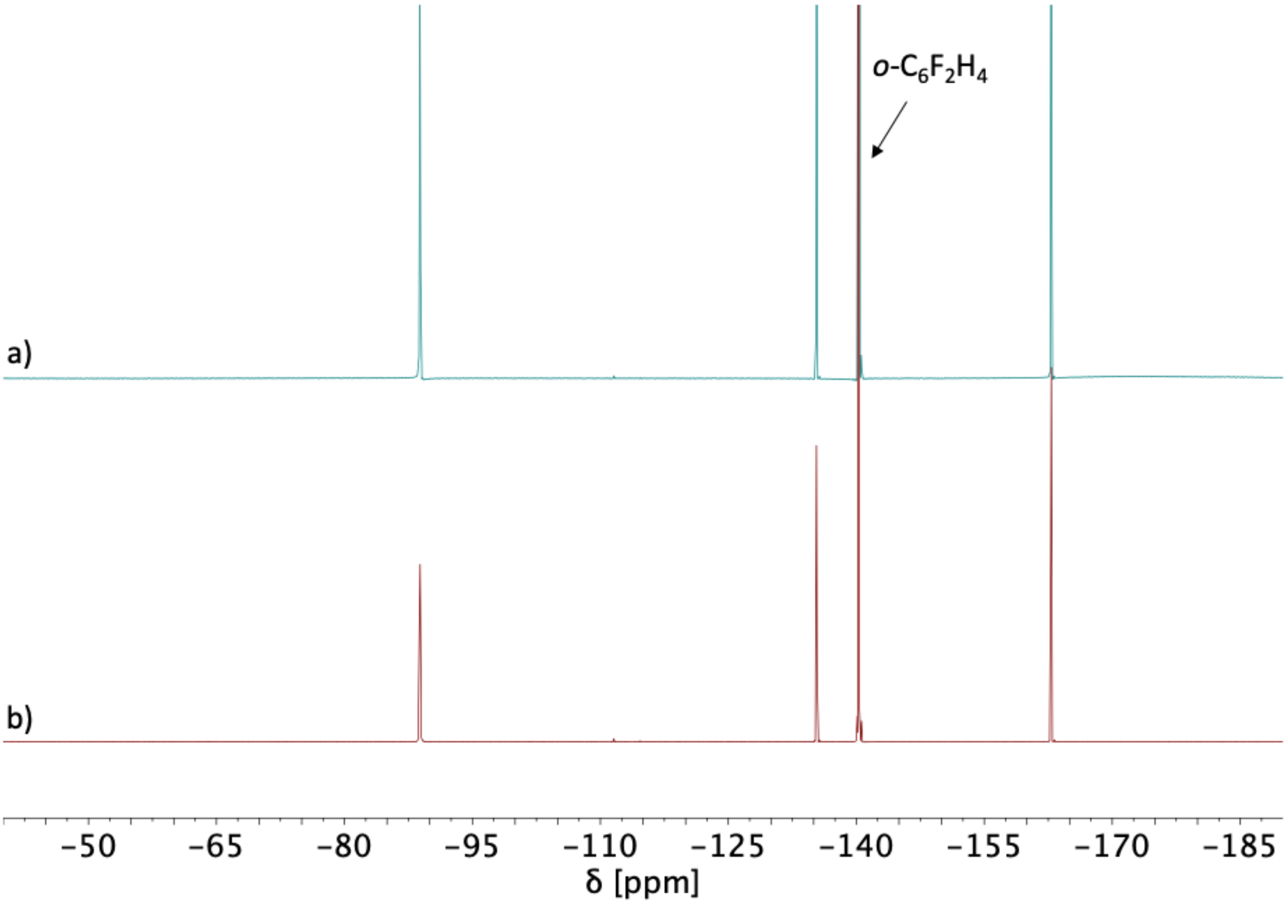
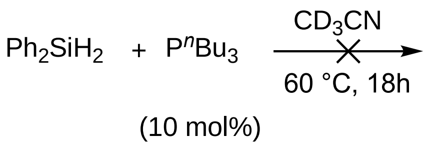


**Figure S24** $^{19}F$ NMR spectra (565 MHz, *o*-difluorobenzene) of the system at t = 0 (spectrum a)) and after 18 hours at 60 °C (spectrum b)).

### 2.2. Reactivity test of $Ph_2SiH_2$ and P*ⁿ*$Bu_3$



P*ⁿ*$Bu_3$ (10 µL, 0.040 mmol, 0.10 equivalent) and $Ph_2SiH_2$ (44 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. The mixture was heated at 60 °C for 18 hours and monitored by $^1H$ and $^{31}P$ NMR spectroscopy, which demonstrated that no reaction occurred.

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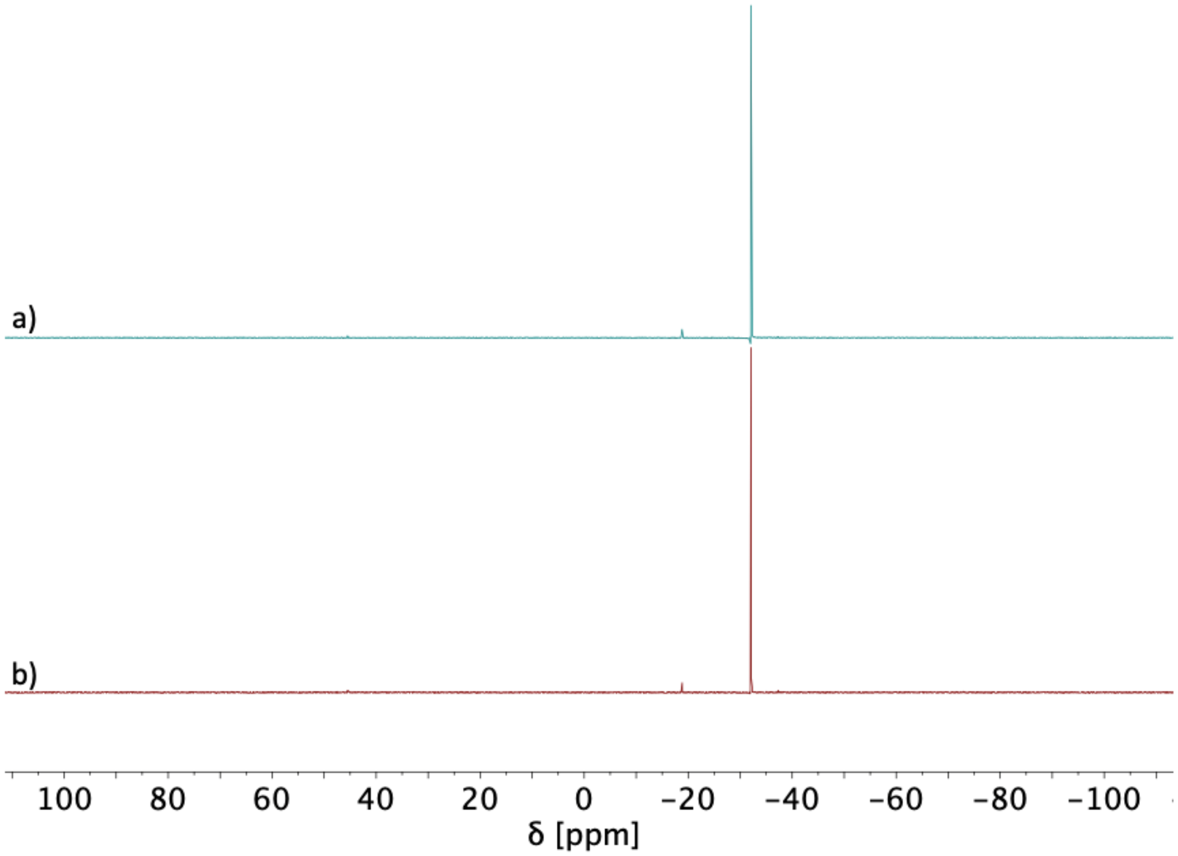
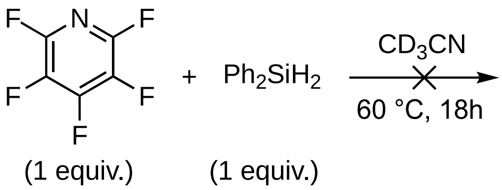


**Figure S25** $\{^1H\}^{31}P$ NMR (243 MHz, $CD_3CN$) spectra of the system at t = 0 (spectrum a)) and after 18 hours at 60 °C (spectrum b)).

### 2.3. Reactivity test of $Ph_2SiH_2$ and pentafluoropyridine



**1**

Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and $Ph_2SiH_2$ (44 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. The mixture was heated at 60 °C for 18 hours and monitored by $^1H$ and $^{19}F$ NMR spectroscopy, which demonstrated that no reaction occurred.

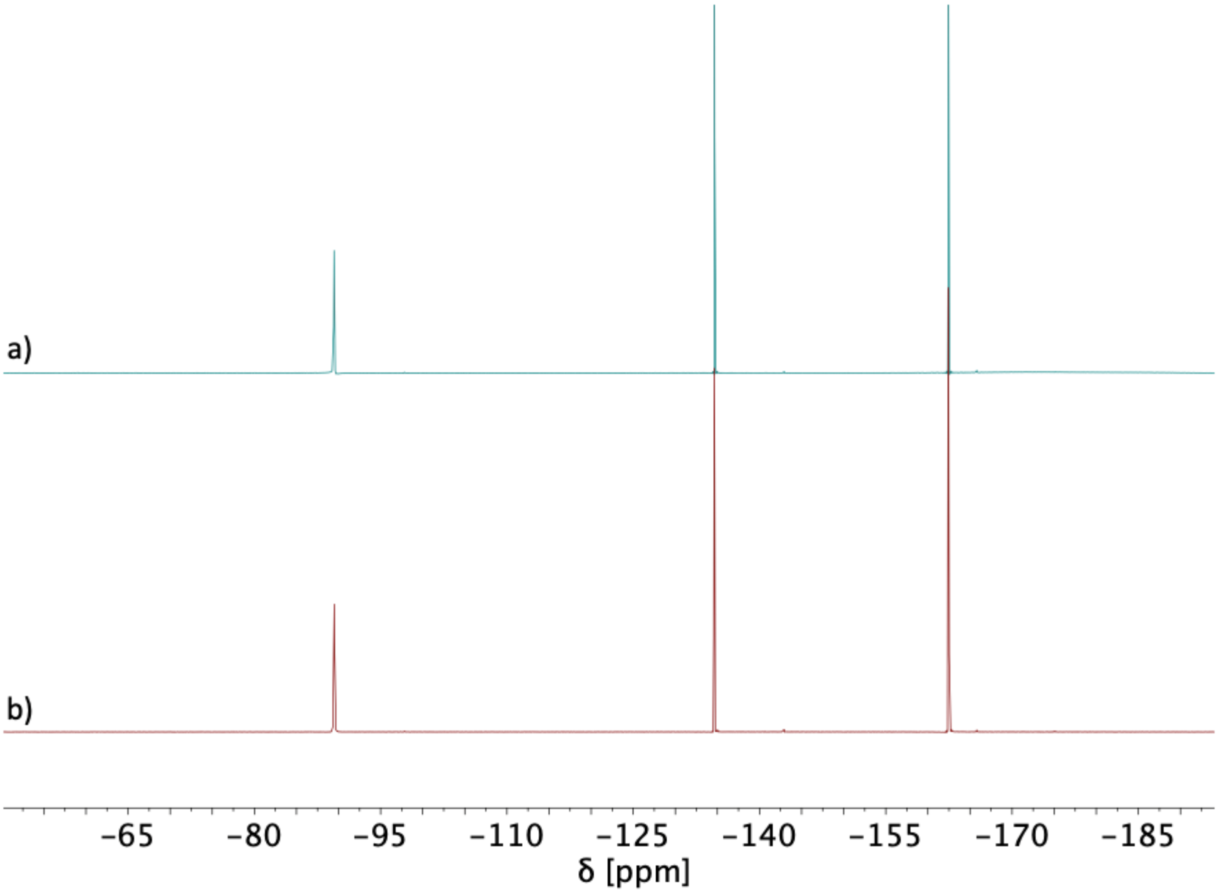
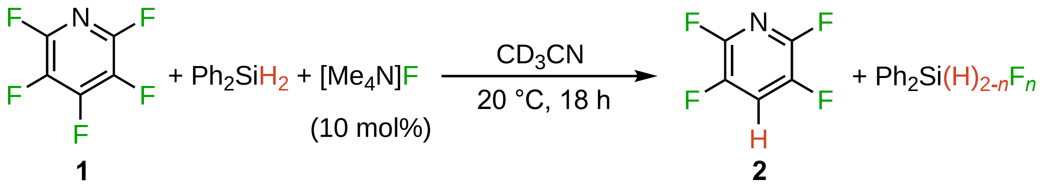


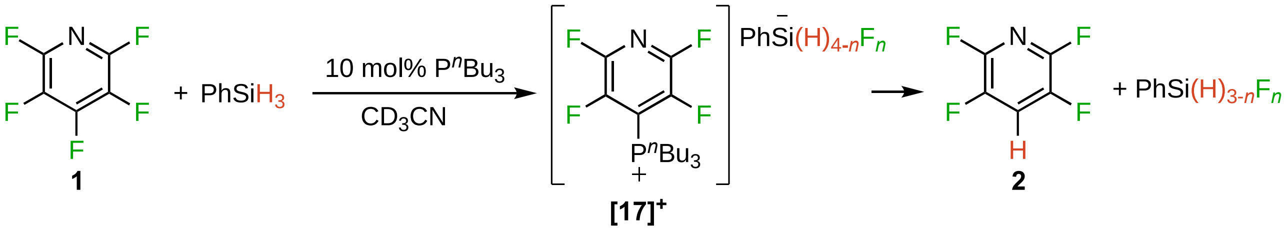
**Figure S26** $^{19}F$ NMR spectra (565 MHz, $CD_3CN$) of the system at t = 0 (spectrum a)) and after 18 hours at 60 °C (spectrum b)).

## 2.4. Reactivity test of $Ph_2SiH_2$ and pentafluoropyridine in the presence of $[Me_4N]F$



Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent), $Ph_2SiH_2$ (44 µL, 0.40 mmol, 1.0 equivalent) and anhydrous $Me_4NF$ (3.7 mg, 0.040 mmol, 0.10 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. The mixture was kept at 20 °C for 18 hours and monitored by $^1H$ and $^{19}F$ NMR spectroscopy. The yields are lower (19% after 20 minutes, 64% after 18 hours) than those of the reaction in the presence of $P^nBu_3$ (Table 1, entry 6, yield 93% after 20 minutes at 20 °C). Hence, direct hydrodefluorination of **1** by catalytic hydrosilicate anions, formed *in situ* by reaction of **1** with $P^nBu_3$, is possible, but significantly slower than hydrodefluorination through a phosphine-mediated pathway.

## 2.5. Characterisation of phosphonium salt [17][$PhSi(H)_{4-n}F_n$]



Pentafluoropyridine (44 µL, 0.40 mmol, 1.0 equivalent) and $PhSiH_3$ (50 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of the tested solvent and placed into a J-Young NMR tube. $P^nBu_3$ (9.9 µL, 0.10 mmol) was added and the progress of the reaction was monitored after 1 hour at 20 °C and 2 hours at 60 °C. The reaction mixture was analysed by $^1H$, $^{31}P$ and quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

The $^{31}P$ NMR spectrum showed the clean conversion of $P^nBu_3$ into a new species **[17]$^+$** after 1 hour at 20 °C.

**[17]$^+$**: $^1H$ NMR (600 MHz, $CD_3CN$): δ 2.68 (td, *J* = 12.7, 8.4 Hz, 6H), 1.69 – 1.59 (m, 6H), 1.54 (h, *J* = 7.1 Hz, 6H), 0.99 (t, $^3J_{HH}$ = 7.3 Hz, 9H). {$^1H$}$^{31}P$ NMR (243 MHz, $CD_3CN$): δ 38.11 (mc, 1P). $^{19}F$ NMR (565 MHz, $CD_3CN$): δ –88.48 (mc, 2F), –130.32 (mc, 2F).

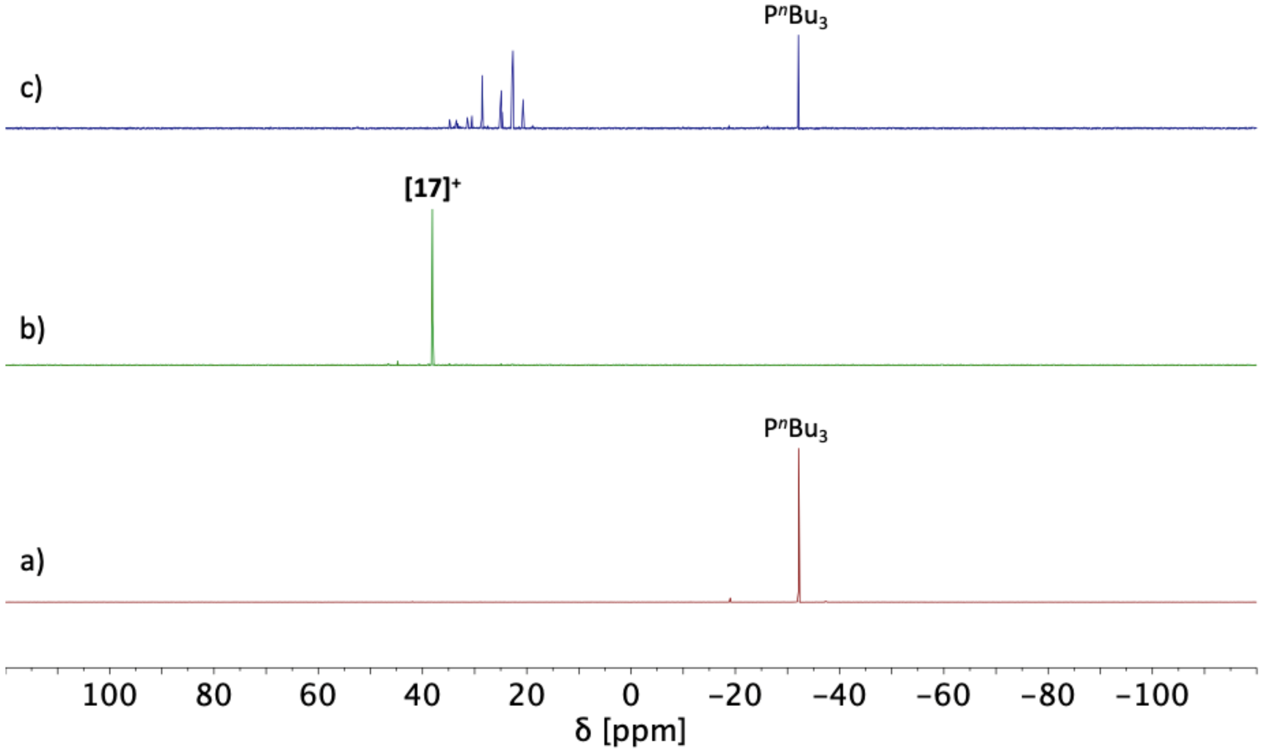


**Figure S27** {$^1$H}$^{31}$P NMR (243 MHz, CD$_3$CN) spectra of the system at t = 0 (spectrum a)), after 1 hour at 20 °C (spectrum b)) and after 2 hours at 60 °C (spectrum c)).

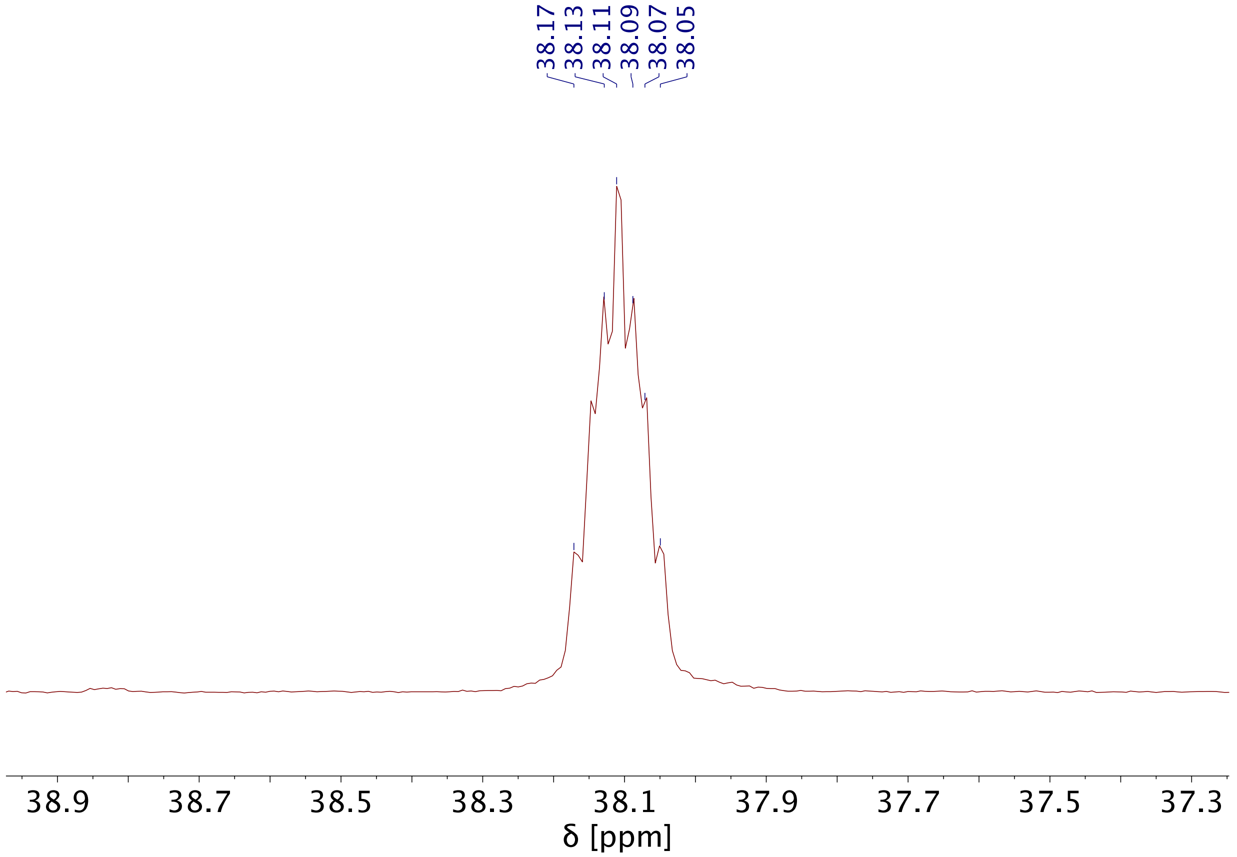


**Figure S28** {$^1$H}$^{31}$P NMR (243 MHz, CD$_3$CN) spectrum of the system after 1 hour at 20 °C (species **[17]$^+$**).

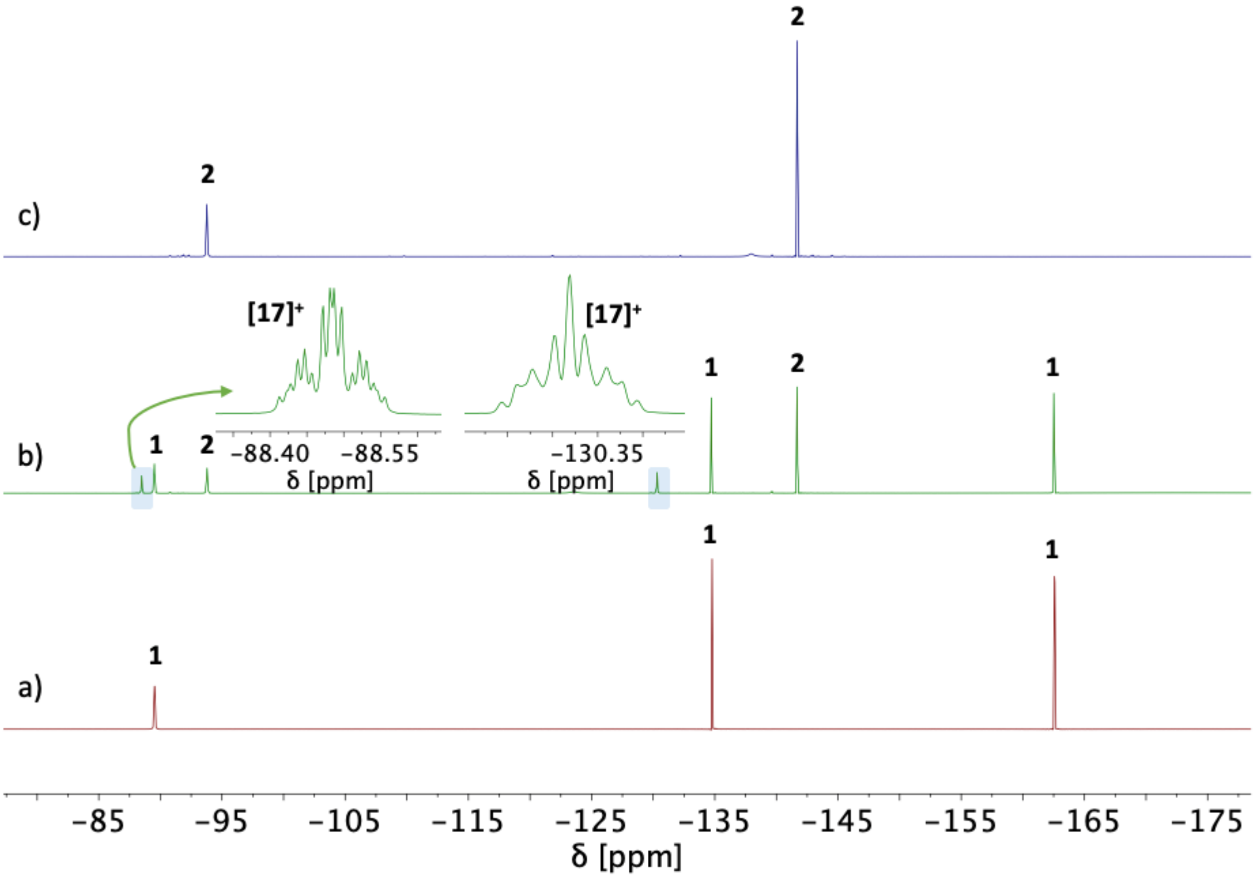


**Figure S29** $^{19}$F NMR (565 MHz, $CD_3CN$) spectra of the system at t = 0 (spectrum a)), after 1 hour at 20 °C (spectrum b)) and after 2 hours at 60 °C (spectrum c)).

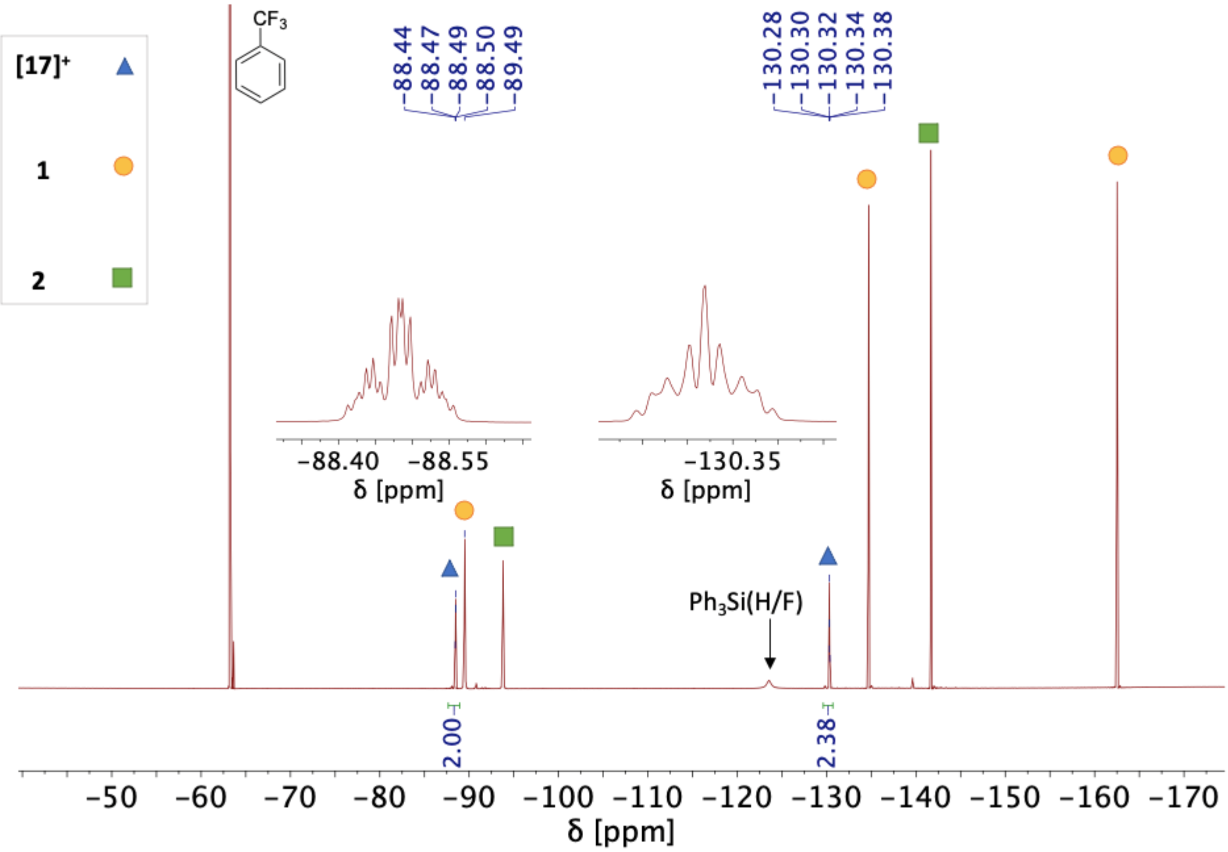


**Figure S30** $^{19}$F NMR (565 MHz, $CD_3CN$) spectrum of the system after 1 hour at 20 °C.

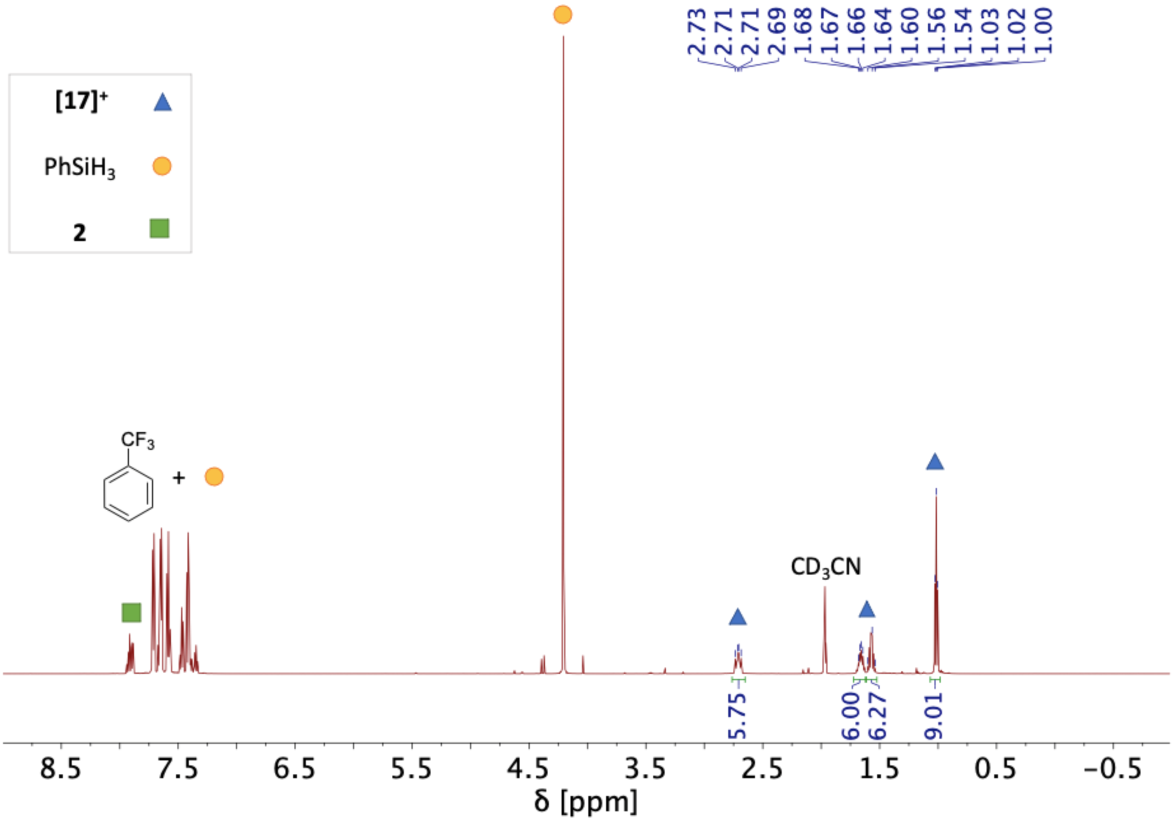
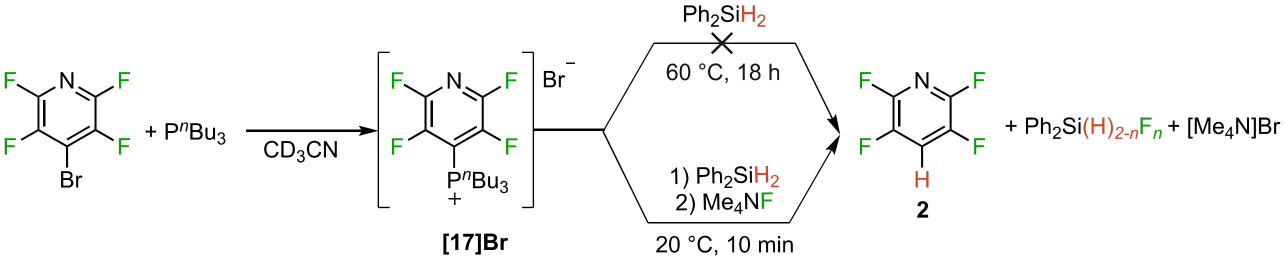


**Figure S31** $^1$H NMR (600 MHz, $CD_3CN$) spectrum of the system after 1 hour at 20 °C (species **[17]**$^+$).

### 2.6. Characterisation and reactivity of phosphonium salt [17]Br



Pentafluoropyridine (22 µL, 0.20 mmol, 1.0 equivalent) and P$^n$Bu$_3$ (49 µL, 0.20 mmol, 1.0 equivalent) were dissolved in 0.4 mL of CD$_3$CN and placed into a J-Young NMR tube. The mixture turned immediately brown and $^1$H, $^{19}$F and $^{31}$P NMR analyses showed the formation of **[17]Br**. Heating the system at 40 °C for 18 hours did not make any change in the reaction mixture. Ph$_2$SiH$_2$ (37 µL, 0.20 mmol, 1.0 equivalent) was added and the system was heated at 40 °C for other 18 hours. $^1$H, $^{19}$F and $^{31}$P NMR analyses demonstrated that no further reaction occurred. The addition of anhydrous [Me$_4$N]F (20 mg, 0.20 mmol, 1.0 equivalent) induced the formation of a white solid corresponding to [Me$_4$N]Br, **2**, fluorosilane Ph$_2$Si(H)$_{2\text{-}n}$F$_n$ and some unreacted **[17]Br**.

**[17]Br:** $^1$H NMR (500 MHz, CD$_3$CN): δ 2.92 (td, *J* = 13.0, 8.5 Hz, 6H), 1.66 (dq, *J* = 16.5, 8.5 Hz, 6H), 1.52 (h, *J* = 7.3 Hz, 6H), 0.96 (t, *J* = 7.3 Hz, 9H). {$^1$H}$^{31}$P NMR (202 MHz, CD$_3$CN): δ 37.87 (mc, 1P). $^{19}$F NMR (471 MHz, CD$_3$CN): δ –89.23 (mc, 2F, *ortho*-F), –130.29 (mc, 2F, *meta*-F).

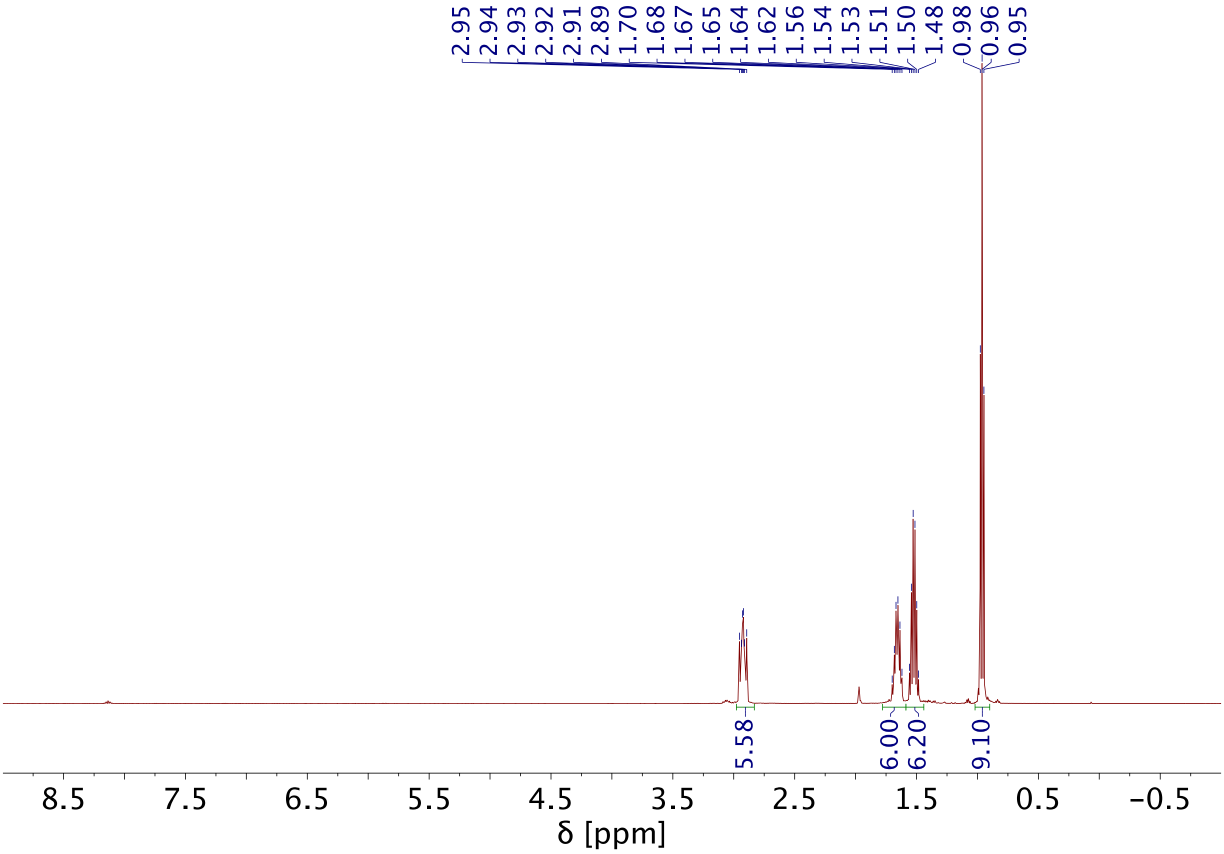


**Figure S32** $^1$H NMR (500 MHz, CD$_3$CN) spectrum of the system after 18 hours at 40 °C.

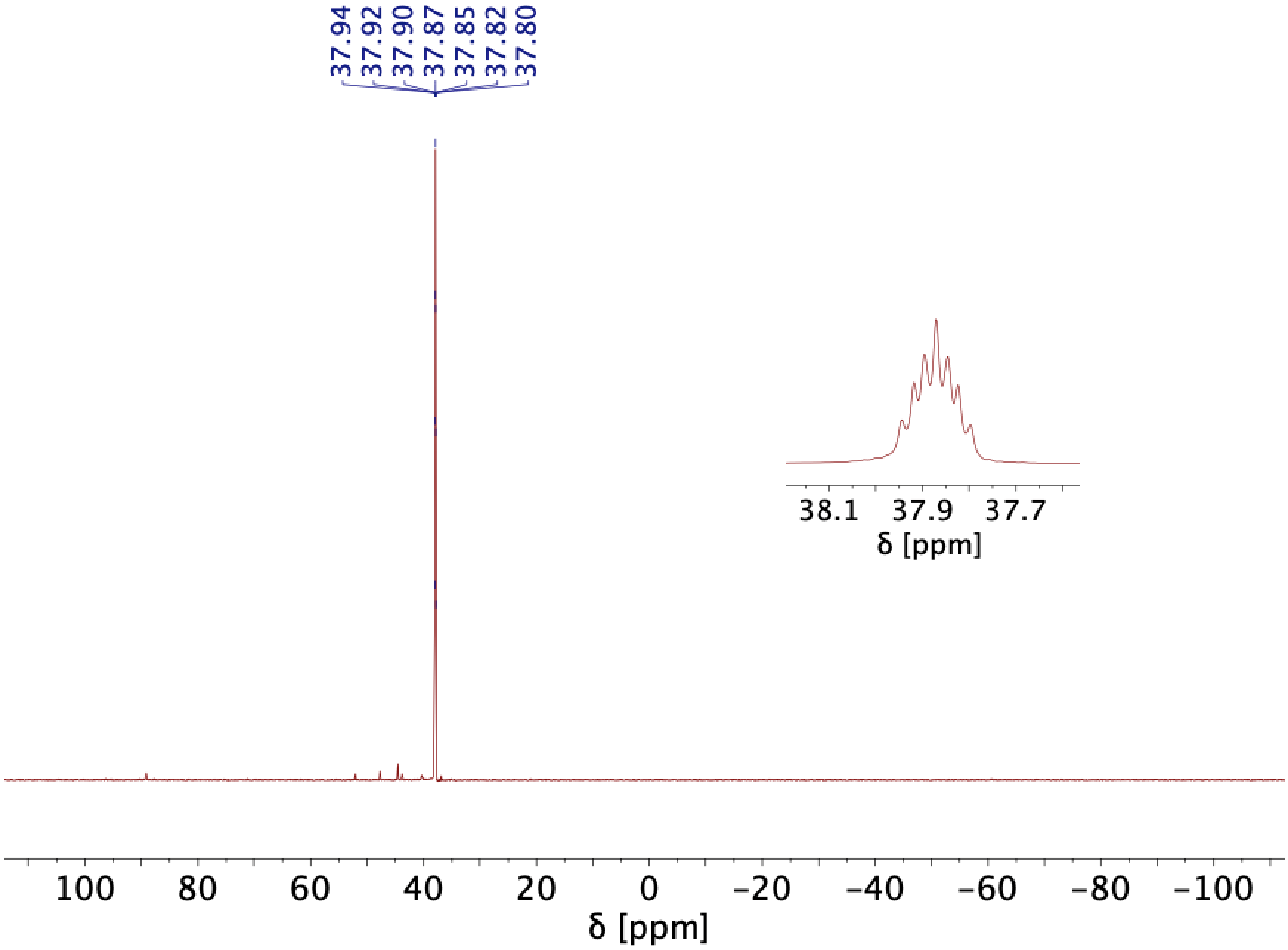


**Figure S33** {$^1$H}$^{31}$P NMR (202 MHz, $CD_3CN$) spectrum of the system after 18 hours at 40 °C.

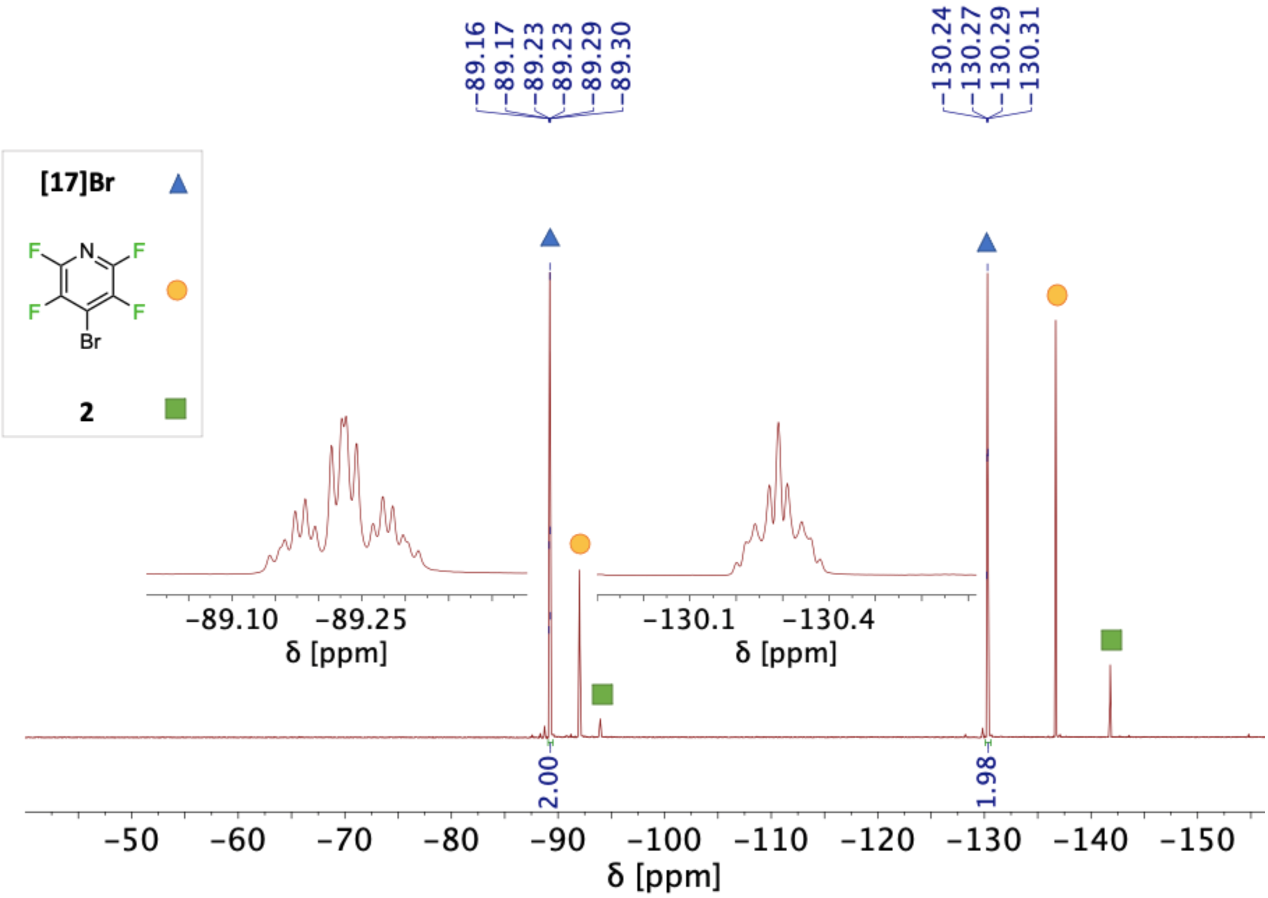


**Figure S34** $^{19}$F NMR (471 MHz, CD$_3$CN) spectrum of the system after 18 hours at 40 °C.

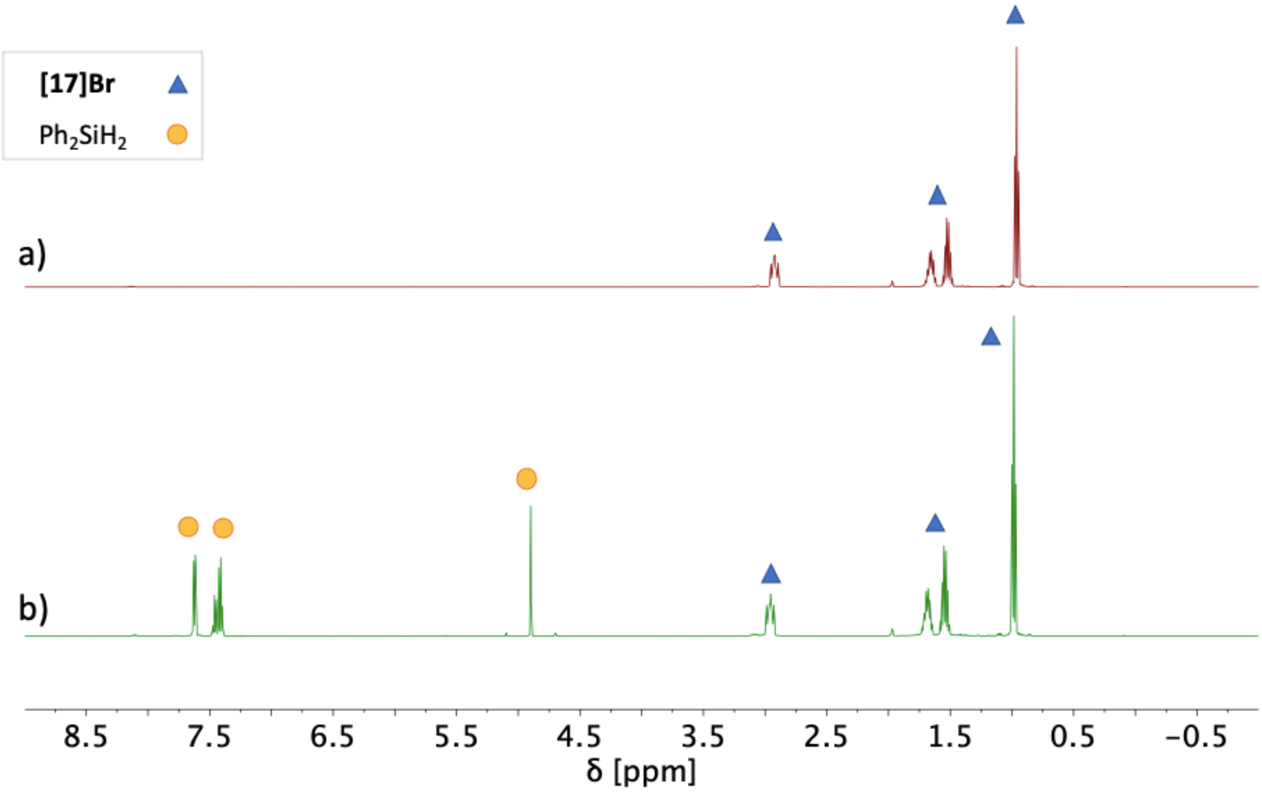


**Figure S35** $^1$H NMR (500 MHz, $CD_3CN$) spectra of the system after 18 hours at 40 °C (spectrum a)) and after 18 hours at 40 °C from the addition of $Ph_2SiH_2$ (spectrum b)).

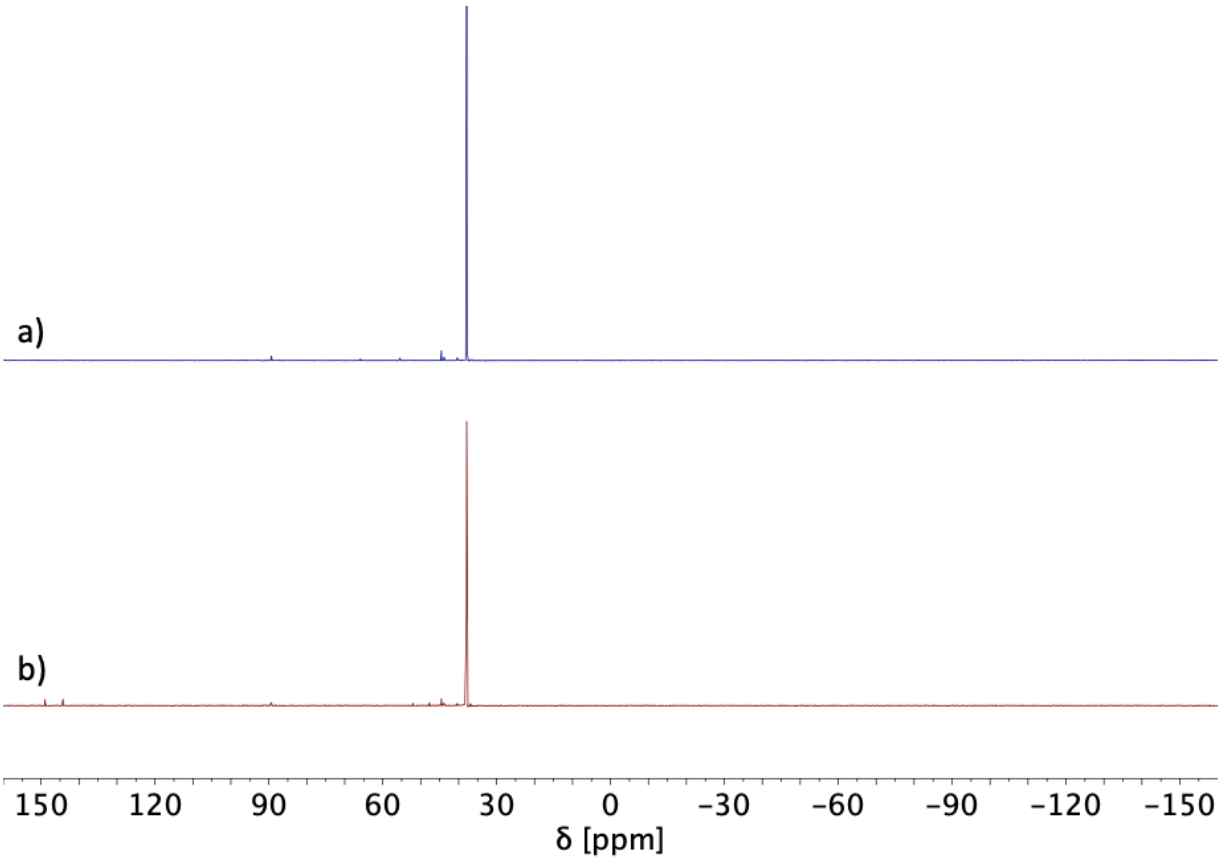


**Figure S36** $\{^1H\}^{31}P$ NMR (202 MHz, $CD_3CN$) spectra of the system after 18 hours at 40 °C (spectrum a)) and after 18 hours at 40 °C from the addition of $Ph_2SiH_2$ (spectrum b)).

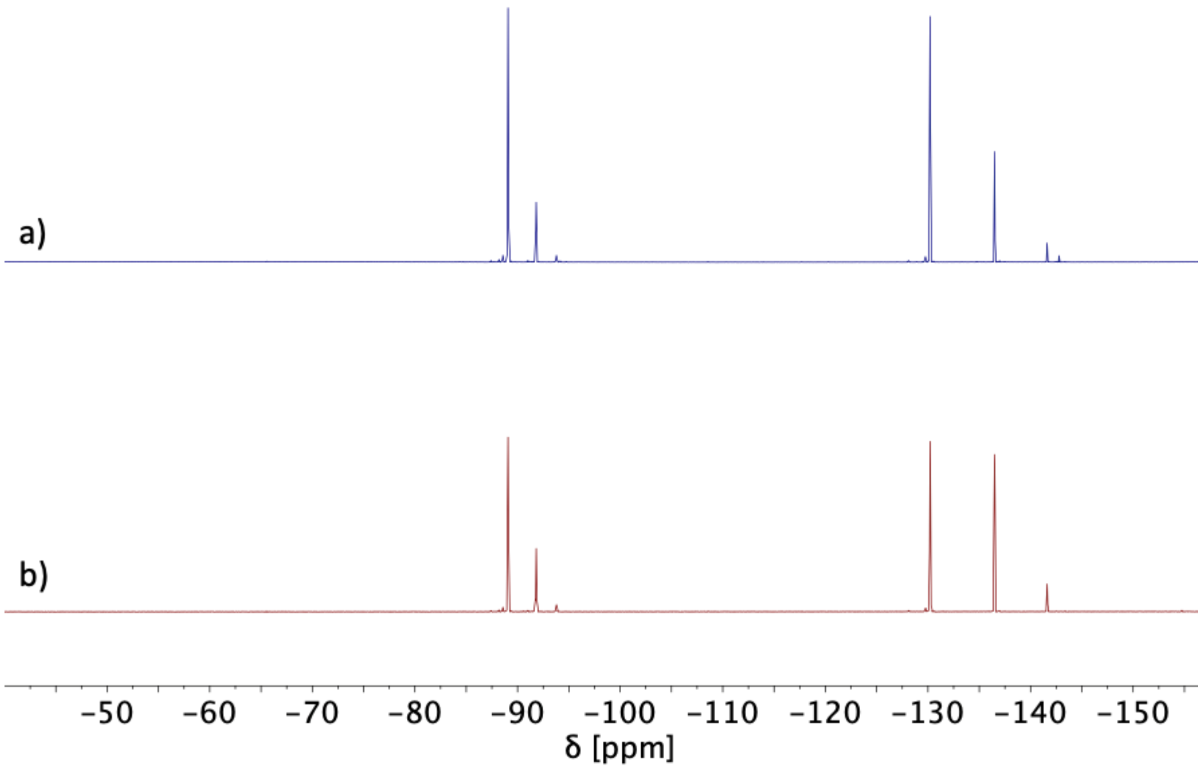


**Figure S37** $^{19}$F NMR (471 MHz, $CD_3CN$) spectra of the system after 18 hours at 40 °C (spectrum a)) and after 18 hours at 40 °C from the addition of $Ph_2SiH_2$ (spectrum b)).

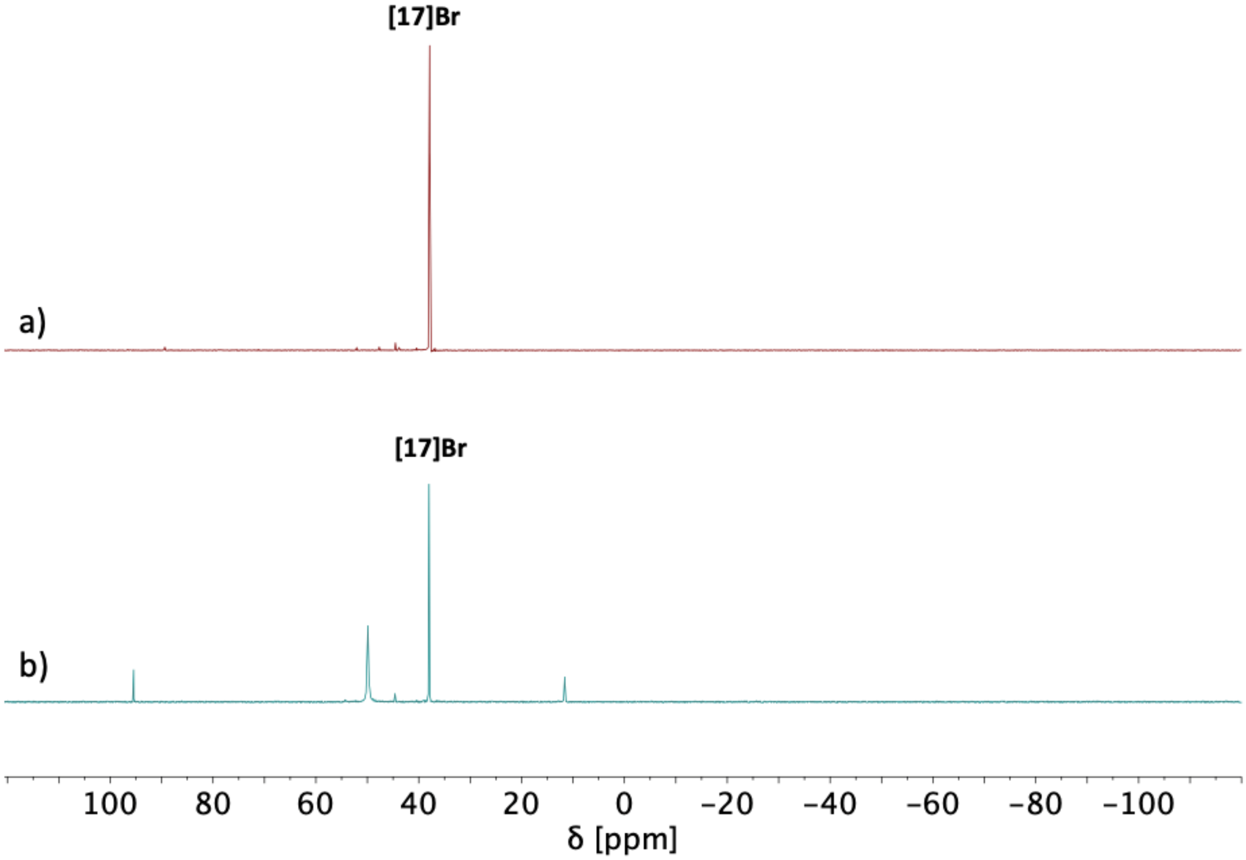


**Figure S38** {$^1$H}$^{31}$P NMR (202 MHz, $CD_3CN$) spectra of the system after 18 hours at 40 °C from the addition of $Ph_2SiH_2$ (spectrum a)) and after 10 minutes at 20 °C from the addition of $[Me_4N]F$ (spectrum b)).

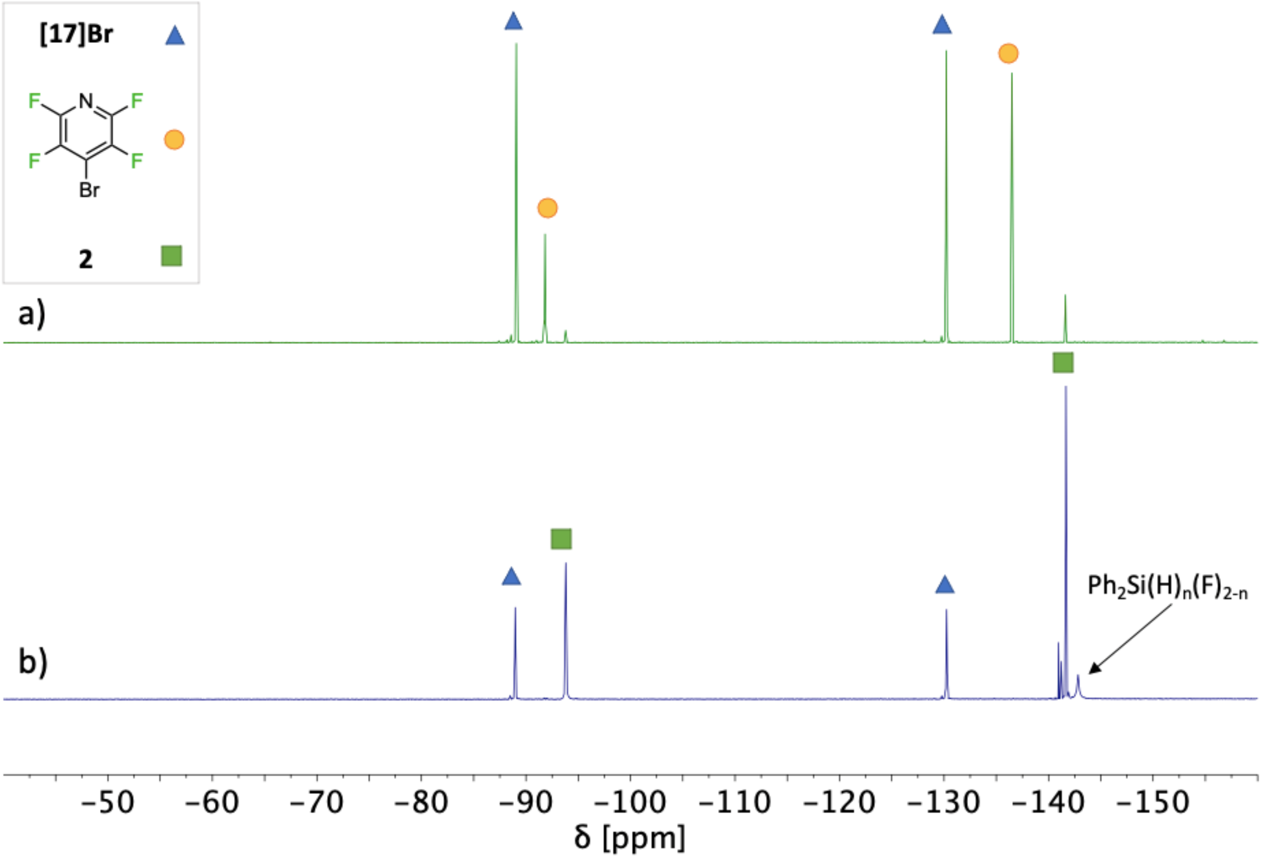
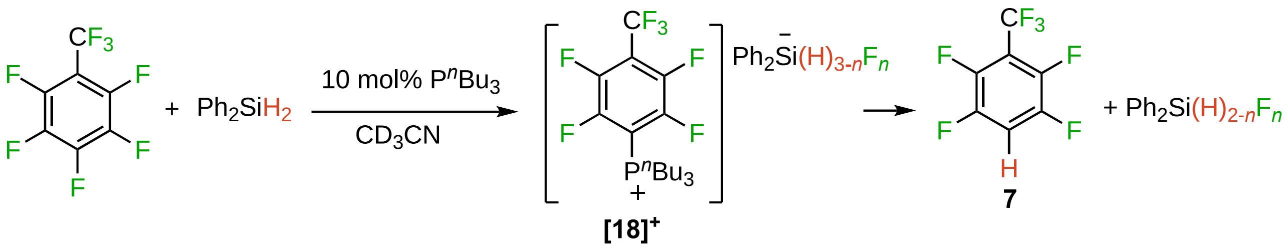


**Figure S39** $^{19}$F NMR (471 MHz, $CD_3CN$) spectra of the system after 18 hours at 40 °C from the addition of $Ph_2SiH_2$ (spectrum a)) and after 10 minutes at 20 °C from the addition of $[Me_4N]F$ (spectrum b)).

## 2.7. Observation of the phosphonium salt [18][$Ph_2Si(H)_{3\text{-}n}F_n$]



Perfluorotoluene (57 µL, 0.40 mmol, 1.0 equivalent) and $Ph_2SiH_2$ (74 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. $P^nBu_3$ (10 µL, 0.040 mmol, 0.10 equivalent) was added and the progress of reaction was monitored by $^1H$, $^{31}P$ and quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7. After 10 minutes at 20 °C from the start of the reaction an apparent septet (coupling constant of *ca.* 4 Hz) was observed in the $^{31}P$ NMR spectrum.

**[18]$^+$:** {$^1H$}$^{31}P$ NMR (202 MHz, $CD_3CN$): δ 38.10 ppm (mc, 1P). $^{19}F$ NMR (471 MHz, $CD_3CN$): δ –58.0 (t, $^4J_{FF}$ = 18 Hz, 3F), –126.8 (mc, 2F), –137.3 (mc, 2F). $^1H$ signals of **[18]$^+$** were not identified due to their low intensity.

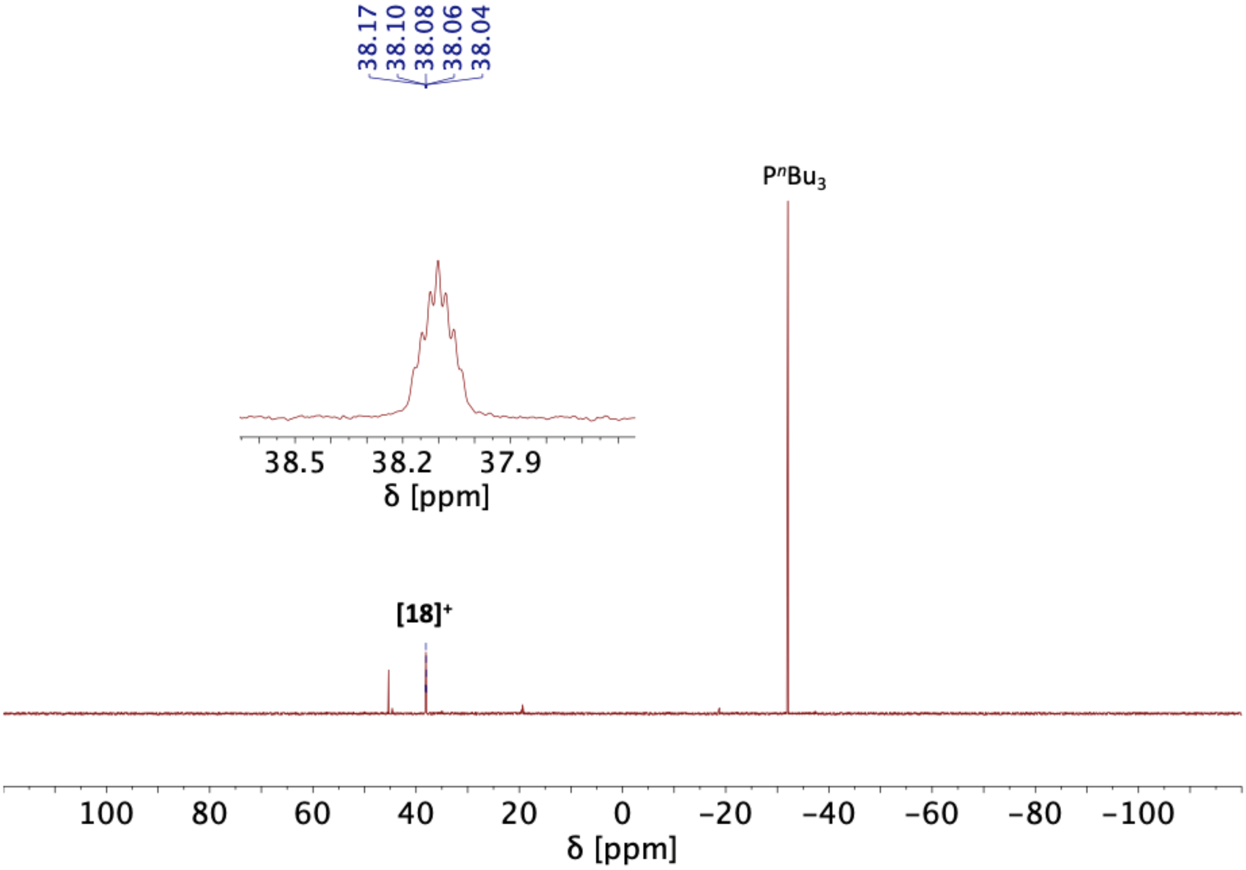


**Figure S40** {$^1H$}$^{31}P$ NMR (202 MHz, $CD_3CN$) spectrum of the system after 10 minutes at 20 °C.

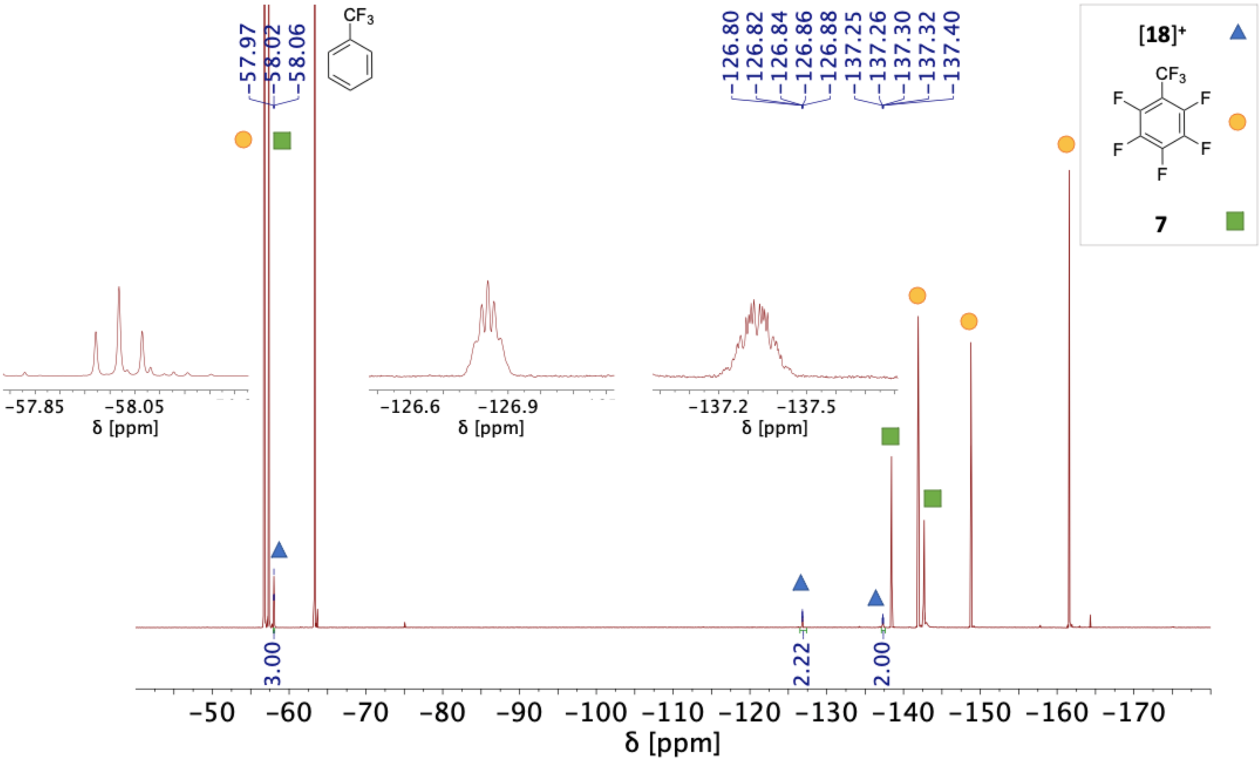
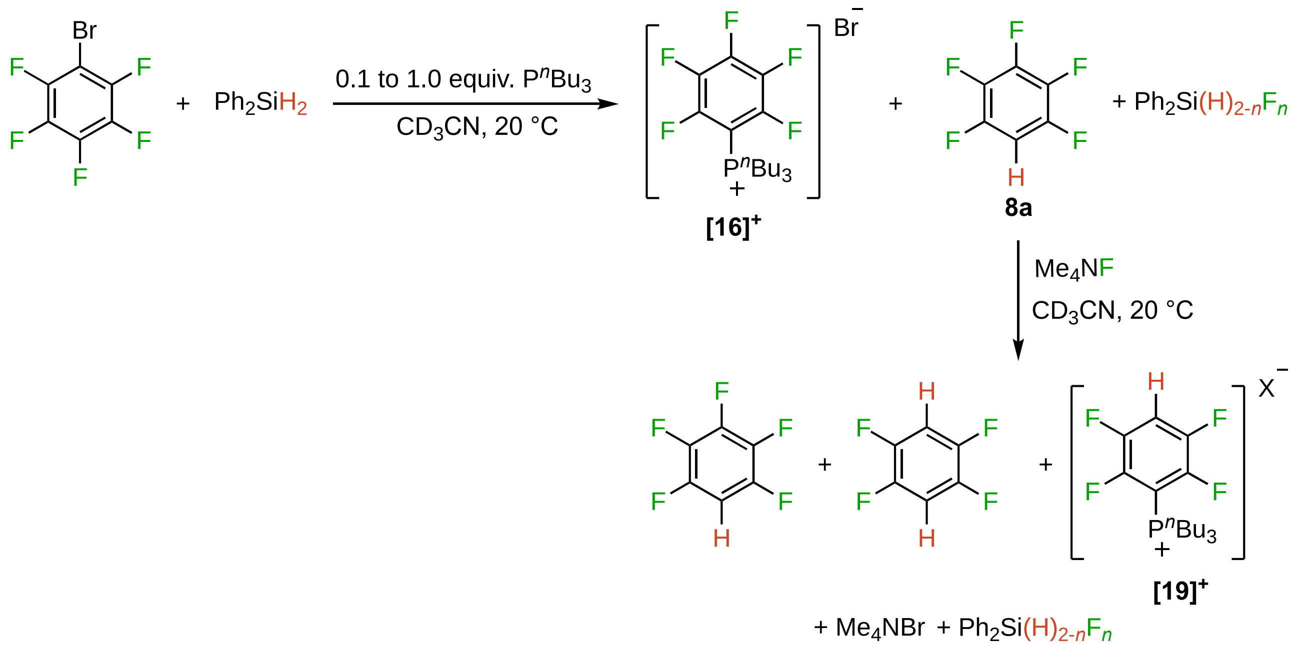


**Figure S41** $^{19}$F NMR (471 MHz, $CD_3CN$) spectrum of the system after 10 minutes at 20 °C.

## 2.8. Characterisation and reactivity of the phosphonium salt [16]Br



Bromopentafluorobenzene (51 µL, 0.40 mmol, 1.0 equivalent) and $Ph_2SiH_2$ (74 µL, 0.40 mmol, 1.0 equivalent) were dissolved in 0.4 mL of $CD_3CN$ and placed into a J-Young NMR tube. $P^nBu_3$ (10 µL, 0.040 mmol, 0.10 equivalent) was added and the reaction mixture was monitored by quantitative $^{19}F$ NMR with trifluorotoluene (25 µL, 0.20 mmol, 0.50 equivalent) used as an internal standard, as described in section 1.7.

The formation of **[16]Br** (11% conversion) and pentafluorobenzene (3% conversion) was observed. More $P^nBu_3$ (90 µL, 0.36 mmol, 0.90 equivalent) was added in the mixture and the system was monitored over 18 hours at 20 °C by $^{31}P$ and $^{19}F$ NMR spectroscopy. The amount of **[16]Br** and pentafluorobenzene increased. The introduction of anhydrous $[NMe_4]F$ (37 mg, 0.40 mmol, 1.0 equivalent) in the mixture led to an increase in the amount of pentaflurobenzene, the formation of **8a** and the precipitation of a white solid identified as $[NMe_4]Br$ . The system was monitored over 18 hours at 20 °C by $^{31}P$ and $^{19}F$ NMR spectroscopy.

**[16]Br:** $^1H$ NMR (500 MHz, $CD_3CN$): δ 2.93 (td, $J$ = 12.9, 8.6 Hz, 6H), 1.65 (dq, $J$ = 16.6, 8.6 Hz, 6H), 1.59 – 1.49 (m, 6H), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 9H). $\{^1H\}^{31}P$ NMR (202 MHz, $CD_3CN$): δ 36.79 – 36.50 (m, 1P). $^{19}F$ NMR (471 MHz, $CD_3CN$): δ –128.37 (mc, 2F), –143.48 (mc, 1F), –158.54 (mc, 2F).

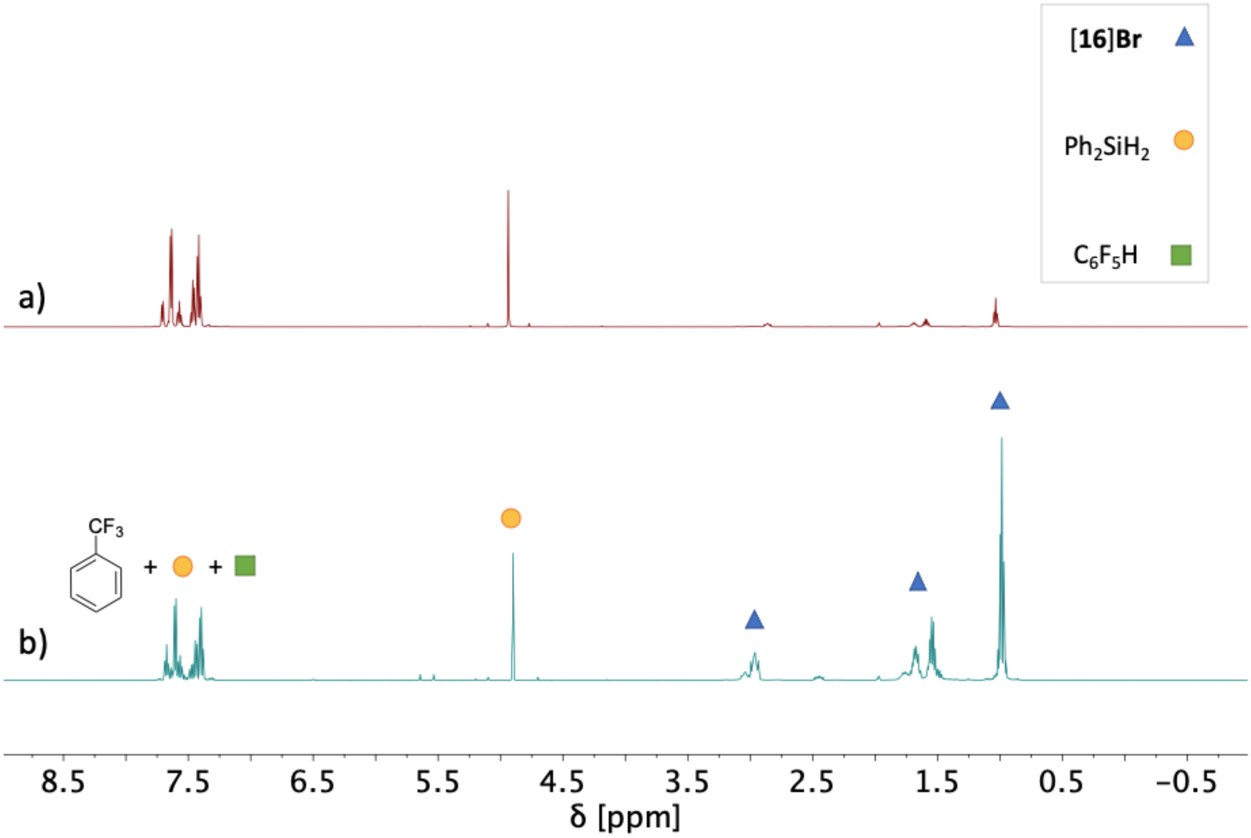


**Figure S42** $^1$H NMR (600 MHz, CD$_3$CN) spectra of the system after 10 minutes at 20 °C from the addition of 10 mol% of P$^n$Bu$_3$ (spectrum a)) and after 18 hours at 20 °C from the further addition of 0.9 equivalents of P$^n$Bu$_3$ (spectrum b)).

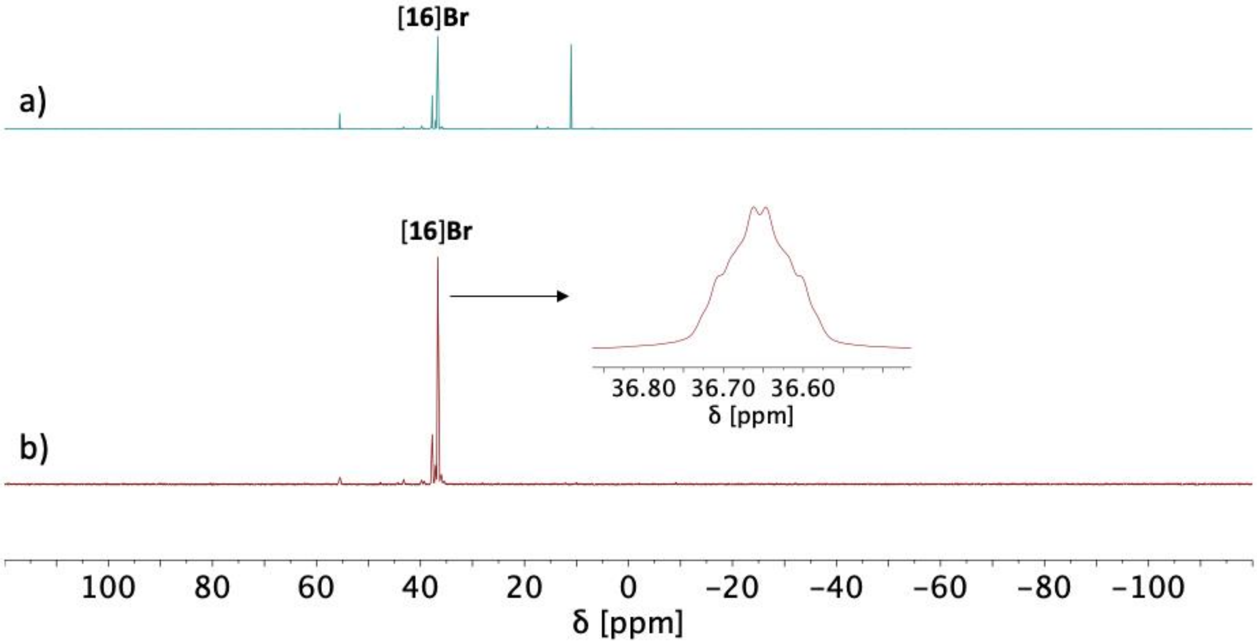


**Figure S43** {$^1$H}$^{31}$P NMR (202 MHz, CD$_3$CN) spectra of the system after 10 minutes at 20 °C from the addition of 10 mol% of P$^n$Bu$_3$ (spectrum a)) and after 18 hours at 20 °C from the further addition of 0.9 equivalents of P$^n$Bu$_3$ (spectrum b)).

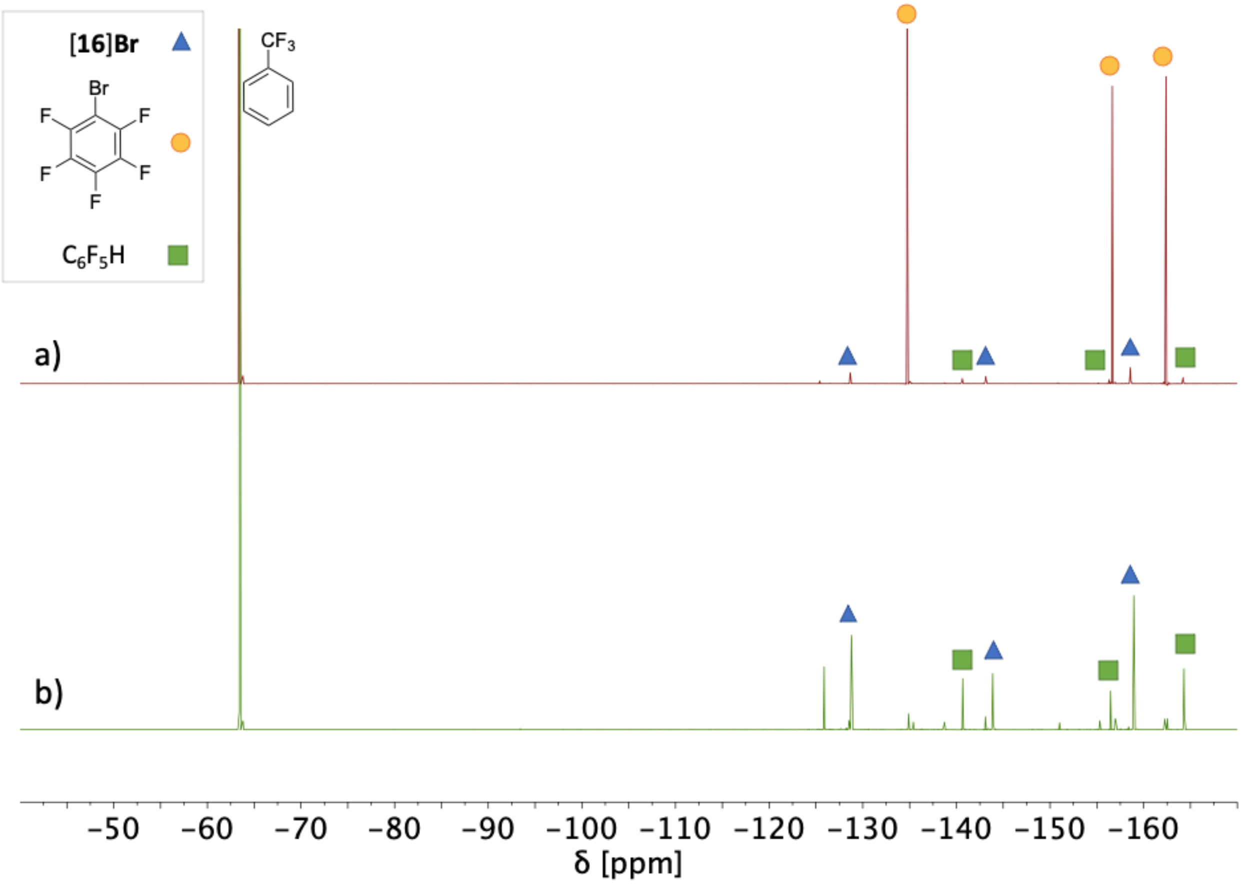


**Figure S44** $^{19}$F NMR (471 MHz, $CD_3CN$) spectra of the system after 10 minutes at 20 °C from the addition of 10 mol% of $P^{n}Bu_3$ (spectrum a)) and after 18 hours at 20 °C from the further addition of 0.9 equivalents of $P^{n}Bu_3$ (spectrum b)).

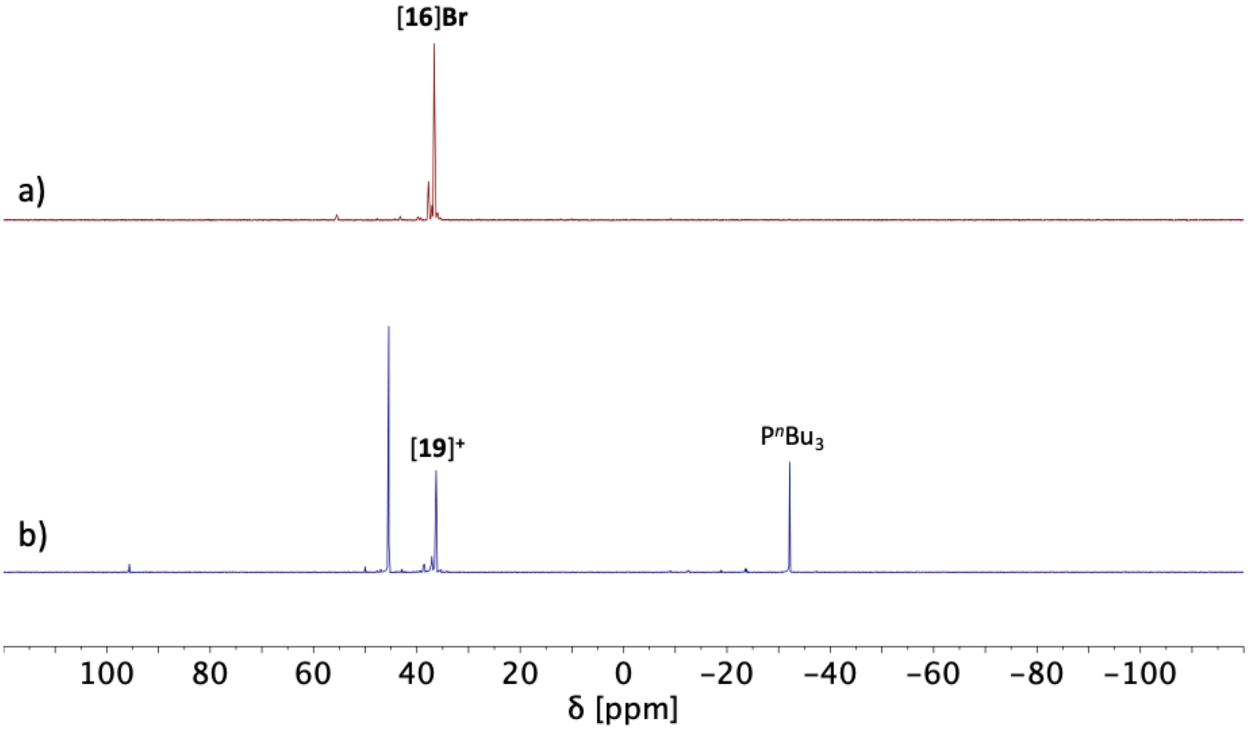


**Figure S45** {$^1$H}$^{31}$P NMR (202 MHz, $CD_3CN$) spectra of the system after 18 hours at 20 °C from the further addition of 0.9 equivalents of P$^n$Bu$_3$ (spectrum a)) and after 10 minutes at 20 °C from the addition of $[Me_4N]F$ (spectrum b)).

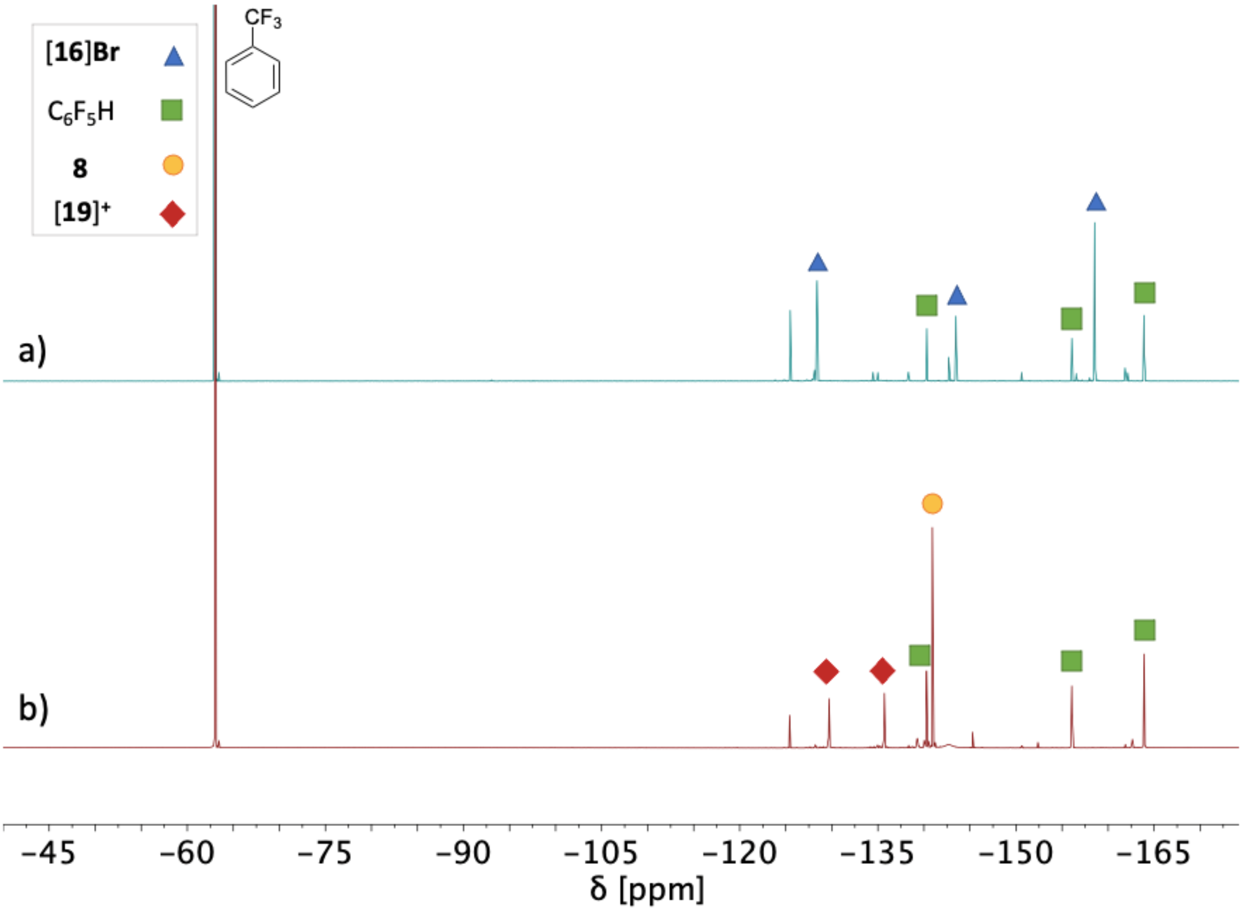


**Figure S46** $^{19}$F NMR (471 MHz, $CD_3CN$) spectra of the system after 18 hours at 20 °C from the further addition of 0.9 equivalents of $P^nBu_3$ (spectrum a)) and after 10 minutes at 20 °C from the addition of $[Me_4N]F$ (spectrum b)).

## 3. Computational Chemistry

Initial optimisations were performed at the (RI-)BP86/SV(P) level, followed by frequency calculations at the same level. Transition states were located by initially performing a constrained minimisation (by freezing internal coordinates that change most during the reaction) of a structure close to the anticipated transition state. This was followed by a frequency calculation to identify the transition vector to follow during a subsequent transition state optimisation. A final frequency calculation was then performed on the optimised transition-state structure. All minima were confirmed as such by the absence of imaginary frequencies and all transition states were identified by the presence of only one imaginary frequency.

Single-point calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the flexible def2-TZVPP basis set. The (RI-)PBE0/def2-TZVPP SCF energies were corrected for their zero-point energies, thermal energies and entropies (obtained from the (RI-)BP86/SV(P)-level frequency calculations). No symmetry constraints were applied during optimisations. All calculations were performed using the TURBOMOLE V6.40 package using the resolution of identity (RI) approximation.[12–22] Solvation effects were modelled using the COSMO module of TURBOMOLE.[23] The dielectric constant used was for MeCN ($\varepsilon$ = 35.9 at 25 °C).[24]

Both enthalpies and Gibbs energies at 298.15 K are shown on the PES'. Gibbs energy changes are discussed in the main section of the manuscript. The difficulty in assessing entropy changes in solution from gas-phase calculations is acknowledged.[25–27] Single-point DFT-D3 corrections (on the (RI-)BP86/SV(P) geometries) have been applied at the PBE0-D3 level using Grimme's DFT-D3 V3.0 Rev 2 program (with BJ-damping)[28,29] and data presented in the main section of the paper includes this correction. Both DFT-D3 and DFT data are presented below.

Structures were visualised and modified using Facio,[30] Jmol,[31] and gOpenMol.

### 3.1. Tabulated energies for mechanism presented in scheme 4

Table S1: Energies and corrections at the PBE0/def2-TZVPP//BP86/SV(P) level. As described above, vibrational frequencies and derived corrections were at the BP86/SV(P) level and electronic energies, both in the gas phase and COSMO solvation, in addition to DFT-D3 corrections were at the PBE0/def2-TZVPP level.

| | SCF (a.u.) | DFT-D3 corr. (a.u.) | COSMO (MeCN) (a.u.) | ZPE (a.u.) | Chem. Pot. (kJ/mol) | Energy (kJ/mol) | Entropy (kJ/K/mol) | Entropy at 1 mol/dm3 (kJ/K/mol) |
|---|---|---|---|---|---|---|---|---|
| $Ph_2SiH_2$ | -753.483828 | -0.0272 | -753.492017 | 0.193283 | 398.96 | 538.61 | 0.4767 | 0.4500 |
| $Ph_2SiHF$ | -852.752370 | -0.0276 | -852.762224 | 0.188550 | 386.01 | 528.26 | 0.4854 | 0.4587 |
| $[Ph_2SiH_2F]^-$ | -853.358399 | -0.0279 | -853.443879 | 0.194003 | 401.36 | 543.07 | 0.4836 | 0.4569 |
| **1** | -744.021127 | -0.0094 | -744.026087 | 0.047281 | 34.67 | 146.81 | 0.3844 | 0.3577 |
| **M1** | -460.870945 | -0.0087 | -460.876044 | 0.108851 | 208.40 | 303.74 | 0.3281 | 0.3014 |
| **TS$_{12}$** | -1204.869012 | -0.0257 | -1204.889163 | 0.156088 | 292.08 | 453.44 | 0.5495 | 0.5228 |
| **M2** | -1204.924023 | -0.0264 | -1204.934966 | 0.158689 | 302.77 | 459.48 | 0.5339 | 0.5072 |
| **M3** | -1204.927511 | -0.0265 | -1204.939349 | 0.159287 | 304.61 | 460.72 | 0.5319 | 0.5052 |
| **M4** | -1104.895087 | -0.0247 | -1104.978201 | 0.157190 | 304.30 | 451.77 | 0.5029 | 0.4762 |
| **M5** | -1105.666078 | -0.0259 | -1105.676025 | 0.164088 | 314.91 | 472.54 | 0.5370 | 0.5103 |
| **M6** | -1105.658139 | -0.0258 | -1105.665154 | 0.163477 | 316.35 | 470.38 | 0.5250 | 0.4983 |
| **TS$_{61}$** | -1105.624638 | -0.0265 | -1105.642515 | 0.160201 | 307.65 | 461.22 | 0.5234 | 0.4967 |
| **2** | -644.842167 | -0.0091 | -644.848657 | 0.055077 | 58.55 | 164.65 | 0.3642 | 0.3375 |

Table S2: Relative energies of different states in the gas phase, with COSMO solvation in MeCN and with both COSMO solvation and DFT-D3 corrections.

| | | | | | **Gas Phase 298.15 K** | | | **COSMO MeCN 298.15 K** | | | **DFT-D3 COSMO MeCN 298.15 K** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Electronic E gas (kJ/mol)** | **Electronic E+D gas (kJ/mol)** | **Electronic E MeCN (kJ/mol)** | **Electronic E+D MeCN (kJ/mol)** | **Rel H (kJ/mol)** | **Rel S (J/K/mol)** | **Rel G (kJ/mol)** | **Rel H (kJ/mol)** | **Rel S (J/K/mol)** | **Rel G (kJ/mol)** | **Rel H (kJ/mol)** | **Rel S (J/K/mol)** | **Rel G (kJ/mol)** |
| $Ph_2SiH_2$ | | | | | | | | | | | | | |
| $Ph_2SiHF$ | | | | | | | | | | | | | |
| $[Ph_2SiH_2F]^-$ | | | | | | | | | | | | | |
| **1** | | | | | | | | | | | | | |
| **M1** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **$TS_{12}$** | 61 | 41 | 34 | 14 | 61 | -163 | 110 | 34 | -136 | 75 | 14 | -136 | 55 |
| **M2** | -84 | -106 | -86 | -108 | -77 | -179 | -24 | -80 | -152 | -34 | -102 | -152 | -56 |
| **M3** | -93 | -115 | -98 | -120 | -85 | -181 | -32 | -90 | -154 | -44 | -112 | -154 | -66 |
| **M4** | 321 | 302 | -73 | -93 | 325 | -203 | 385 | -70 | -176 | -18 | -89 | -176 | -37 |
| **M5** | -112 | -133 | -116 | -137 | -103 | -167 | -53 | -107 | -140 | -65 | -128 | -140 | -86 |
| **M6** | -91 | -112 | -87 | -108 | -84 | -179 | -31 | -80 | -152 | -35 | -101 | -152 | -56 |
| **$TS_{61}$** | -3 | -26 | -28 | -51 | -5 | -180 | 49 | -30 | -154 | 16 | -53 | -154 | -7 |
| **2** | -235 | -236 | -244 | -244 | -228 | -12 | -224 | -236 | -12 | -233 | -237 | -12 | -233 |

### 3.2. 3-component alternative mechanism for Si-H activation (c.f. Piers' mechanism)

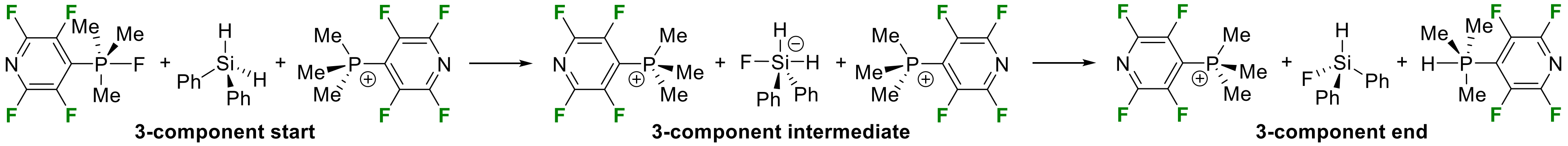


Table S3: Energies and corrections at the PBE0/def2-TZVPP//BP86/SV(P) level. As described above, vibrational frequencies and derived corrections were at the BP86/SV(P) level and electronic energies, both in the gas phase and COSMO solvation, in addition to DFT-D3 corrections were at the PBE0/def2-TZVPP level.

| | SCF (a.u.) | DFT-D3 corr. (a.u.) | COSMO (MeCN) (a.u.) | ZPE (a.u.) | Chem. Pot. (kJ/mol) | Energy (kJ/mol) | Entropy (kJ/K/mol) | ln q(vib) | HOMO (eV) | LUMO (eV) | Entropy at 1 mol/dm3 (kJ/K/mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Start | -3063.326992 | -0.096063 | -3063.403577 | 0.511531 | 1102.95 | 1467.39 | 1.2307 | 58.08 | -9.1374 | -5.6136 | 1.2040 |
| TS1 | -3063.316750 | -0.098043 | -3063.390751 | 0.510491 | 1105.55 | 1462.63 | 1.2060 | 55.99 | -9.2997 | -5.4042 | 1.1793 |
| Intermediate | -3063.327974 | -0.096200 | -3063.405328 | 0.510779 | 1110.60 | 1463.02 | 1.1903 | 54.19 | -8.5633 | -5.0345 | 1.1636 |
| TS2 | -3063.323394 | -0.096075 | -3063.399502 | 0.510378 | 1106.89 | 1461.48 | 1.1976 | 55.27 | -8.6778 | -5.0141 | 1.1709 |
| End | -3063.330657 | -0.095090 | -3063.409383 | 0.511033 | 1095.48 | 1466.34 | 1.2522 | 60.52 | -8.7458 | -5.6035 | 1.2255 |

Table S4: Relative energies of different states in the gas phase, with COSMO solvation in MeCN and with both COSMO solvation and DFT-D3 corrections.

| | | | | | Gas Phase 298.15 K | | | COSMO MeCN 298.15 K | | | DFT-D3 COSMO MeCN 298.15 K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Electronic E gas (kJ/mol) | Electronic E+D gas (kJ/mol) | Electronic E MeCN (kJ/mol) | Electronic E+D MeCN (kJ/mol) | Rel H (kJ/mol) | Rel S (J/K/mol) | Rel G (kJ/mol) | Rel H (kJ/mol) | Rel S (J/K/mol) | Rel G (kJ/mol) | Rel H (kJ/mol) | Rel S (J/K/mol) | Rel G (kJ/mol) |
| Start | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| TS1 | 27 | 22 | 34 | 28 | 22 | -25 | 29 | 29 | -25 | 36 | 24 | -25 | 31 |
| Intermediate | -3 | -3 | -5 | -5 | -7 | -40 | 5 | -9 | -40 | 3 | -9 | -40 | 3 |
| TS2 | 9 | 9 | 11 | 11 | 4 | -33 | 13 | 5 | -33 | 15 | 5 | -33 | 15 |
| End | -10 | -7 | -15 | -13 | -11 | 22 | -17 | -16 | 22 | -23 | -14 | 22 | -20 |

### 3.3. xyz coordinates

**Ph$_2$SiH$_2$**
25

| | | | |
|---|---|---|---|
| Si | -2.13544 | -1.15576 | 1.18329 |
| H | -2.66898 | -0.67759 | 2.51312 |
| C | -2.39619 | 0.15300 | -0.15735 |
| C | -0.30609 | -1.58561 | 1.41980 |
| C | -2.77697 | 2.11772 | -2.17239 |
| C | -3.29755 | 0.82407 | -2.34243 |
| C | -3.10879 | -0.14682 | -1.34272 |
| C | -1.87792 | 1.46292 | -0.00669 |
| C | -2.06627 | 2.43638 | -1.00112 |
| H | -2.92531 | 2.88119 | -2.95443 |
| H | -3.85556 | 0.56819 | -3.25878 |
| H | -3.52727 | -1.15780 | -1.48939 |
| H | -1.31504 | 1.73178 | 0.90462 |
| H | -1.65658 | 3.45109 | -0.86247 |
| C | 2.41767 | -2.30569 | 1.77081 |
| C | 1.92209 | -2.02393 | 0.48540 |
| C | 0.57415 | -1.66646 | 0.31403 |
| C | 0.21278 | -1.86822 | 2.70573 |
| C | 1.56062 | -2.22629 | 2.88192 |
| H | 3.47621 | -2.58456 | 1.90683 |
| H | 2.59133 | -2.08072 | -0.38968 |
| H | 0.20371 | -1.44160 | -0.70154 |
| H | -0.44538 | -1.80530 | 3.59010 |
| H | 1.94525 | -2.44090 | 3.89319 |
| H | -2.92247 | -2.38111 | 0.77816 |

**Ph$_2$SiHF**
25

| | | | |
|---|---|---|---|
| Si | -2.11942 | -1.27531 | 1.04004 |
| H | -2.78336 | -1.00456 | 2.36511 |
| C | -2.37445 | 0.11332 | -0.20137 |
| C | -0.30342 | -1.64426 | 1.34591 |
| C | -2.80078 | 2.21433 | -2.05595 |
| C | -3.44072 | 0.97602 | -2.23453 |
| C | -3.23105 | -0.06448 | -1.31324 |
| C | -1.73495 | 1.36606 | -0.03903 |
| C | -1.94687 | 2.40891 | -0.95563 |
| H | -2.96661 | 3.03164 | -2.77787 |
| H | -4.10914 | 0.81872 | -3.09774 |
| H | -3.73786 | -1.03291 | -1.46040 |
| H | -1.05456 | 1.53459 | 0.81486 |
| H | -1.44117 | 3.37867 | -0.81293 |
| C | 2.42920 | -2.23183 | 1.82053 |
| C | 1.99081 | -1.92284 | 0.52036 |
| C | 0.63785 | -1.62832 | 0.28735 |
| C | 0.15768 | -1.95615 | 2.64748 |
| C | 1.51191 | -2.24688 | 2.88539 |

| | | | |
|---|---|---|---|
| H | 3.49258 | -2.45989 | 2.00465 |
| H | 2.70963 | -1.90820 | -0.31588 |
| H | 0.30915 | -1.37967 | -0.73670 |
| H | -0.55274 | -1.97129 | 3.49287 |
| H | 1.85375 | -2.48609 | 3.90633 |
| F | -2.88046 | -2.59756 | 0.40442 |

**$[Ph_2SiH_2F]^-$**
26

| | | | |
|---|---|---|---|
| Si | -1.73148 | -0.37400 | 1.56008 |
| H | -0.93286 | 0.97100 | 1.87951 |
| C | -2.36134 | 0.41207 | -0.12408 |
| C | -0.04536 | -1.37686 | 1.61003 |
| C | -3.26532 | 1.58539 | -2.57299 |
| C | -3.60649 | 0.25903 | -2.24935 |
| C | -3.16262 | -0.31125 | -1.04224 |
| C | -2.03201 | 1.74137 | -0.47683 |
| C | -2.47463 | 2.32796 | -1.67759 |
| H | -3.61372 | 2.03750 | -3.51953 |
| H | -4.22689 | -0.33450 | -2.94661 |
| H | -3.42941 | -1.34613 | -0.77530 |
| H | -1.40397 | 2.32258 | 0.22390 |
| H | -2.19946 | 3.37122 | -1.92038 |
| C | 2.42862 | -2.81312 | 1.69920 |
| C | 2.40279 | -1.42546 | 1.92795 |
| C | 1.18128 | -0.72738 | 1.88114 |
| C | 0.00987 | -2.77480 | 1.38432 |
| C | 1.22315 | -3.48580 | 1.42560 |
| H | 3.38398 | -3.36813 | 1.73319 |
| H | 3.34333 | -0.88493 | 2.14291 |
| H | 1.16073 | 0.36406 | 2.05798 |
| H | -0.93995 | -3.29104 | 1.17276 |
| H | 1.23184 | -4.57665 | 1.24360 |
| F | -2.61600 | -1.87221 | 1.19538 |
| H | -2.57307 | -0.22693 | 2.84036 |

**1**
11

| | | | |
|---|---|---|---|
| C | 0.22445 | -1.15121 | 0.52387 |
| F | 0.44915 | -2.35155 | 1.04738 |
| N | -0.25113 | 1.35707 | -0.56754 |
| C | -0.47824 | 0.27002 | -1.28098 |
| C | -0.25904 | -1.03114 | -0.79315 |
| C | 0.46625 | 0.00980 | 1.28308 |
| C | 0.20319 | 1.24685 | 0.66698 |
| F | -0.93935 | 0.42043 | -2.52370 |
| F | -0.49699 | -2.11758 | -1.52987 |
| F | 0.92417 | -0.08138 | 2.53278 |
| F | 0.42055 | 2.36770 | 1.35715 |

**M1**

13

| | | | |
|---|---|---|---|
| C | -0.72666 | 0.17095 | -1.50065 |
| P | -0.99328 | 0.30647 | 0.34773 |
| H | 0.21015 | -0.37192 | -1.76608 |
| H | -0.68648 | 1.19006 | -1.94485 |
| H | -1.58928 | -0.35964 | -1.96092 |
| C | 0.68237 | 0.97837 | 0.84469 |
| C | -0.74674 | -1.48872 | 0.81766 |
| H | 0.76371 | 0.98507 | 1.95407 |
| H | 0.77736 | 2.03070 | 0.49672 |
| H | 1.52950 | 0.38607 | 0.42732 |
| H | -0.72387 | -1.58176 | 1.92600 |
| H | 0.19340 | -1.92014 | 0.40277 |
| H | -1.60818 | -2.08951 | 0.45054 |

**TS$_{12}$**

24

| | | | |
|---|---|---|---|
| C | 0.87757 | -2.62738 | -1.81662 |
| C | 0.26183 | -3.17652 | 1.01024 |
| C | -0.62973 | -0.16173 | -0.13801 |
| C | 2.36106 | -1.21974 | 0.31060 |
| F | -1.72753 | -1.00109 | -0.52578 |
| P | 0.70338 | -1.83746 | -0.16710 |
| N | 0.02060 | 2.58667 | 0.50142 |
| C | 0.10176 | 2.11751 | -0.73652 |
| C | -0.22717 | 0.81759 | -1.11397 |
| C | -0.72229 | 0.39959 | 1.18471 |
| C | -0.37119 | 1.72508 | 1.43057 |
| F | 0.51896 | 2.97094 | -1.68876 |
| F | -0.06548 | 0.39148 | -2.39785 |
| F | -1.05525 | -0.44282 | 2.20227 |
| F | -0.44607 | 2.17900 | 2.69436 |
| H | 1.21268 | -1.86349 | -2.54787 |
| H | -0.12184 | -2.99183 | -2.13458 |
| H | 1.59684 | -3.47666 | -1.79616 |
| H | 0.20138 | -2.75038 | 2.03281 |
| H | 0.99955 | -4.00988 | 0.98832 |
| H | -0.74345 | -3.56076 | 0.73710 |
| H | 2.30433 | -0.77436 | 1.32744 |
| H | 2.66714 | -0.42116 | -0.39958 |
| H | 3.12494 | -2.02741 | 0.30563 |

**M2**

24

| | | | |
|---|---|---|---|
| C | -0.04471 | -1.54375 | -1.09175 |
| C | -0.26543 | -0.23352 | 1.75930 |
| C | 0.02591 | 1.70712 | -0.78296 |
| C | 1.96285 | 0.00153 | 0.05237 |
| F | -1.69831 | 0.12976 | -0.24687 |

|  |  |  |  |
|---|---|---|---|
| P | 0.05767 | -0.02155 | -0.04644 |
| N | -0.03658 | 4.31625 | -1.85330 |
| C | -0.35998 | 3.27487 | -2.59688 |
| C | -0.36137 | 1.95406 | -2.11139 |
| C | 0.36669 | 2.83389 | -0.01758 |
| C | 0.31323 | 4.11426 | -0.59830 |
| F | -0.70497 | 3.50029 | -3.86825 |
| F | -0.70698 | 0.95492 | -2.93959 |
| F | 0.74544 | 2.70964 | 1.27115 |
| F | 0.63287 | 5.17929 | 0.14293 |
| H | -0.15340 | -1.22694 | -2.14854 |
| H | -0.95897 | -2.10289 | -0.81293 |
| H | 0.86217 | -2.17365 | -0.98846 |
| H | -0.73729 | 0.69457 | 2.13873 |
| H | 0.65719 | -0.44733 | 2.33548 |
| H | -1.00450 | -1.05184 | 1.87661 |
| H | 2.32218 | 0.85052 | 0.67384 |
| H | 2.40768 | 0.10042 | -0.96357 |
| H | 2.33761 | -0.94490 | 0.50440 |

**M3**
24

|  |  |  |  |
|---|---|---|---|
| C | -0.11912 | -1.24603 | -1.31472 |
| C | 0.03649 | -0.35629 | 1.87288 |
| F | 1.67469 | -0.28249 | 0.04752 |
| C | 0.20185 | 1.75816 | -0.41885 |
| C | -2.08117 | 0.09189 | 0.11228 |
| P | -0.05378 | 0.00009 | 0.05675 |
| N | -4.92085 | -0.15449 | 0.27764 |
| C | -4.35400 | 0.96927 | -0.11332 |
| C | -2.95622 | 1.14100 | -0.21441 |
| C | -2.73450 | -1.08850 | 0.51442 |
| C | -4.13477 | -1.16988 | 0.58741 |
| F | -5.15454 | 1.99380 | -0.43041 |
| F | -2.51976 | 2.34806 | -0.63579 |
| F | -2.00761 | -2.18477 | 0.84076 |
| F | -4.71283 | -2.31096 | 0.98172 |
| H | 0.66425 | -0.96180 | -2.04565 |
| H | -1.11171 | -1.31356 | -1.80177 |
| H | 0.16086 | -2.23262 | -0.89184 |
| H | -0.91273 | -0.16498 | 2.41028 |
| H | 0.85405 | 0.27359 | 2.27844 |
| H | 0.33661 | -1.41598 | 2.00112 |
| H | -0.29876 | 2.43030 | 0.30540 |
| H | -0.23598 | 1.94982 | -1.41884 |
| H | 1.29154 | 1.94538 | -0.43602 |

**[M4]$^+$**
23

|  |  |  |  |
|---|---|---|---|
| C | -0.33833 | -1.28278 | -2.67444 |
| C | -1.18497 | -2.48407 | -0.10772 |

| | | | |
|---|---|---|---|
| C | 0.02822 | 0.22113 | -0.08018 |
| C | 1.71471 | -2.12862 | -0.71870 |
| P | 0.05171 | -1.41099 | -0.90383 |
| N | 0.03781 | 2.64653 | 1.31522 |
| C | -0.22892 | 2.63308 | 0.02563 |
| C | -0.25177 | 1.44070 | -0.73452 |
| C | 0.31240 | 0.27761 | 1.30335 |
| C | 0.30172 | 1.52516 | 1.95740 |
| F | -0.48402 | 3.77808 | -0.58259 |
| F | -0.53240 | 1.48970 | -2.03875 |
| F | 0.59020 | -0.84726 | 1.98174 |
| F | 0.56435 | 1.57807 | 3.25123 |
| H | 0.40559 | -0.64697 | -3.19679 |
| H | -1.35253 | -0.85904 | -2.82349 |
| H | -0.30389 | -2.31119 | -3.09714 |
| H | -0.96279 | -2.58129 | 0.97507 |
| H | -1.15280 | -3.48843 | -0.58385 |
| H | -2.19801 | -2.04732 | -0.24059 |
| H | 1.96823 | -2.22733 | 0.35711 |
| H | 2.46043 | -1.47230 | -1.21648 |
| H | 1.73206 | -3.13247 | -1.19668 |

**M5**

24

| | | | |
|---|---|---|---|
| C | -0.09198 | -1.24529 | -1.32713 |
| C | 0.08214 | -0.35769 | 1.87204 |
| H | 1.55197 | -0.24021 | 0.03097 |
| C | 0.23799 | 1.76721 | -0.41005 |
| C | -2.10241 | 0.09304 | 0.11372 |
| P | 0.07498 | -0.01120 | 0.05016 |
| N | -4.94073 | -0.17060 | 0.28248 |
| C | -4.38020 | 0.95577 | -0.11509 |
| C | -2.98353 | 1.12994 | -0.21674 |
| C | -2.74539 | -1.08443 | 0.52002 |
| C | -4.14550 | -1.17823 | 0.59622 |
| F | -5.19222 | 1.97391 | -0.43606 |
| F | -2.54644 | 2.34131 | -0.64584 |
| F | -2.01138 | -2.18253 | 0.85396 |
| F | -4.71816 | -2.32264 | 0.99847 |
| H | 0.73811 | -1.06395 | -2.04334 |
| H | -1.07595 | -1.19073 | -1.83540 |
| H | 0.03917 | -2.25874 | -0.89119 |
| H | -0.86503 | -0.06520 | 2.36882 |
| H | 0.94354 | 0.19495 | 2.30593 |
| H | 0.25633 | -1.44418 | 2.01893 |
| H | -0.33537 | 2.39722 | 0.29722 |
| H | -0.18841 | 1.93075 | -1.42024 |
| H | 1.31050 | 2.05054 | -0.40289 |

**M6**

24

| | | | |
|---|---|---|---|
| C | -0.06232 | -1.61127 | -1.05202 |
| C | -0.27460 | -0.29629 | 1.76328 |
| C | 0.04434 | 1.76108 | -0.79523 |
| C | 1.93860 | 0.01075 | 0.03830 |
| H | -1.48767 | 0.11315 | -0.25069 |
| P | 0.00313 | -0.03138 | -0.05707 |
| N | -0.06648 | 4.36543 | -1.86897 |
| C | -0.35480 | 3.31721 | -2.61809 |
| C | -0.32147 | 1.99847 | -2.12801 |
| C | 0.35001 | 2.89231 | -0.02661 |
| C | 0.27438 | 4.17199 | -0.60917 |
| F | -0.68526 | 3.53581 | -3.89572 |
| F | -0.63933 | 0.97764 | -2.95012 |
| F | 0.72061 | 2.77933 | 1.26778 |
| F | 0.56400 | 5.24731 | 0.13167 |
| H | -0.13712 | -1.33248 | -2.12390 |
| H | -0.98707 | -2.16140 | -0.77552 |
| H | 0.83764 | -2.24375 | -0.90397 |
| H | -0.47595 | 0.69116 | 2.22924 |
| H | 0.60873 | -0.74855 | 2.26010 |
| H | -1.17341 | -0.93514 | 1.89405 |
| H | 2.27335 | 0.86584 | 0.66603 |
| H | 2.36581 | 0.13804 | -0.98236 |
| H | 2.34389 | -0.93024 | 0.47499 |

**TS$_{61}$**

24

| | | | |
|---|---|---|---|
| C | -0.28167 | -2.94270 | -1.54688 |
| C | -0.88049 | -2.85079 | 1.41185 |
| C | -0.23144 | -0.27684 | -0.05966 |
| C | 1.78854 | -2.43269 | 0.40075 |
| H | -1.64144 | -1.09639 | -0.41019 |
| P | -0.00314 | -2.04456 | 0.02406 |
| N | -0.15212 | 2.59771 | -0.08013 |
| C | 0.19247 | 1.88551 | -1.14439 |
| C | 0.25625 | 0.49486 | -1.17405 |
| C | -0.40191 | 0.52865 | 1.12330 |
| C | -0.43052 | 1.91602 | 1.02449 |
| F | 0.55211 | 2.56610 | -2.24616 |
| F | 0.66951 | -0.15541 | -2.30031 |
| F | -0.68060 | -0.08831 | 2.30487 |
| F | -0.71229 | 2.62910 | 2.12842 |
| H | 0.18872 | -2.37286 | -2.37275 |
| H | -1.36594 | -3.04823 | -1.74347 |
| H | 0.19933 | -3.94225 | -1.46179 |
| H | -0.41570 | -2.55543 | 2.37350 |
| H | -0.77813 | -3.94915 | 1.27288 |
| H | -1.95099 | -2.56925 | 1.40493 |
| H | 2.08552 | -1.91036 | 1.33600 |

| | | | |
|---|---|---|---|
| H | 2.42278 | -2.05100 | -0.42864 |
| H | 1.96858 | -3.52292 | 0.52261 |

**2**
11

| | | | |
|---|---|---|---|
| C | 0.22952 | -1.18022 | 0.53641 |
| H | 0.41798 | -2.17424 | 0.96915 |
| N | -0.24553 | 1.33702 | -0.55936 |
| C | -0.47384 | 0.25114 | -1.27331 |
| C | -0.25261 | -1.04756 | -0.77157 |
| C | 0.46539 | -0.01834 | 1.28181 |
| C | 0.20731 | 1.22793 | 0.67536 |
| F | -0.93268 | 0.40223 | -2.51812 |
| F | -0.50078 | -2.12300 | -1.52736 |
| F | 0.92290 | -0.08607 | 2.53718 |
| F | 0.42533 | 2.35010 | 1.36581 |

**3-component start**
72

| | | | |
|---|---|---|---|
| C | -0.03967 | 3.99683 | -2.43836 |
| C | -1.16436 | 2.48302 | -0.16343 |
| C | -1.22301 | 5.44992 | -0.07550 |
| C | 1.36529 | 4.01359 | 0.15588 |
| P | -0.26818 | 3.98863 | -0.63711 |
| N | -2.66537 | 7.63284 | 0.92992 |
| C | -2.47632 | 7.51041 | -0.36784 |
| C | -1.75878 | 6.43306 | -0.93550 |
| C | -1.44963 | 5.61413 | 1.30931 |
| C | -2.17987 | 6.73105 | 1.76053 |
| F | -2.97921 | 8.43369 | -1.17198 |
| F | -1.60535 | 6.37040 | -2.26139 |
| F | -0.97430 | 4.71506 | 2.18336 |
| F | -2.38876 | 6.88521 | 3.05890 |
| H | 0.50926 | 4.90471 | -2.76161 |
| H | -1.01719 | 3.95152 | -2.95984 |
| H | 0.55999 | 3.08980 | -2.68586 |
| H | -1.24014 | 2.41184 | 0.94275 |
| H | -0.58332 | 1.60975 | -0.53893 |
| H | -2.17675 | 2.48894 | -0.62061 |
| H | 1.25619 | 3.88265 | 1.25307 |
| H | 1.88134 | 4.97064 | -0.07139 |
| H | 1.95157 | 3.16018 | -0.25644 |
| Si | 2.65242 | -0.23308 | 1.11709 |
| C | 2.36110 | 0.25075 | -0.70208 |
| C | 1.38662 | 0.56589 | 2.28313 |
| C | 1.98167 | 0.95953 | -3.43207 |
| C | 1.06083 | 0.11384 | -2.78292 |
| C | 1.24699 | -0.23950 | -1.43291 |
| C | 3.27601 | 1.10127 | -1.37190 |
| C | 3.09189 | 1.45328 | -2.72317 |
| H | 1.85018 | 1.20855 | -4.49870 |

| | | | |
|---|---|---|---|
| H | 0.20413 | -0.29719 | -3.34412 |
| H | 0.54064 | -0.93913 | -0.94727 |
| H | 4.16956 | 1.47416 | -0.84056 |
| H | 3.83316 | 2.09305 | -3.23119 |
| C | -0.48275 | 1.79275 | 4.03856 |
| C | -0.87827 | 0.71940 | 3.21878 |
| C | 0.04563 | 0.10936 | 2.34956 |
| C | 1.76836 | 1.64475 | 3.11939 |
| C | 0.84478 | 2.25427 | 3.98889 |
| H | -1.20393 | 2.25713 | 4.73160 |
| H | -1.91267 | 0.33908 | 3.27355 |
| H | -0.27366 | -0.74302 | 1.72190 |
| H | 2.81315 | 2.00288 | 3.11321 |
| H | 1.16812 | 3.07851 | 4.64666 |
| H | 4.01476 | 0.29035 | 1.49422 |
| H | 2.62753 | -1.73012 | 1.25225 |
| C | -2.33690 | -3.56792 | -0.35688 |
| C | 0.85043 | -4.33085 | -0.68831 |
| F | -0.29427 | -2.38385 | 0.35787 |
| C | -0.51778 | -4.29721 | 2.09958 |
| C | -1.21773 | -6.08963 | -0.04706 |
| P | -0.71975 | -4.20855 | 0.27790 |
| N | -1.95598 | -8.70897 | -0.87269 |
| C | -1.78143 | -8.42434 | 0.40155 |
| C | -1.41809 | -7.13982 | 0.86626 |
| C | -1.42220 | -6.44290 | -1.39596 |
| C | -1.78460 | -7.74924 | -1.76280 |
| F | -1.96022 | -9.40113 | 1.29136 |
| F | -1.27945 | -6.98016 | 2.19701 |
| F | -1.27198 | -5.50810 | -2.36505 |
| F | -1.96738 | -8.04557 | -3.05073 |
| H | -2.68388 | -2.78199 | 0.34217 |
| H | -3.09688 | -4.36834 | -0.45389 |
| H | -2.16335 | -3.09821 | -1.34581 |
| H | 1.14717 | -5.38310 | -0.86815 |
| H | 1.63305 | -3.79399 | -0.11682 |
| H | 0.71616 | -3.81249 | -1.65868 |
| H | 0.17903 | -5.11719 | 2.36173 |
| H | -1.49481 | -4.51786 | 2.57503 |
| H | -0.12587 | -3.32905 | 2.45999 |

**3-component TS1**
72

| | | | |
|---|---|---|---|
| C | 0.73972 | 3.48712 | -1.73214 |
| C | -1.01596 | 3.71189 | 0.64234 |
| C | 0.16200 | 6.17641 | -0.49199 |
| C | 1.91383 | 4.22269 | 0.87850 |
| P | 0.45184 | 4.38843 | -0.18752 |
| N | -0.29968 | 8.92555 | -0.80033 |
| C | -0.07938 | 8.17133 | -1.85723 |
| C | 0.15921 | 6.78105 | -1.76720 |
| C | -0.07674 | 7.01868 | 0.61699 |

| | | | |
|---|---|---|---|
| C | -0.30359 | 8.39243 | 0.40606 |
| F | -0.08224 | 8.73992 | -3.05321 |
| F | 0.37522 | 6.07827 | -2.88259 |
| F | -0.08711 | 6.51397 | 1.86161 |
| F | -0.52825 | 9.17915 | 1.44739 |
| H | 1.64939 | 3.86570 | -2.24096 |
| H | -0.13263 | 3.57959 | -2.40973 |
| H | 0.87360 | 2.41366 | -1.46123 |
| H | -1.23694 | 4.29554 | 1.55901 |
| H | -0.80690 | 2.65427 | 0.92419 |
| H | -1.88314 | 3.75284 | -0.05021 |
| H | 1.75234 | 4.75405 | 1.83851 |
| H | 2.80458 | 4.63771 | 0.36083 |
| H | 2.05116 | 3.12965 | 1.06105 |
| Si | 0.69234 | -0.19510 | 0.72304 |
| C | 0.11815 | -0.07633 | -1.09023 |
| C | -0.52840 | 0.16272 | 2.14544 |
| C | -0.64601 | 0.20463 | -3.82453 |
| C | -1.60625 | 0.31950 | -2.80312 |
| C | -1.22683 | 0.17596 | -1.45490 |
| C | 1.06937 | -0.18141 | -2.13588 |
| C | 0.69526 | -0.04954 | -3.48642 |
| H | -0.94325 | 0.30474 | -4.88154 |
| H | -2.66244 | 0.51002 | -3.05948 |
| H | -2.00207 | 0.25433 | -0.67245 |
| H | 2.13167 | -0.37009 | -1.89545 |
| H | 1.45481 | -0.14970 | -4.28011 |
| C | -2.26486 | 0.81693 | 4.30994 |
| C | -2.70274 | -0.03562 | 3.28156 |
| C | -1.83839 | -0.36982 | 2.22426 |
| C | -0.11416 | 1.02826 | 3.18886 |
| C | -0.96126 | 1.34128 | 4.26682 |
| H | -2.93624 | 1.06622 | 5.14834 |
| H | -3.72237 | -0.45526 | 3.31151 |
| H | -2.17717 | -1.07204 | 1.44756 |
| H | 0.90442 | 1.45634 | 3.16779 |
| H | -0.60207 | 1.99523 | 5.07940 |
| H | 1.39779 | 1.20794 | 0.76717 |
| H | 1.93378 | -1.00710 | 0.98909 |
| C | -1.74004 | -3.66578 | -0.66877 |
| C | 1.45919 | -3.77851 | -0.40971 |
| F | -0.19909 | -2.13988 | 0.62128 |
| C | -0.37285 | -4.37070 | 2.03025 |
| C | -0.23197 | -6.03100 | -0.35271 |
| P | -0.21708 | -4.20018 | 0.21529 |
| N | -0.21986 | -8.62143 | -1.49712 |
| C | -0.31251 | -8.46267 | -0.19310 |
| C | -0.32247 | -7.19509 | 0.43317 |
| C | -0.13304 | -6.25005 | -1.74282 |
| C | -0.13132 | -7.55345 | -2.26749 |
| F | -0.40033 | -9.55078 | 0.56773 |
| F | -0.41929 | -7.15698 | 1.77220 |
| F | -0.03826 | -5.19543 | -2.58003 |

|  |  |  |  |
|---|---|---|---|
| F | -0.03713 | -7.73063 | -3.58356 |
| H | -2.39322 | -3.15147 | 0.06257 |
| H | -2.27027 | -4.53038 | -1.11553 |
| H | -1.46104 | -2.93520 | -1.45305 |
| H | 2.01835 | -4.68963 | -0.70342 |
| H | 1.99331 | -3.22994 | 0.39010 |
| H | 1.34929 | -3.10050 | -1.27957 |
| H | 0.49296 | -4.94004 | 2.42430 |
| H | -1.29815 | -4.92986 | 2.27402 |
| H | -0.40213 | -3.35531 | 2.46348 |

**3-component intermediate**
72

|  |  |  |  |
|---|---|---|---|
| C | -0.19692 | 3.90900 | -1.73470 |
| C | -0.99242 | 3.83071 | 1.10194 |
| C | 0.45228 | 6.20319 | 0.10783 |
| C | 1.89569 | 3.63031 | 0.34466 |
| P | 0.29587 | 4.37717 | -0.05454 |
| N | 0.74905 | 8.96626 | 0.50997 |
| C | 0.43888 | 8.50120 | -0.68272 |
| C | 0.27618 | 7.12292 | -0.94787 |
| C | 0.78850 | 6.73991 | 1.37079 |
| C | 0.92270 | 8.13357 | 1.51811 |
| F | 0.27221 | 9.36476 | -1.67469 |
| F | -0.04038 | 6.72713 | -2.18489 |
| F | 0.98097 | 5.92921 | 2.42380 |
| F | 1.23359 | 8.63247 | 2.70634 |
| H | 0.56928 | 4.22107 | -2.47161 |
| H | -1.17374 | 4.36429 | -1.99529 |
| H | -0.27935 | 2.79708 | -1.74946 |
| H | -0.72021 | 4.10808 | 2.13991 |
| H | -1.07315 | 2.72030 | 1.04385 |
| H | -1.96021 | 4.29944 | 0.82366 |
| H | 2.19952 | 3.92693 | 1.36960 |
| H | 2.65386 | 3.97952 | -0.38865 |
| H | 1.81473 | 2.50409 | 0.29339 |
| Si | 0.78925 | -0.35916 | 0.15964 |
| C | 0.43710 | 0.23440 | -1.64422 |
| C | -0.17475 | 0.31116 | 1.69392 |
| C | 0.03381 | 1.12515 | -4.32840 |
| C | -1.05145 | 0.65983 | -3.56408 |
| C | -0.84465 | 0.20143 | -2.24873 |
| C | 1.50888 | 0.72446 | -2.43102 |
| C | 1.32100 | 1.14477 | -3.76052 |
| H | -0.12152 | 1.46208 | -5.36706 |
| H | -2.06328 | 0.63532 | -4.00404 |
| H | -1.69912 | -0.20179 | -1.68040 |
| H | 2.52148 | 0.76669 | -1.98990 |
| H | 2.18209 | 1.48963 | -4.35848 |
| C | -1.50973 | 1.35181 | 3.99595 |
| C | -2.24585 | 0.74721 | 2.96124 |
| C | -1.58217 | 0.21716 | 1.83820 |

| | | | |
|---|---|---|---|
| C | 0.53987 | 0.93605 | 2.74569 |
| C | -0.10901 | 1.43335 | 3.89079 |
| H | -2.02502 | 1.74733 | 4.88740 |
| H | -3.34406 | 0.67105 | 3.03973 |
| H | -2.16851 | -0.29289 | 1.05652 |
| H | 1.63895 | 1.02224 | 2.66808 |
| H | 0.47966 | 1.88504 | 4.70776 |
| H | 1.92692 | 0.73906 | 0.34152 |
| H | 1.80454 | -1.48539 | 0.36099 |
| C | -1.13104 | -4.17907 | -1.55034 |
| C | 1.25139 | -4.47074 | 0.21201 |
| F | -0.49924 | -1.68119 | -0.04675 |
| C | -1.43791 | -4.13328 | 1.37745 |
| C | -0.67870 | -6.69812 | -0.04048 |
| P | -0.50711 | -4.86659 | 0.00850 |
| N | -0.84305 | -9.49343 | -0.23542 |
| C | -1.46084 | -8.86149 | 0.74131 |
| C | -1.41484 | -7.45740 | 0.89306 |
| C | -0.02877 | -7.41110 | -1.07161 |
| C | -0.14426 | -8.81332 | -1.12366 |
| F | -2.15391 | -9.57532 | 1.61798 |
| F | -2.06577 | -6.88648 | 1.91145 |
| F | 0.69586 | -6.75888 | -1.99505 |
| F | 0.46695 | -9.47894 | -2.09393 |
| H | -1.00500 | -3.07552 | -1.42876 |
| H | -2.20240 | -4.44291 | -1.67684 |
| H | -0.54096 | -4.55877 | -2.40867 |
| H | 1.62283 | -4.89339 | 1.16952 |
| H | 1.32849 | -3.35605 | 0.23082 |
| H | 1.83829 | -4.88128 | -0.63485 |
| H | -1.04710 | -4.47781 | 2.35599 |
| H | -2.51743 | -4.37253 | 1.29620 |
| H | -1.26281 | -3.03801 | 1.23605 |

**3-component TS2**
72

| | | | |
|---|---|---|---|
| C | 0.23160 | 4.32416 | -1.66814 |
| C | -1.18180 | 3.90563 | 1.11383 |
| C | 0.31444 | 6.26561 | 0.47387 |
| C | 1.83341 | 3.72487 | 0.81368 |
| P | 0.28878 | 4.42673 | 0.16022 |
| N | 0.14842 | 9.04620 | 0.86816 |
| C | -0.78009 | 8.42353 | 0.16792 |
| C | -0.74406 | 7.03443 | -0.05467 |
| C | 1.28268 | 6.96280 | 1.22351 |
| C | 1.14780 | 8.36058 | 1.38361 |
| F | -1.77785 | 9.13765 | -0.33722 |
| F | -1.71729 | 6.44116 | -0.76911 |
| F | 2.32737 | 6.34405 | 1.78792 |
| F | 2.06581 | 9.01297 | 2.08549 |
| H | 0.70044 | 5.23709 | -2.09619 |
| H | -0.82045 | 4.25245 | -2.00788 |

| | | | |
|---|---|---|---|
| H | 0.76853 | 3.41302 | -1.99634 |
| H | -1.17521 | 4.44835 | 2.08429 |
| H | -1.16305 | 2.80801 | 1.27370 |
| H | -2.09363 | 4.18392 | 0.54589 |
| H | 1.86811 | 3.84014 | 1.91558 |
| H | 2.70343 | 4.24377 | 0.36223 |
| H | 1.84486 | 2.64790 | 0.53752 |
| Si | 0.28540 | 0.42132 | -0.46510 |
| C | -0.52513 | 0.25045 | -2.19425 |
| C | -0.75214 | 0.15617 | 1.12459 |
| C | -1.73542 | 0.04627 | -4.77005 |
| C | -2.24599 | 0.94557 | -3.81788 |
| C | -1.63265 | 1.05468 | -2.55738 |
| C | -0.04085 | -0.65895 | -3.16683 |
| C | -0.62409 | -0.74986 | -4.44326 |
| H | -2.20062 | -0.03057 | -5.76687 |
| H | -3.12051 | 1.57143 | -4.06402 |
| H | -2.02844 | 1.78686 | -1.83068 |
| H | 0.82095 | -1.30029 | -2.92082 |
| H | -0.20997 | -1.44857 | -5.19012 |
| C | -2.27694 | -0.17106 | 3.51734 |
| C | -2.91701 | -0.13984 | 2.26517 |
| C | -2.16307 | 0.02718 | 1.08864 |
| C | -0.12987 | 0.11540 | 2.39823 |
| C | -0.87842 | -0.03975 | 3.58056 |
| H | -2.86660 | -0.29466 | 4.44093 |
| H | -4.01399 | -0.24266 | 2.20477 |
| H | -2.69082 | 0.05386 | 0.11816 |
| H | 0.96948 | 0.20371 | 2.47485 |
| H | -0.36644 | -0.06139 | 4.55797 |
| H | -0.07325 | 2.01226 | -0.43302 |
| H | 1.75948 | 0.76545 | -0.26952 |
| C | -0.96543 | -3.79632 | -0.90593 |
| C | 1.98707 | -4.09283 | -0.67655 |
| F | 0.78547 | -1.34661 | -0.46546 |
| C | 0.36379 | -3.50545 | 1.71022 |
| C | 0.19626 | -6.21292 | 0.37076 |
| P | 0.39183 | -4.39914 | 0.13588 |
| N | -0.09760 | -8.99672 | 0.57274 |
| C | -0.10046 | -8.25148 | 1.65879 |
| C | 0.04298 | -6.84615 | 1.62194 |
| C | 0.19559 | -7.04522 | -0.77004 |
| C | 0.04394 | -8.43612 | -0.61279 |
| F | -0.24408 | -8.84719 | 2.83452 |
| F | 0.03014 | -6.15538 | 2.76619 |
| F | 0.33899 | -6.51573 | -1.99592 |
| F | 0.04275 | -9.21400 | -1.68623 |
| H | -0.74211 | -2.71312 | -1.04808 |
| H | -1.93464 | -3.93344 | -0.38192 |
| H | -0.97664 | -4.32671 | -1.87931 |
| H | 2.81619 | -4.44776 | -0.02862 |
| H | 2.02789 | -2.98554 | -0.80390 |
| H | 2.02676 | -4.60545 | -1.65905 |

|  |  |  |  |
|---|---|---|---|
| H | 1.19851 | -3.82814 | 2.36463 |
| H | -0.60319 | -3.64657 | 2.23323 |
| H | 0.48385 | -2.43785 | 1.41114 |

**3-component end**
72

|  |  |  |  |
|---|---|---|---|
| C | 1.36516 | 4.14510 | -1.75554 |
| C | -1.51733 | 4.24399 | -0.31261 |
| C | 0.38337 | 6.13181 | 0.13952 |
| C | 1.34203 | 3.71571 | 1.28366 |
| P | 0.33470 | 4.08087 | -0.22853 |
| N | 0.22583 | 8.88227 | 0.86531 |
| C | 0.62909 | 8.51857 | -0.33623 |
| C | 0.71088 | 7.17013 | -0.74641 |
| C | -0.06414 | 6.57150 | 1.39657 |
| C | -0.11957 | 7.93838 | 1.72081 |
| F | 0.96589 | 9.48124 | -1.19912 |
| F | 1.11459 | 6.93285 | -2.01600 |
| F | -0.46896 | 5.67365 | 2.33548 |
| F | -0.54040 | 8.31397 | 2.93263 |
| H | 2.18402 | 4.88134 | -1.64304 |
| H | 0.73763 | 4.45619 | -2.61513 |
| H | 1.76833 | 3.13130 | -1.95309 |
| H | -1.88279 | 4.51739 | 0.69949 |
| H | -1.98705 | 3.29051 | -0.63022 |
| H | -1.77747 | 5.06887 | -1.00905 |
| H | 0.66712 | 3.38015 | 2.09701 |
| H | 1.91422 | 4.60114 | 1.62765 |
| H | 2.03182 | 2.88490 | 1.02426 |
| Si | 0.19354 | 0.20654 | -0.61650 |
| C | 0.25160 | 0.61273 | -2.44960 |
| C | -1.44954 | 0.36468 | 0.28279 |
| C | 0.42353 | 1.14570 | -5.23282 |
| C | -0.68517 | 1.59639 | -4.49493 |
| C | -0.76610 | 1.33636 | -3.11653 |
| C | 1.35769 | 0.16021 | -3.21247 |
| C | 1.44665 | 0.42802 | -4.58902 |
| H | 0.49145 | 1.35640 | -6.31277 |
| H | -1.49031 | 2.15842 | -4.99634 |
| H | -1.63679 | 1.71081 | -2.55225 |
| H | 2.16949 | -0.41011 | -2.72758 |
| H | 2.32016 | 0.07667 | -5.16288 |
| C | -3.90703 | 0.48096 | 1.70178 |
| C | -3.89177 | 0.09872 | 0.34893 |
| C | -2.67426 | 0.03730 | -0.35215 |
| C | -1.48653 | 0.73887 | 1.64893 |
| C | -2.70090 | 0.79721 | 2.35281 |
| H | -4.86186 | 0.53580 | 2.25016 |
| H | -4.83573 | -0.14654 | -0.16578 |
| H | -2.68482 | -0.26616 | -1.41371 |
| H | -0.55009 | 0.99776 | 2.17360 |
| H | -2.70849 | 1.09684 | 3.41389 |

|  |  |  |  |
|---|---|---|---|
| H | 0.16382 | 2.53810 | -0.40125 |
| H | 1.38672 | 0.58945 | 0.20789 |
| C | -0.20295 | -4.41161 | -1.78162 |
| C | 1.60762 | -4.17306 | 0.56718 |
| F | 0.42637 | -1.50099 | -0.64571 |
| C | -1.29961 | -3.74797 | 0.87760 |
| C | -0.20198 | -6.50878 | 0.31949 |
| P | -0.03491 | -4.70975 | 0.00348 |
| N | -0.32991 | -9.28063 | 0.71353 |
| C | -1.19560 | -8.48982 | 1.31334 |
| C | -1.18285 | -7.08518 | 1.15460 |
| C | 0.70919 | -7.38969 | -0.30487 |
| C | 0.59983 | -8.77458 | -0.07329 |
| F | -2.11403 | -9.03312 | 2.09662 |
| F | -2.09058 | -6.34144 | 1.79317 |
| F | 1.67058 | -6.90933 | -1.11037 |
| F | 1.45348 | -9.59865 | -0.65985 |
| H | -0.05264 | -3.31963 | -1.93300 |
| H | -1.21816 | -4.71006 | -2.11909 |
| H | 0.56283 | -4.98656 | -2.34120 |
| H | 1.69996 | -4.33028 | 1.66278 |
| H | 1.68149 | -3.08976 | 0.32535 |
| H | 2.39945 | -4.74166 | 0.03789 |
| H | -1.20843 | -3.87910 | 1.97483 |
| H | -2.31714 | -4.04368 | 0.55144 |
| H | -1.10429 | -2.68764 | 0.60107 |

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