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Supporting Information for:

Air- and water-stable Lewis acids: synthesis and reactivity of *P*-trifluoromethyl electrophilic phosphonium cations

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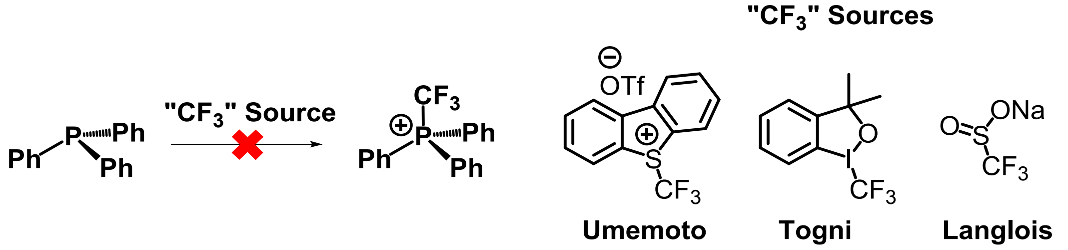
1. General Remarks

Unless otherwise indicated all manipulations were conducted under inert nitrogen atmosphere. 5-(Trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (Umemoto's reagent), 1-Trifluoromethyl-1,2-benziodoxol-3-(1H)-one (Togni's reagent), sodium triflinate (Langlois reagent), Ph_3P, Ph_2POPh, $TMSCF_3$, CsF and all the reagents for the catalysis screening were purchased from commercial sources and used as received unless otherwise stated. Tris(pentafluorophenyl)fluorophosphonium tetrakis(pentafluorophenyl)borate $[(C_6F_5)_3PF][BArF]$,[1] triphenylphosphonium anhydride trifluoromethane sulfonate (Hendrickson reagent)[2] and [K][BArF][3] were synthesized in accordance with the literature. Dichloromethane, d_2-dichloromethane, *d*-chloroform were dried over CaH_2 and distilled and degassed before use. Solvents for column chromatography were of technical grade and used without further purification. Column chromatography was performed on silica gel (230-400 mesh). NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz ^1H; 100 MHz ^{13}C; 128 MHz ^{11}B; 376 MHz ^{19}F; 79 MHz ^{29}Si, 162 MHz ^{31}P). ^1H NMR chemical shifts are reported in ppm relative to *protio* impurities in the deuterated solvents and ^{13}C NMR chemical shifts using the solvent resonances unless otherwise stated. ^{11}B NMR spectra were referenced to external $BF_3:Et_2O$, ^{19}F to Cl_3CF, ^{29}Si to $Si(CH_3)_4$ and ^{31}P to 85% H_3PO_4.). Coupling constants *J* are given in Hertz (Hz), while the multiplicity of the signals are indicated as "s", "d", "t", "q", "pent", "sept" or "m" for singlet, doublet, triplet, quartet, pentet, septet or multiplet, respectively. Mass spectra were recorded on a Waters QTOF mass spectrometer.

2. Attempted trifluoromethylations of phosphines

2.1 Electrophilic / radical trifluoromethylation



Umemoto's: the use of Umemoto's reagent was found to be unsuccessful under a range of conditions (this is consistent with already reported by Umemoto and co-workers).[4]

Togni's: under inert atmosphere, in a J. Youngs NMR tube, Ph_3P (15 mg, 0.06 mmol, 1.5 eq.) was dissolved in anhydrous DCM (0.5 mL), followed by the addition of 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (13 mg, 0.04 mmol, 1.0 eq.). After heating the reaction mixture at 60°C for 18 hours, no significant reactivity was observed.

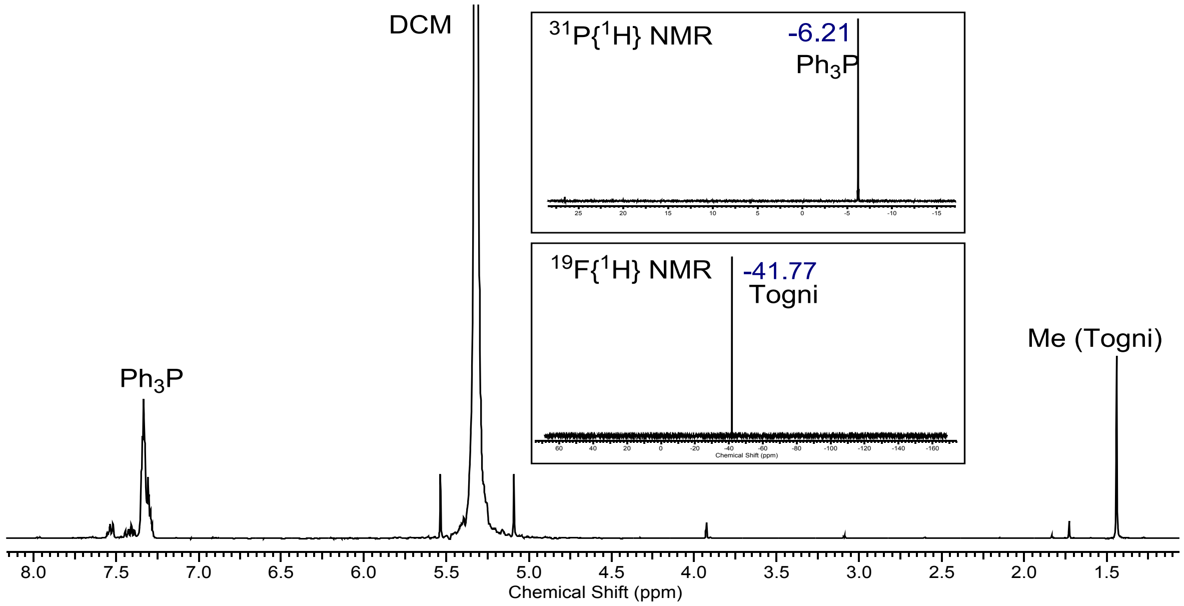


Figure S1. *In situ* ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reaction between Ph_3P and Togni's reagent in anhydrous DCM after 18 h at 60°C.

Langlois's: under inert atmosphere, in a J. Youngs NMR tube, Ph_3P (10 mg, 0.04 mmol, 1.0 eq.), sodium triflinate (19 mg, 0.12 mmol, 3.0 eq.) and CuCl (4 mg, 0.04 mmol, 1.0 eq.) were dissolved in anhydrous DCM (0.5 mL), followed by the addition of a 5.5 M solution of tert-butyl hydroperoxide in nonane (35 µL, 0.20 mmol, 5.0 eq.). After heating the reaction mixture at 60°C for 1 hours, although some $CuCF_3$ was observed (thus suggesting CF_3 radical formation), Ph_3P was oxidized to Ph_3PO.

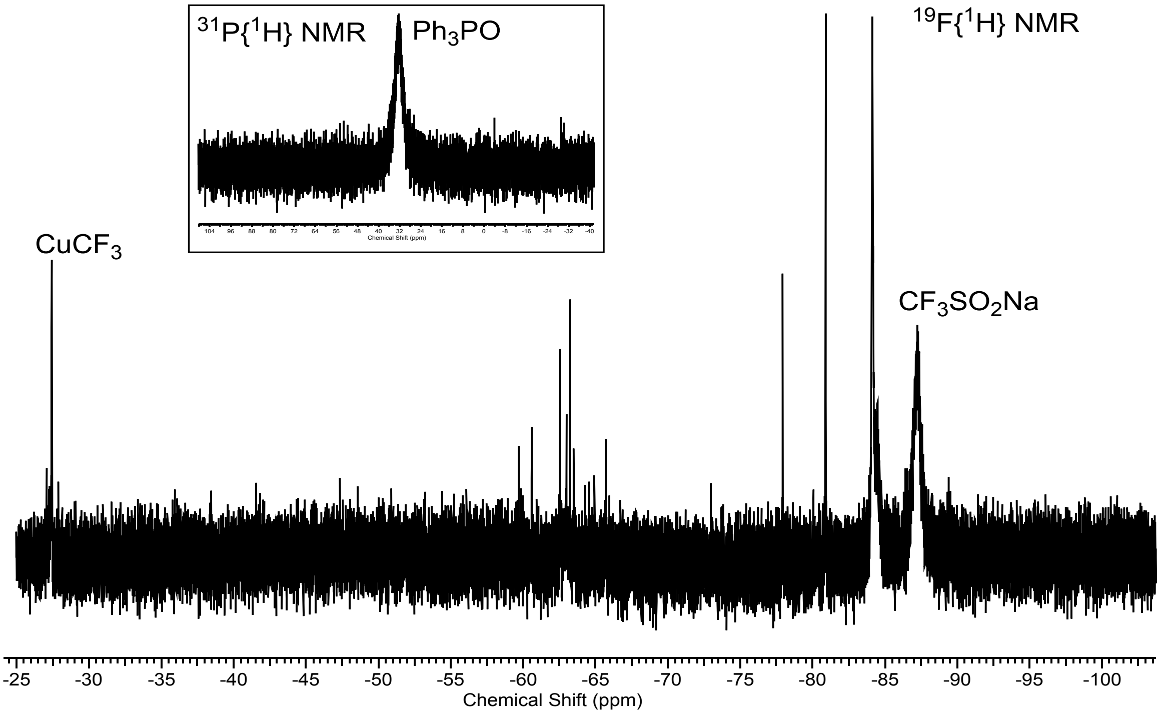
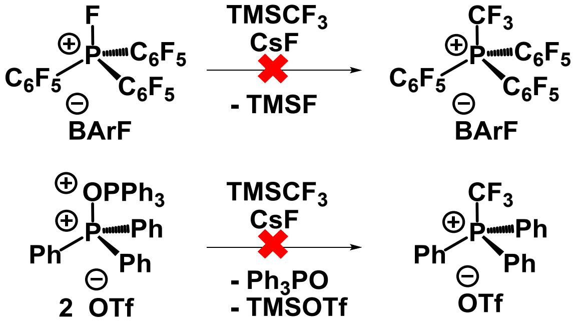


Figure S2. *In situ* ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of the reaction with Ph$_3$P, CF$_3$SO$_2$Na, CuCl and TBHP in anhydrous DCM after 1 h at 60^{o}C.

2.2 Nucleophilic trifluoromethylation



[(C$_6$F$_5$)$_3$PF][BArF]: Under inert atmosphere, in a J. Youngs NMR tube, [(C$_6$F$_5$)$_3$PF][BArF] (49 mg, 0.04 mmol, 1.0 eq.) was dissolved in anhydrous DCM (0.5 mL), followed by the addition of TMSCF$_3$ (9 µL, 0.06 mmol, 1.5 eq.) and CsF (3 mg, 0.02 mmol, 0.5 eq.). After inverting the reaction mixture at R.T. for 18 hours, (C$_6$F$_5$)$_3$PF$_2$ was observed; the high fluorophilicity of the starting phosphonium sequestered the fluoride preventing TMSCF$_3$ activation, while in absence of CsF no reaction was observed at R.T.). Diagnostic peaks: ^{31}P{^{1}H} NMR δ = -48.1 ppm (t, $^{1}J_{P-F}$ = 695 Hz) and ^{19}F{^{1}H} NMR δ = 1.60 ppm (d, $^{1}J_{P-F}$ = 695 Hz), in accordance with those reported in the literture.[1]

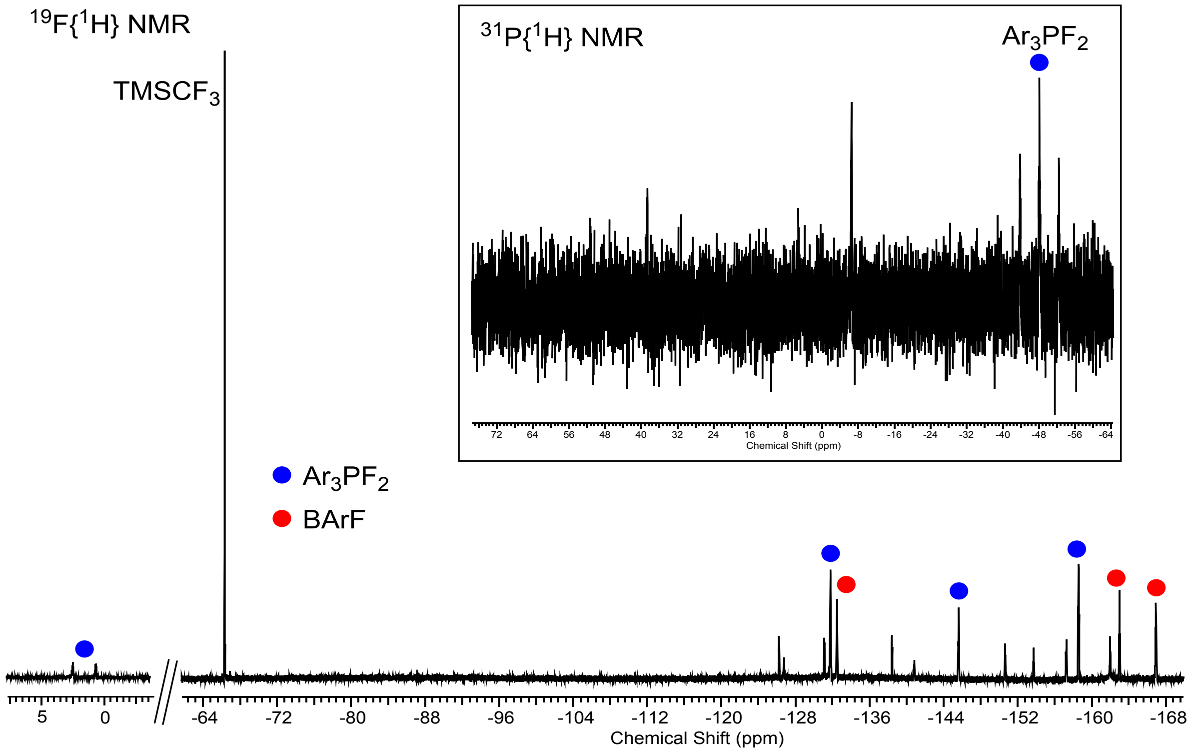


Figure S3. *In situ* $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$-NMR spectra of the reaction with $[(C_6F_5)_3PF][BArF]$, $TMSCF_3$ and CsF in anhydrous DCM, after 18 h at R.T.

$[Ph_3POPPh_3][OTf]_2$: Under inert atmosphere, in a vial Ph_3PO (45 mg, 0.16 mmol, 2.0 eq.) was dissolved in anhydrous DCM (0.5 mL), followed by the addition of Tf_2O (14 µL, 0.08 mmol, 1.0 eq.). After 10 minutes at R.T., a white solid was formed ($^{31}P/^{19}F$ NMR analysis revealed full conversion of Ph_3PO to $[Ph_3POPPh_3][OTf]_2$).[2] Then, to the reaction mixture $TMSCF_3$ (25 µL, 0.17 mmol, 2.1 eq.) and CsF (25 mg, 0.16 mmol, 2.0 eq.) were added. After leaving the reaction mixture stirring at R.T. for 4 hours, Ph_3PF was detected as major species with minimal $TMSCF_3$ activation observed). Diagnostic peaks: $^{31}P\{^{1}H\}$ NMR δ = 94.7 ppm (d, $^{1}J_{P\text{-}F}$ = 996 Hz) and $^{19}F\{^{1}H\}$ NMR δ = -128.0 ppm (d, $^{1}J_{P\text{-}F}$ = 996 Hz), in accordance with those reported in the literature.[5]

Note: in the $[Ph_3POPPh_3][OTf]_2$ formation, the small peaks at 65 ppm and 52 ppm are related to the coordination of one or two $[OTf]^-$ to the dication, respectively.[2]

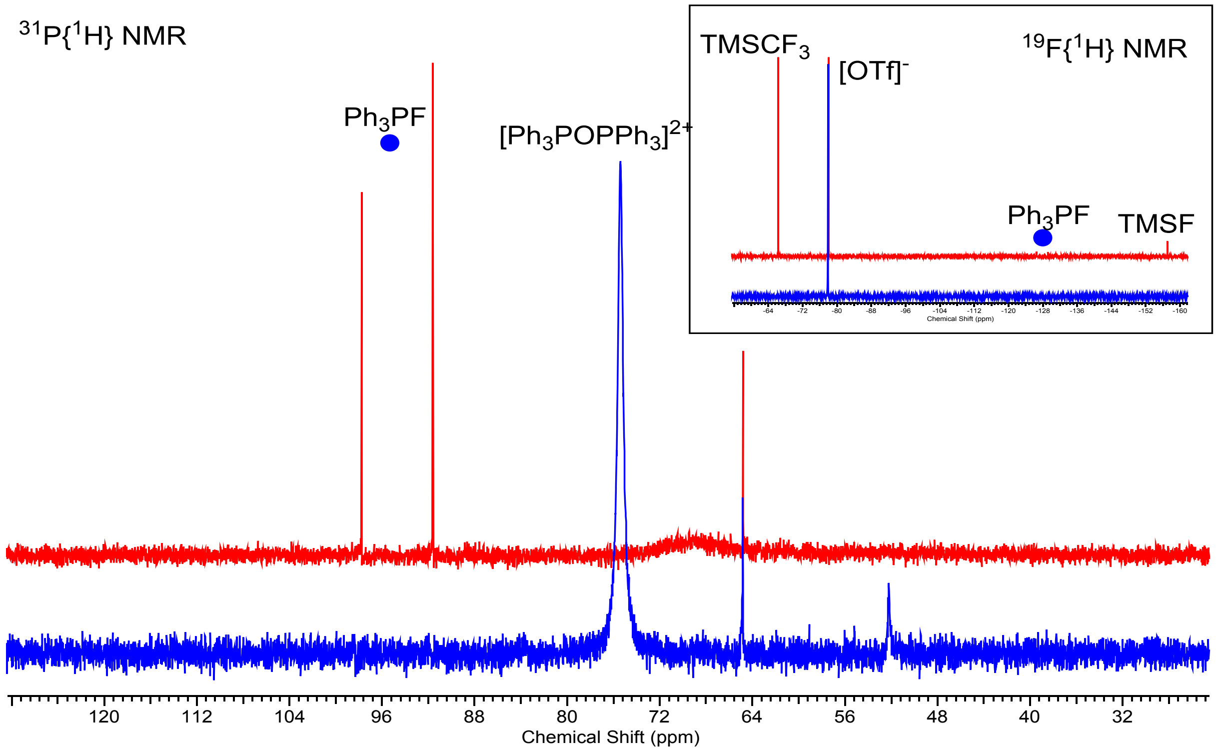
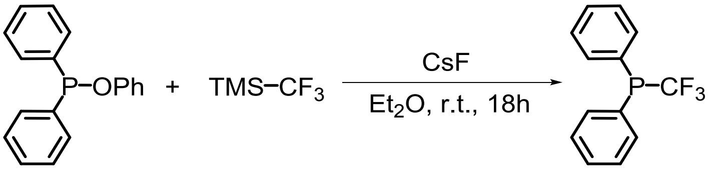


Figure S4. *In situ* $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reaction with $[Ph_3POPPh_3][OTf]_2$, $TMSCF_3$ and CsF in anhydrous DCM, after 18 h at R.T.

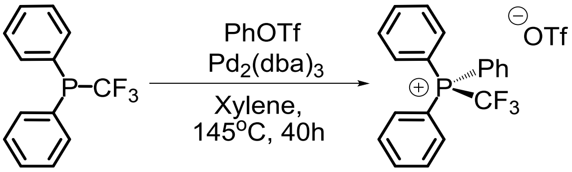
3. Catalyst synthesis

3.1 Synthesis of diphenyl(trifluoromethyl)phosphine (Ph_2PCF_3)



Under anhydrous conditions, an ampoule was charged with diphenyl phenoxy phosphine (2.40 g, 8.45 mmol, 1.00 eq.) and caesium fluoride (0.76 g, 4.75 mmol, 0.56 eq.) in distilled Et_2O (15 mL), followed by the addition of trifluoromethyl trimethylsilane (1.90 mL, 12.70 mmol, 1.50 eq.). The ampoule was sealed and the solution stirred at room temperature for 18 hours. The obtained orange solution was then filtered and the solvent removed. The resulting crude oil was purified by flash chromatography on silica gel (100% hexane), yielding diphenyl(trifluoromethyl)phosphine as a colourless oil (1.83 g, 7.2 mmol, 85%). R_f = 0.22. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.65 (m, 4H), 7.40-7.52 (m, 6H) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 2.57 ppm (q, *J* = 73.2 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -55.1 ppm (d, *J* = 72.7 Hz). The results are in accordance with those reported in the literature.[6]

3.2 Synthesis of triphenyl(trifluoromethyl)phosphonium trifluoromethanesulfonate ([1][OTf])



Under anhydrous conditions, an ampoule was charged with tris(dibenzylideneacetone)dipalladium(0) (0.12 g, 0.12 mmol, 0.05 eq.) in distilled xylene (1 mL), followed by the addition of phenyltriflate (1.01 mL, 6.11 mmol, 2.50 eq.) and diphenyl(trifluoromethyl)phosphine (0.50 mL, 2.45 mmol, 1.00 eq.). The ampoule was sealed and the solution stirred at 145°C for 40 hours. Upon heating, a dark orange solution with a whitish precipitate was found. The solvent was removed under vacuum and the crude left was washed with hexane. The solid left was dissolved in DCM and filtered . The obtained orange solution was concentrated and a recrystallization in DCM/hexane was performed twice to obtain triphenyl(trifluoromethyl)- phosphonium trifluoromethanesulfonate **[1][OTf]** as a pale brown solid after the removal of the solvent (1.00 g, 2.08 mmol, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97-8.12 (m, 3H), 7.72-7.95 (m, 12H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.0 (d, *J* = 2.9 Hz), 134.8 (d, *J* = 11.7 Hz), 131.6 (d, *J* = 13.7 Hz), 109.6 (d, *J* = 86.1 Hz) ppm (the trifluoromethyl carbons could not be detected). $^{31}P\{^1H\}$

NMR (162 MHz, $CDCl_3$): δ 27.5 ppm (q, *J* = 92.3 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -58.2 ppm (d, *J* = 92.3 Hz), -78.2 (s) ppm. Elemental analysis for $C_{20}H_{15}F_6O_3PS$: calcd C 50.01 H 3.15, found C 50.20 H 3.37. HRMS (MS ESI+) for **[1]**$^+$: *m/z* 331.0856 (calcd 331.0858).

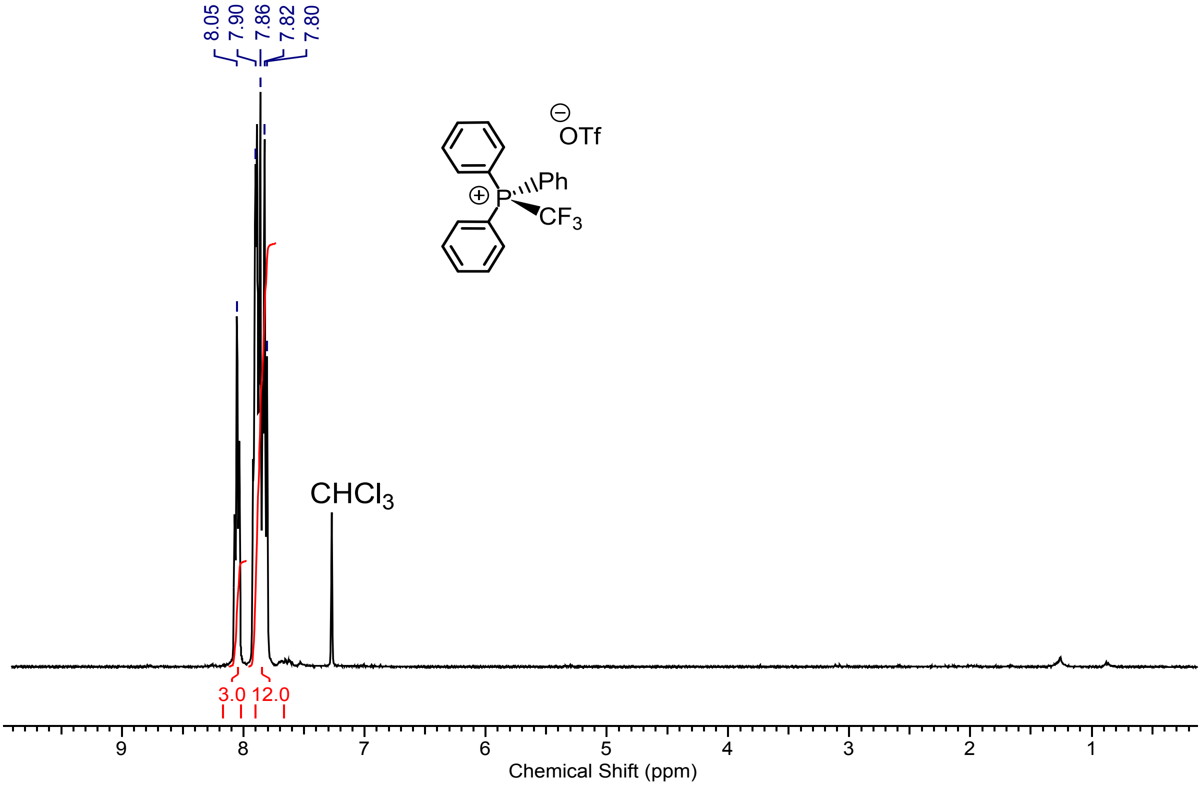


Figure S5. ^1H-NMR spectrum of **[1][OTf]** in dried $CDCl_3$.

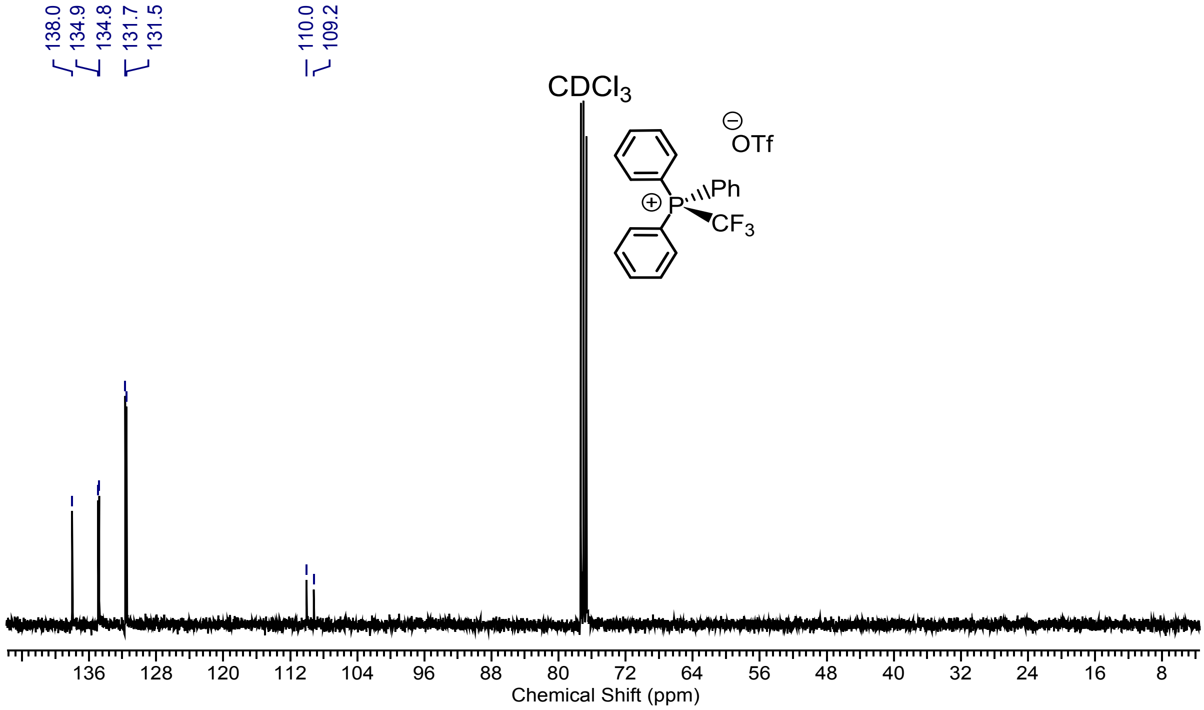


Figure S6. $^{13}C\{^1H\}$-NMR spectrum of **[1][OTf]** in dried $CDCl_3$.

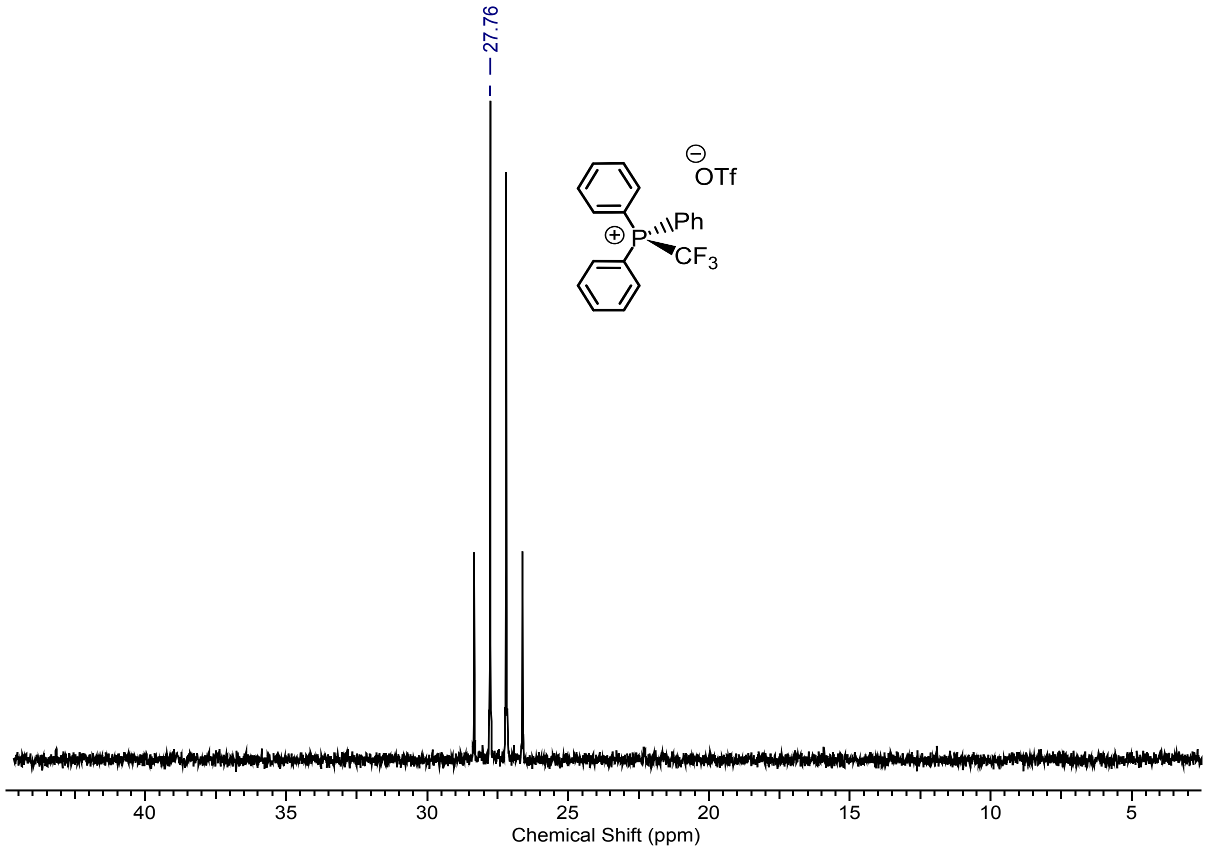


Figure S7. $^{31}P\{^{1}H\}$-NMR spectrum of **[1][OTf]** in dried $CDCl_3$.

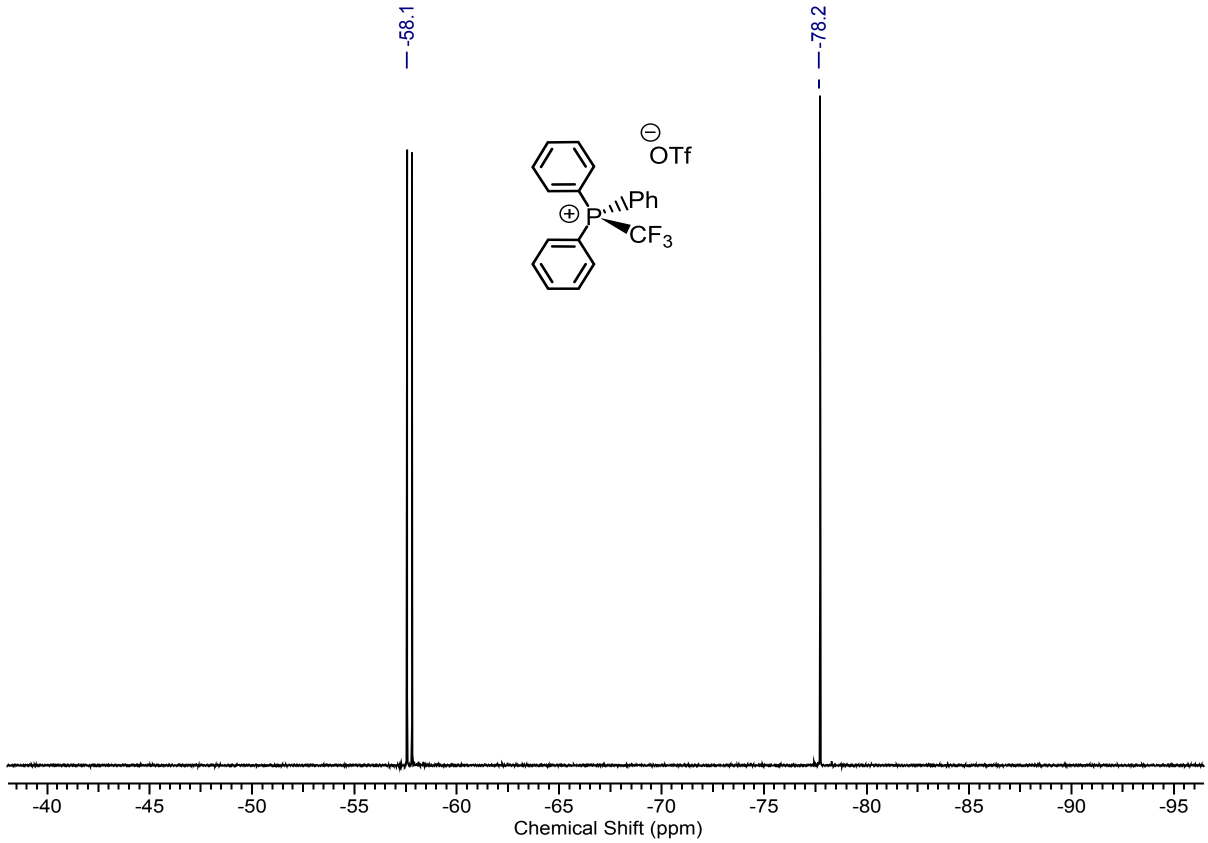
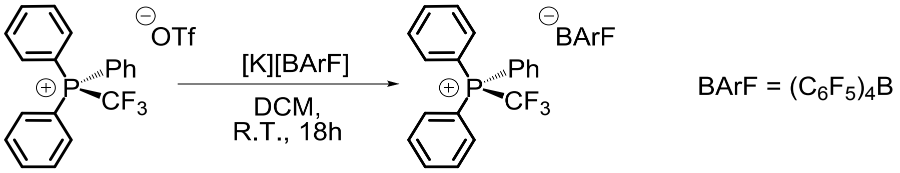


Figure S8. $^{19}F\{^{1}H\}$-NMR spectrum of **[1][OTf]** in dried $CDCl_3$.

3.3 Synthesis of triphenyl(trifluoromethyl)phosphonium tetrakis(pentafluorophenyl)borate ([1][BArF])



Under anhydrous conditions, in a 20 mL vial potassium tetrakis(pentafluorophenyl)-borate (329 mg, 0.46 mmol, 1.10 eq.) was dissolved in distilled DCM (15 mL), followed by the addition of **[1][OTf]** (200 mg, 0.42 mmol, 1.00 eq.). The vial was sealed and the light brown suspension was stirred at ambient temperature for 18 hours. The resultant suspension was filtered over celite. The obtained solution was precipitated with hexane, decanted, and dried under vacuum. The crude left was washed with hexane and dried under vacuum. The obtained solid was recrystallized in DCM/hexane, providing **[1][BArF]** as a light brown solid (371 mg, 0.37 mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.76 (m(br), 6H), 7.81 (m(br), 6H), 8.03 ppm (m(br), 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 109.7 (d, *J* = 86.5 Hz), 124.0 (m,(br)), 131.8 (d, *J* = 13.7 Hz), 134.6 (d, *J* = 10.9 Hz), 136.3 (d(br), *J* = 240 Hz), 138.2 (d(br), *J* = 240 Hz), 138.4 (d, *J* = 3.3 Hz), 148.2 ppm (d(br), *J* = 238 Hz) (the trifluoromethyl carbon). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 27.5 ppm (q, *J* = 94.8 Hz). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ -58.0 ppm (d, *J* = 95.4 Hz), -132.6 (s), -163.1 (t, *J* = 20.5 Hz), -166.9 ppm (t, *J* = 16.0 Hz). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ -16.7 ppm (s). Elemental analysis for $C_{43}H_{15}BF_{23}P$: calcd C 51.12 H 1.50, found C 51.66 H 1.60.

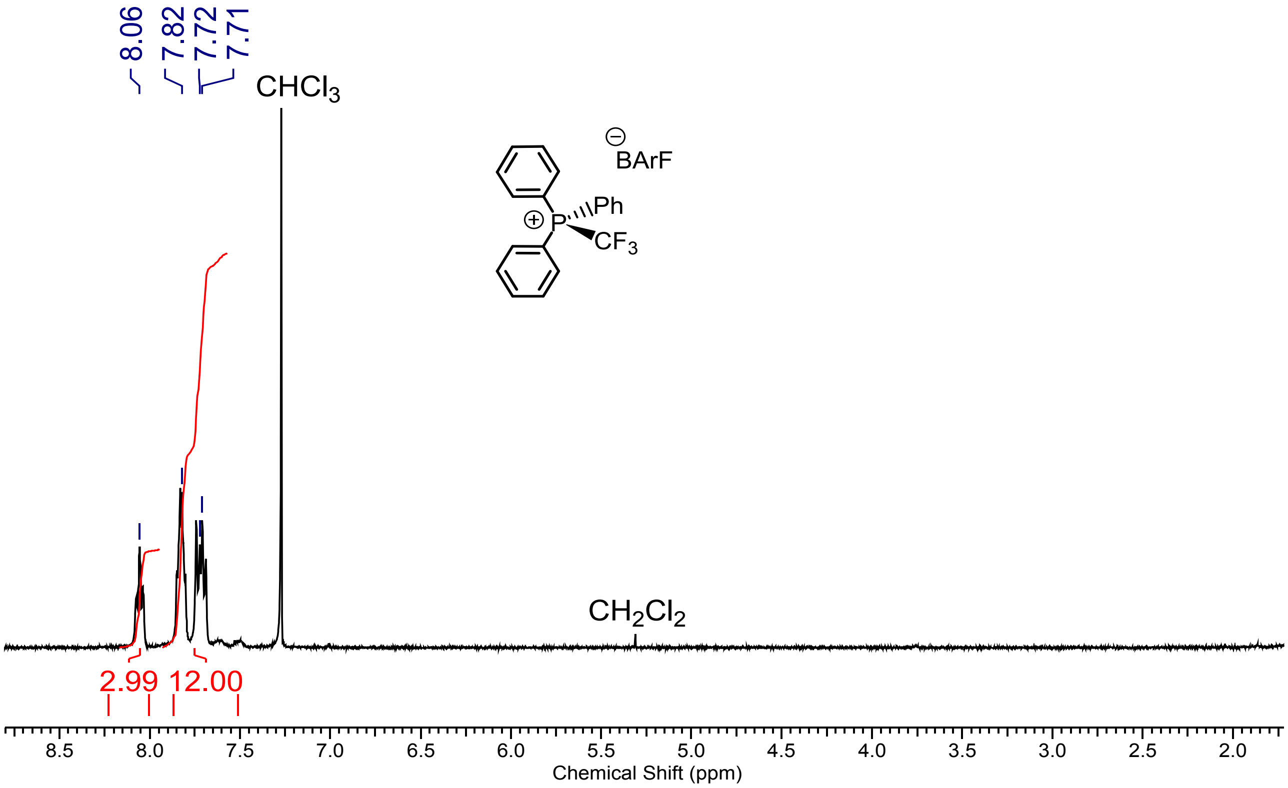


Figure S9. ^{1}H-NMR spectrum of **[1][BArF]** in dried $CDCl_3$.

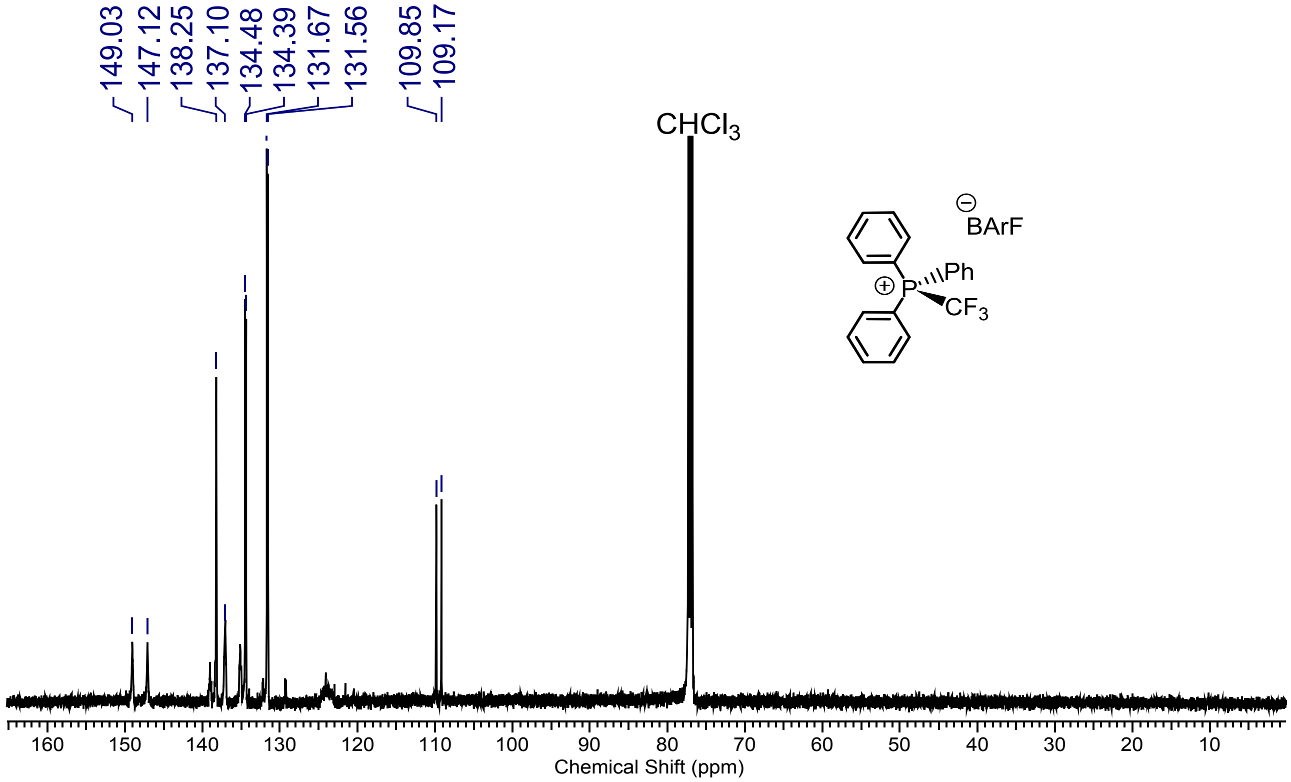


Figure S10. $^{13}C\{^{1}H\}$-NMR spectrum of **[1][BArF]** in dried $CDCl_3$.

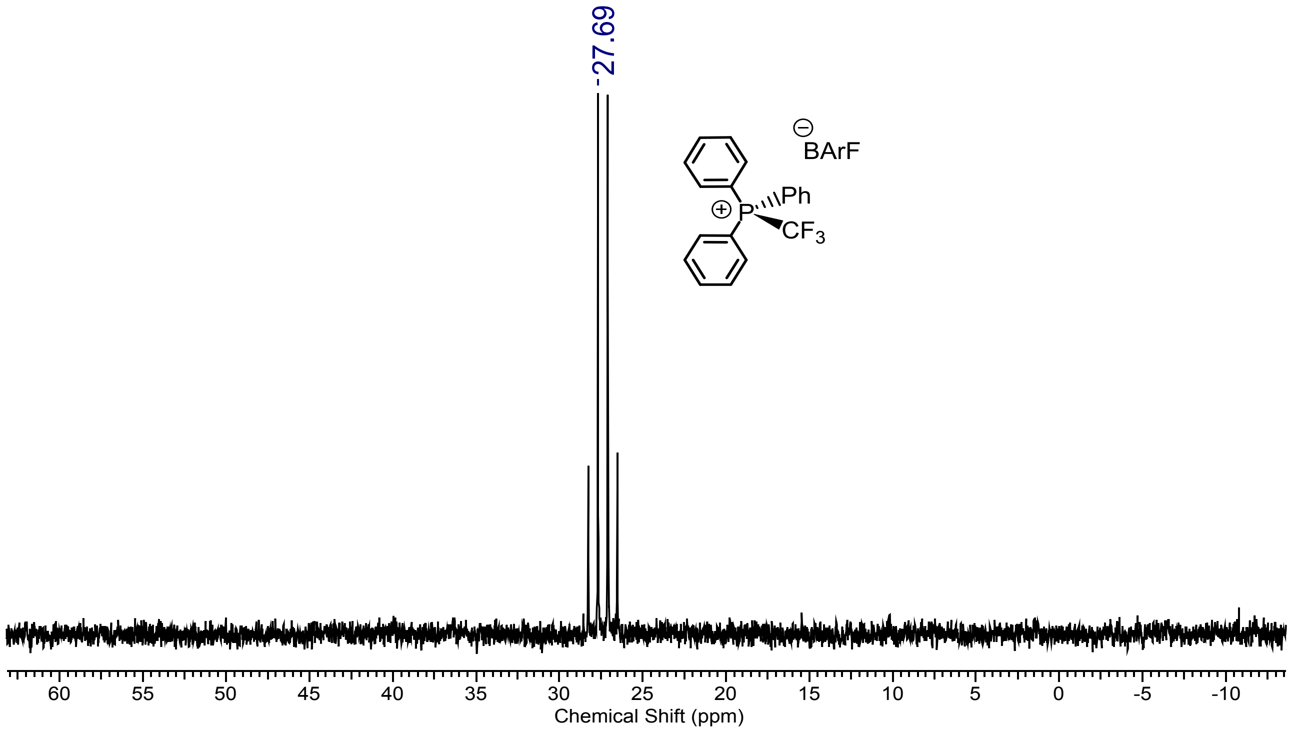


Figure S11. $^{31}P\{^{1}H\}$-NMR spectrum of **[1][BArF]** in dried $CDCl_3$.

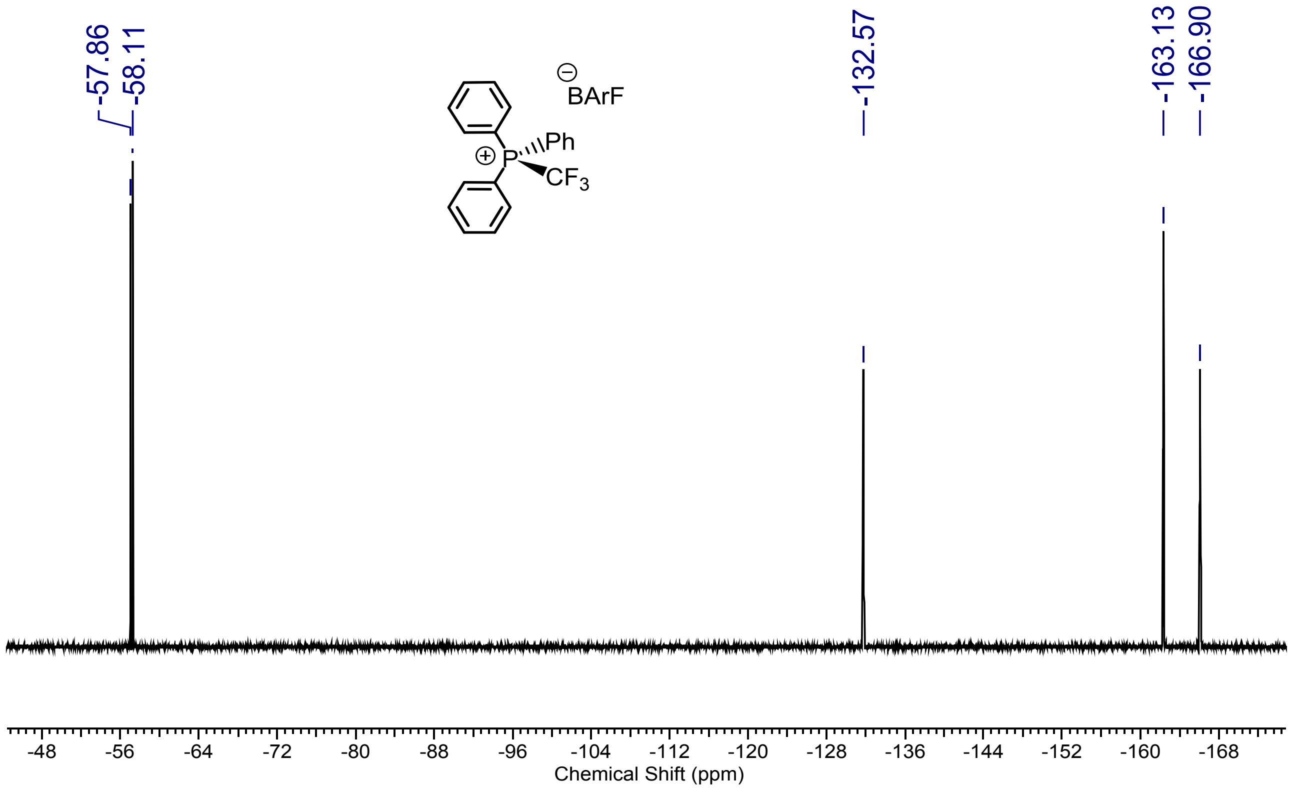


Figure S12. $^{19}F\{^1H\}$-NMR spectrum of **[1][BArF]** in dried $CDCl_3$.

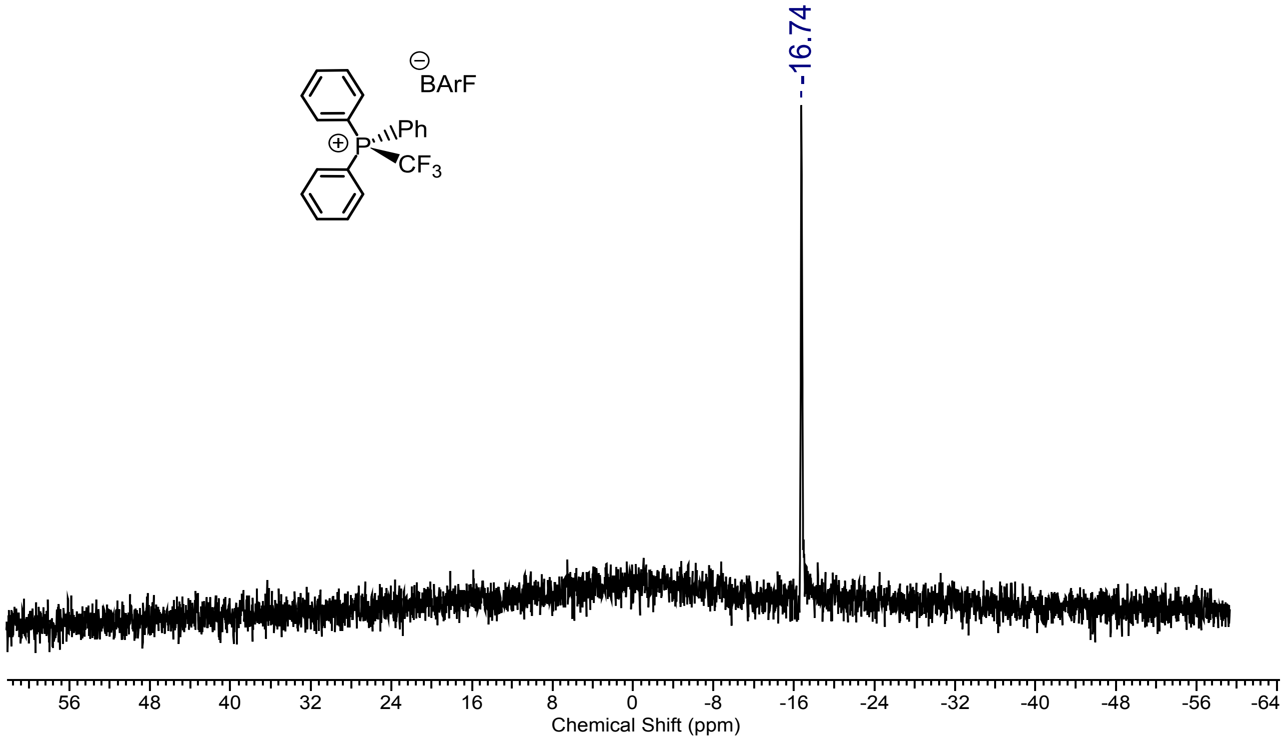
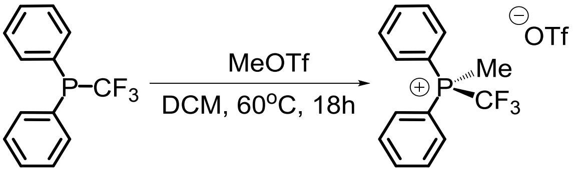


Figure S13. $^{11}B\{^1H\}$-NMR spectrum of **[1][BArF]** in dried $CDCl_3$.

3.4. Synthesis of methyldiphenyl(trifluoromethyl)phosphonium trifluoromethanesulfonate ([2][OTf])



Under anhydrous conditions, an ampoule was charged with diphenyl(trifluoromethyl)phosphine (250 µL, 1.22 mmol, 1.00 eq.) in distilled DCM (3 mL), followed by the addition of methyltriflate (155 µL, 1.34 mmol, 1.10 eq.). The ampoule was sealed and the solution stirred at 60°C for 18 hours. Then, the solvent and the excess of the MeOTf were removed under vacuum, obtaining methyldiphenyl(trifluoromethyl)phosphonium trifluoromethanesulfonate **[2][OTf]** as a white powder (440 mg, 1.05 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-8.10 (m, 6H), 7.70-7.86 (m, 4H), 3.09 (d, *J* = 14.0 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 137.3 (d, *J* = 3.4 Hz), 133.9 (d, *J* = 11.2 Hz), 131.1 (d, *J* = 13.7 Hz), 110.5 (d, *J* = 86.6 Hz), 3.9 (d, *J* = 50.9 Hz) ppm (the trifluoromethyl carbons could not be detected). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 29.6 ppm (q, *J* = 92.3 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -62.9 ppm (d, *J* = 92.3 Hz), -78.5 (s) ppm. Elemental analysis for $C_{15}H_{13}F_6O_3PS$: calcd C 43.07 H 3.13, found C 42.82 H 3.07. HRMS (MS ESI+) for **[2]**$^+$: *m/z* 269.0728 (calcd 269.0701).

Note: MeOTf is a strong methylating agent (use it in a fumehood at all times and quench it with $NaOH_{(aq.)}$ *solution).*

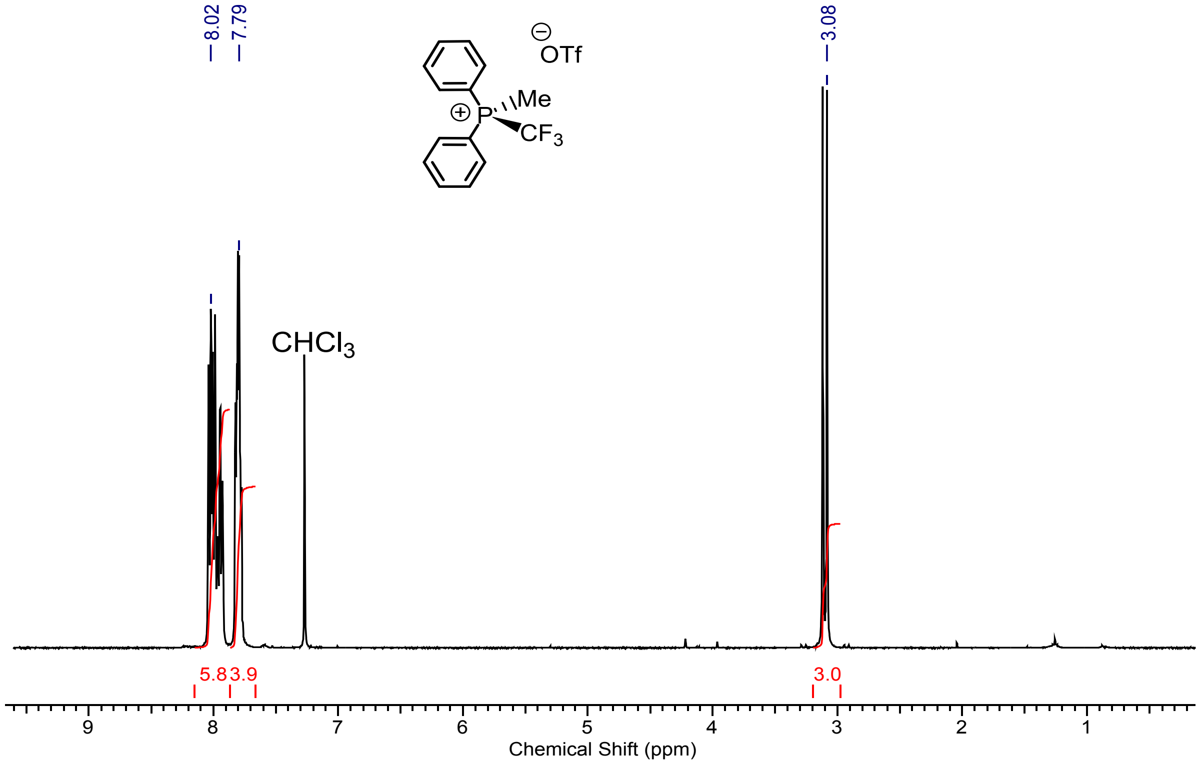


Figure S14. ^{1}H-NMR spectrum of **[2][OTf]** in dried $CDCl_3$.

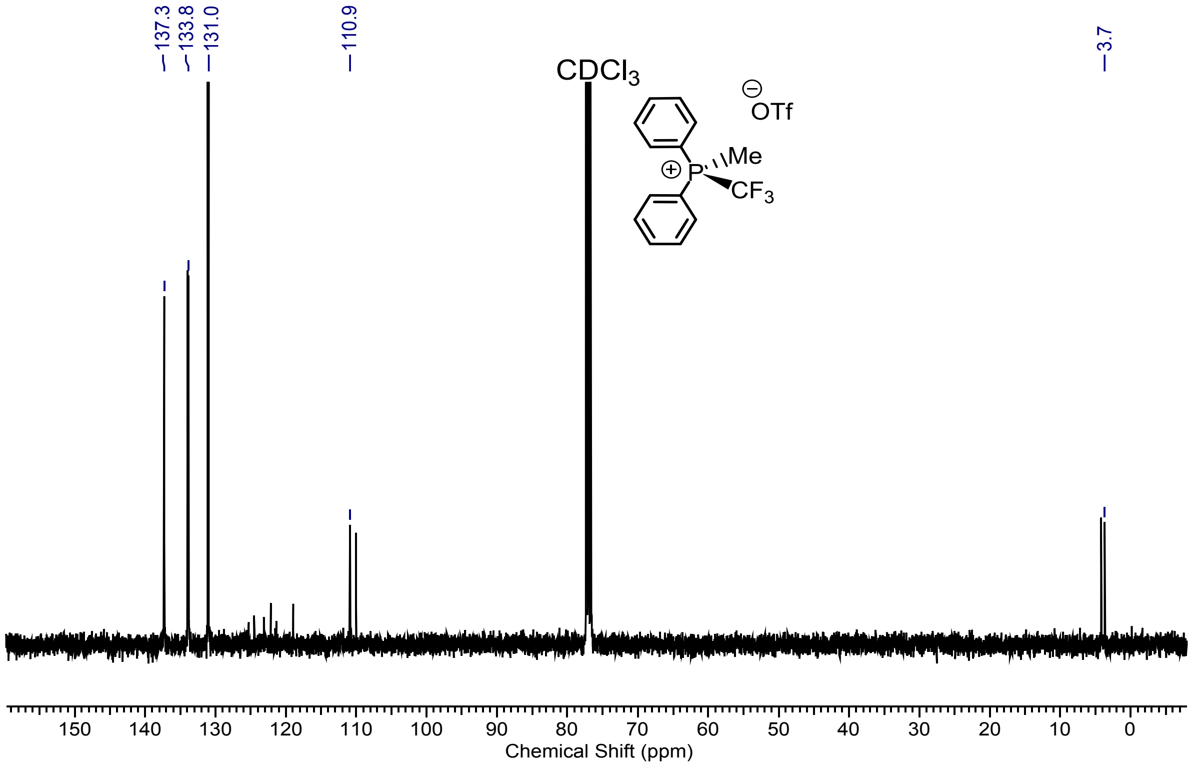


Figure S15. ^{13}C{^{1}H}-NMR spectrum of **[2][OTf]** in dried $CDCl_3$.

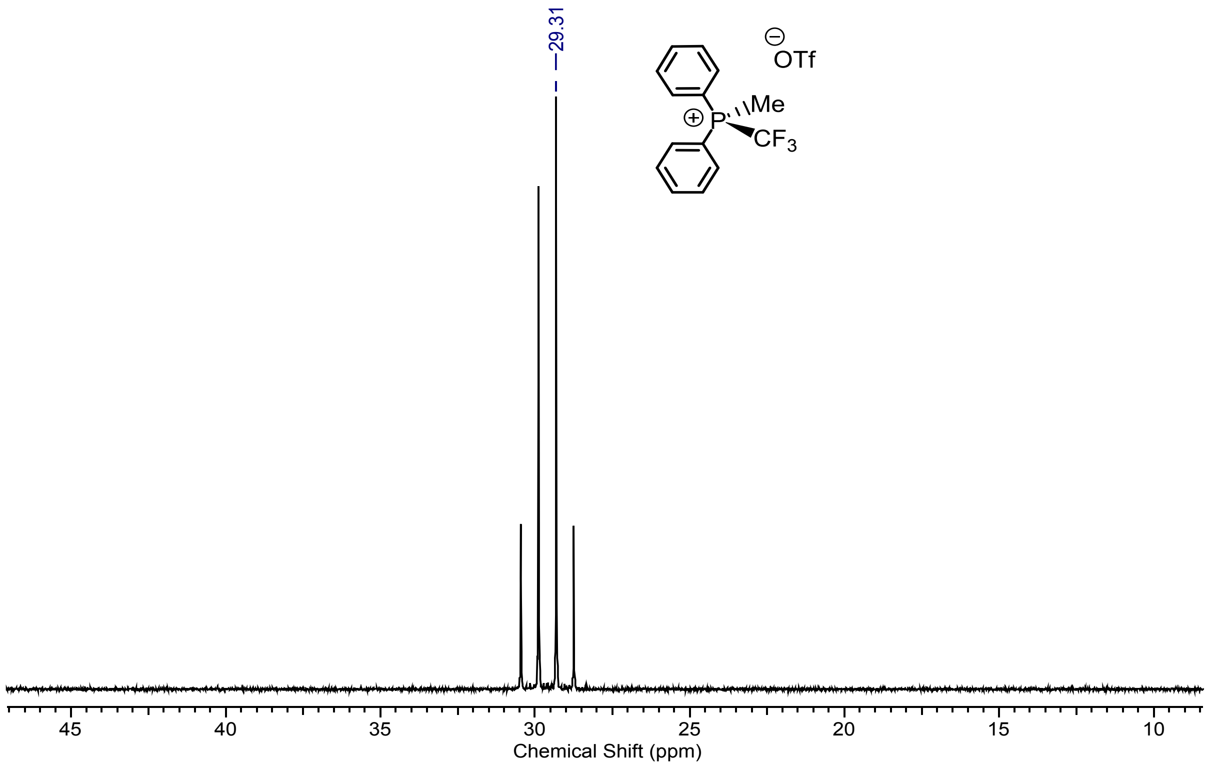


Figure S16. $^{31}P\{^1H\}$-NMR spectrum of **[2][OTf]** in dried $CDCl_3$.

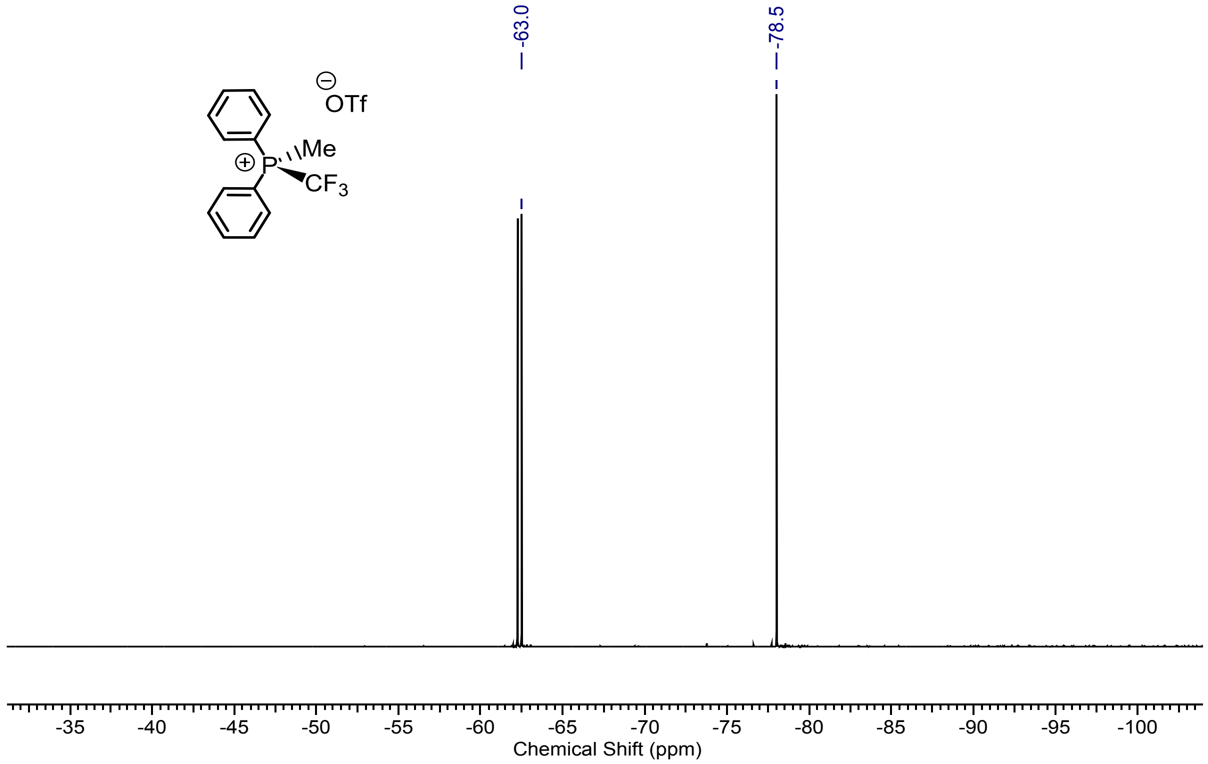


Figure S17. $^{19}F\{^1H\}$-NMR spectrum of **[2][OTf]** in dried $CDCl_3$.

4. Stability test

General procedure: in a J. Young NMR tube the catalyst was dissolved in $CDCl_3$ (0.05 mL), followed by the addition of ROH (R = H, Ph). The system was then heated in an oil bath (see figure captions for the temperatures) and analysed by multinuclear NMR analysis. In the absence of added water, the solutions were made under inert atmosphere with dried $CDCl_3$ (0.5 mL). When aniline was involved in the test, it was added after ROH.

4.1 Water addition

[1][OTf] (9 mg, 1 eq.) + **H_2O** (4 μL, > 10 eq.).

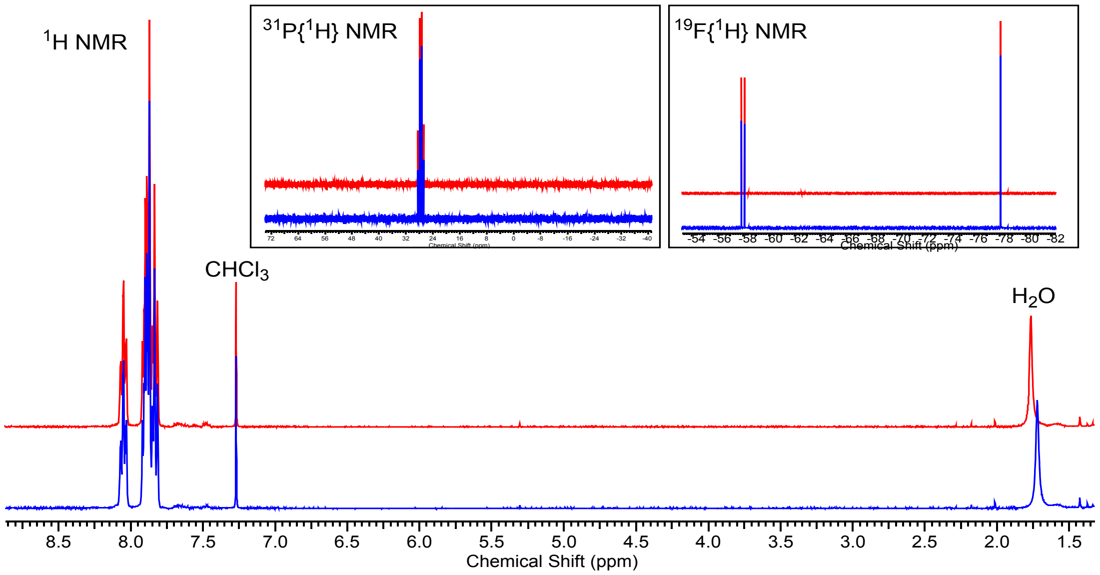


Figure S18. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[1][OTf]** with water in $CDCl_3$. Blue (after 5 min), red (after 18h at 60°C).

[1][BArF] (10 mg, 1 eq.) + **H_2O** (4 μL, > 10 eq.) in $CDCl_3$ (0.5 mL).

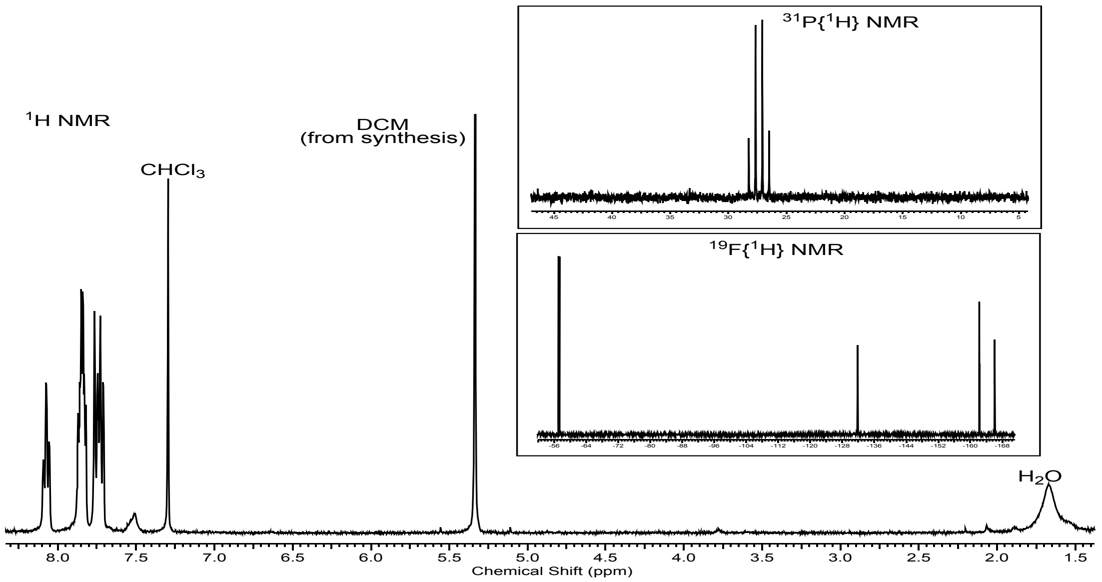


Figure S19. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[1][BArF]** with water in $CDCl_3$ after 18h at 100°C.

[2][OTf] (8 mg, 1 eq.) + **H_2O** (4 µL, > 10 eq.) in $CDCl_3$ (0.5 mL).

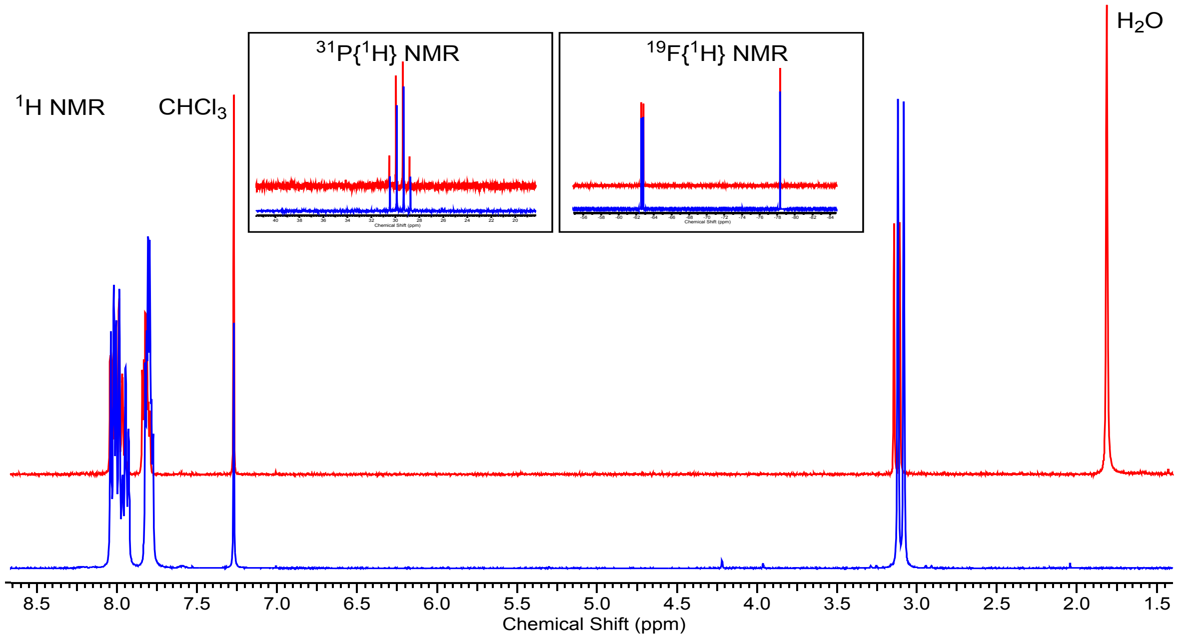


Figure S20. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[2][OTf]** with water in $CDCl_3$. Blue (under anhydrous conditions), red (with water after 18h at 60°C). Note: no significant shift is noted when water is added to the system, indicating a very low degree of water coordination.

4.2 Phenol addition

[1][OTf] (15 mg, 1 eq.) + **PhOH** (3 mg, 1 eq)

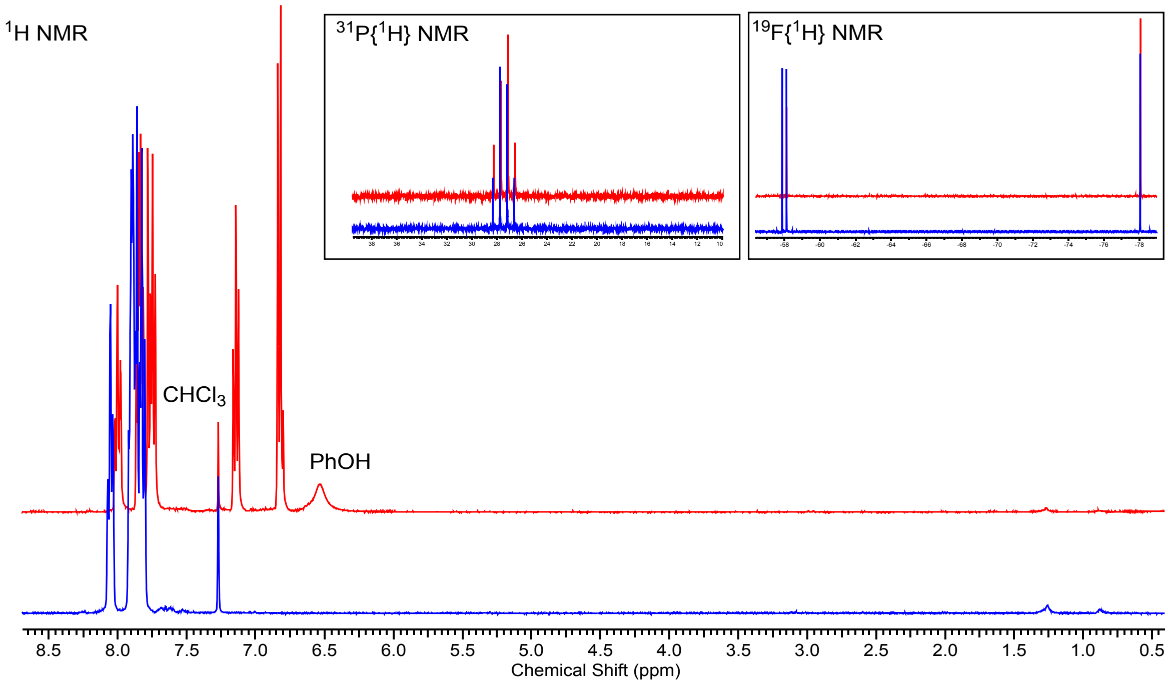


Figure S21. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[1][OTf]** with PhOH in CDCl$_3$. Blue (before PhOH addition), red (after 5 hours at 60ºC from PhOH addition). Note: minimal shift is noted when PhOH is added to the system, indicating a very low degree of PhOH coordination.

[2][OTf] (10 mg, 1 eq.) + **PhOH** (3 mg, 1 eq.)

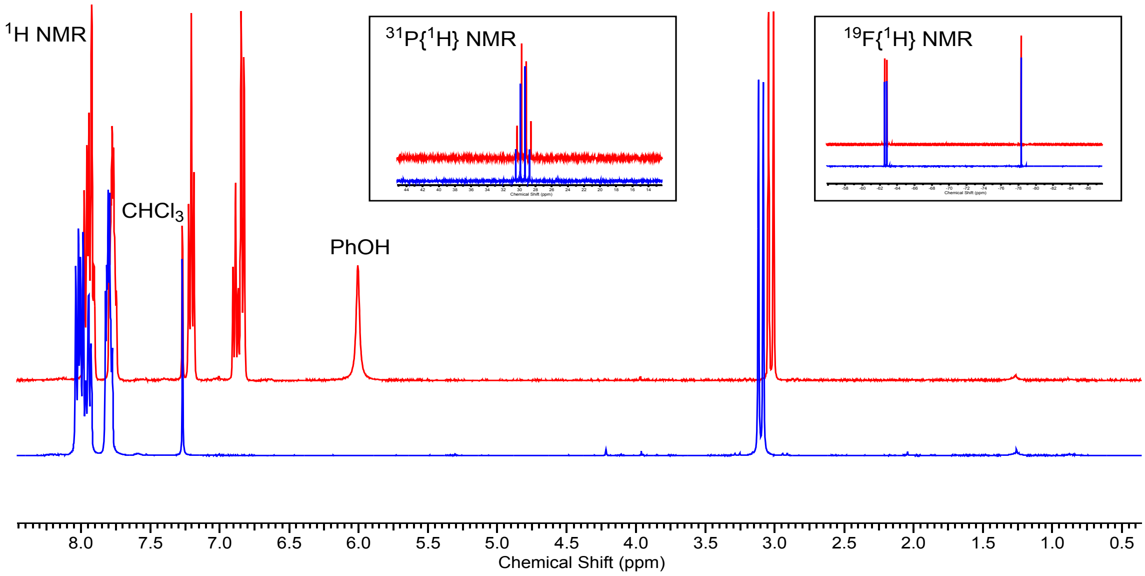


Figure S22. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[2][OTf]** with PhOH in CDCl$_3$. Blue (before PhOH addition), red (after 10 min from PhOH addition). Note: minimal shift is noted when PhOH is added to the system, indicating a very low degree of PhOH coordination.

4.3 Phenol / PhNH$_2$ addition

[1][OTf] (15 mg, 1 eq.) + **PhOH** (3 mg, 1 eq.) + **PhNH$_2$** (3 μL, 1 eq.)

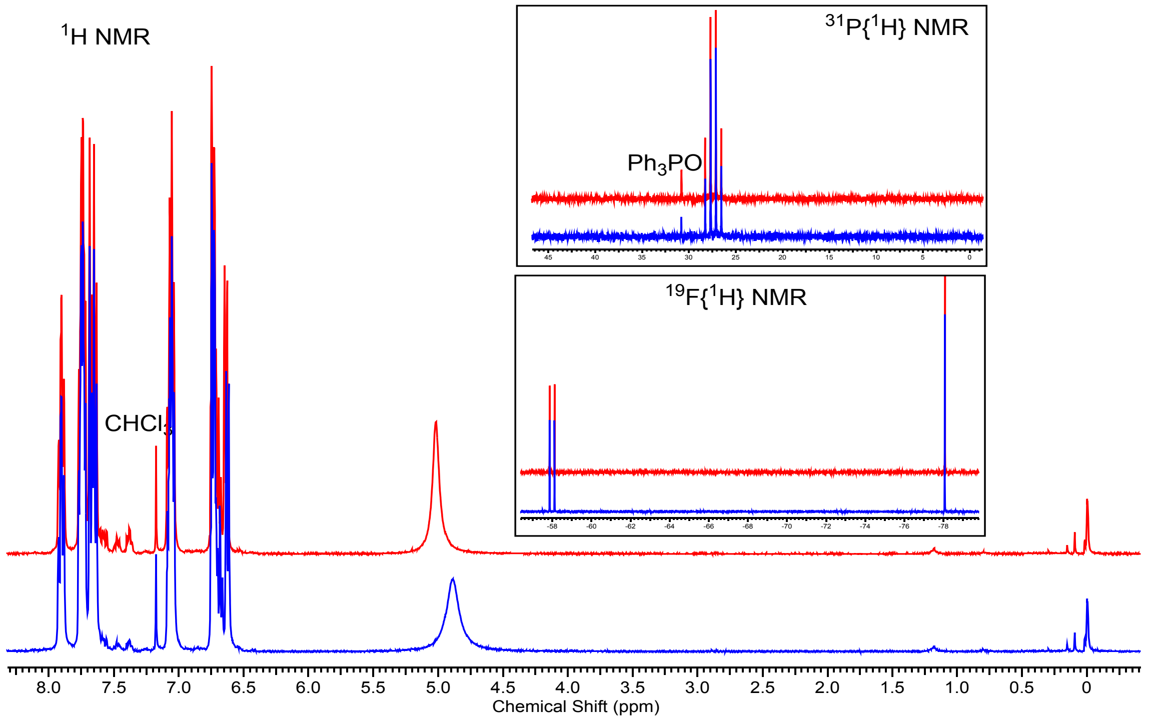


Figure S23. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[1][OTf]** with PhOH / PhNH$_2$ in CDCl$_3$. Blue (after 5 min), red (after 18h at 60ºC). Small Ph$_3$PO formation is observed on heating most likely due to trace water present in phenol/aniline.

[2][OTf] (10 mg, 1 eq.) + **PhOH** (3 mg, 1 eq.) + **PhNH$_2$** (2 μL, 1 eq.) in CDCl$_3$ (0.5 mL).

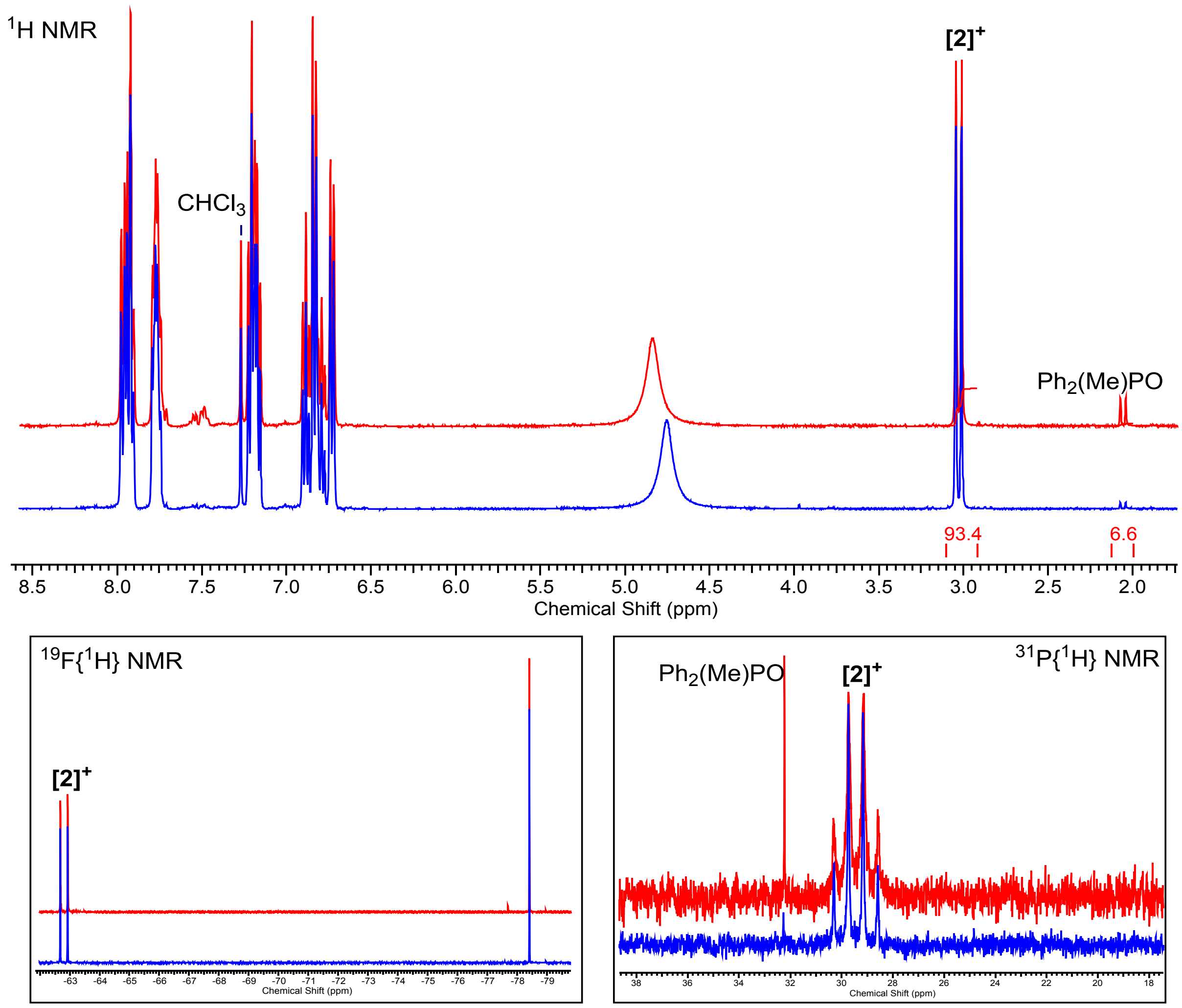


Figure S24. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[2][OTf]** with PhOH / PhNH$_2$ in dried CDCl$_3$. Blue (after 5 min), red (after 18h at 60°C). Note: small Ph$_2$(Me)PO formation (~ 7%) is observed on heating most likely due to trace water present in phenol/aniline.

4.4 Water/ PhNH$_2$ addition

[1][OTf] (24 mg, 1 eq.) + **H$_2$O** (1 µL, 1 eq.) + **PhNH$_2$** (5 µL, 1 eq.). After 5 min upon mixing, effervescence was noted, along with white solid formation. NMR analysis revealed HCF$_3$ (^{1}H δ = 6.6 ppm, q, $^2J_{H\text{-}F}$ = 79 Hz; ^{19}F δ = -77.8 ppm, d, $^2J_{H\text{-}F}$ = 79 Hz) and Ph$_3$PO (^{31}P δ = 29.9 ppm (s)) as major products. The data are in accordance for those reported in the literature.[7] Note: due to [PhNH$_3$]$^+$ formation, the δ ^{31}P value for Ph$_3$PO is slightly downfield due to the H-bonding effect.

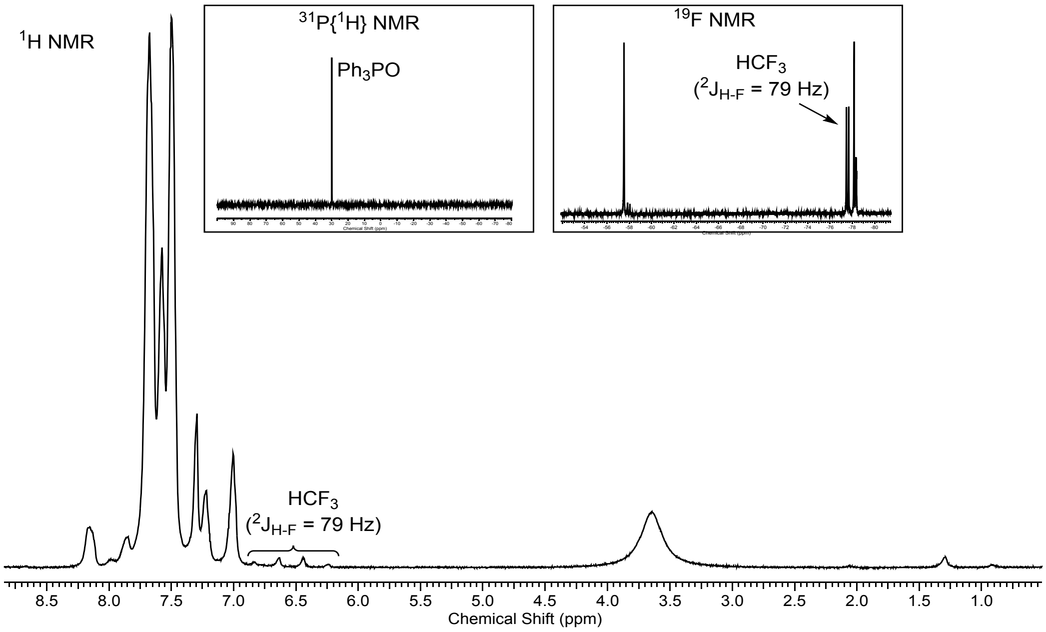


Figure S25. ^{1}H, ^{31}P{^{1}H} and ^{19}F-NMR spectra of **[1][OTf]** with H_2O / $PhNH_2$ in $CDCl_3$, after 5 min at R.T.

[2][OTf] (21 mg, 1 eq.) + **H_2O** (1 μL, 1 eq.) + **$PhNH_2$** (5 μL, 1 eq.). After 5 min upon mixing, effervescence was noted, along with white solid formation. NMR analysis revealed HCF_3 (^{1}H δ = 6.6 ppm, q, $^2J_{H-F}$ = 79 Hz; ^{19}F δ = -77.8 ppm, d, $^2J_{H-F}$ = 79 Hz) and $Ph_2(Me)PO$ (^{31}P δ = 31.4 ppm (s)) as major products. The data are in accordance for those reported in the literature.[7] Note: due to $[PhNH_3]^+$ formation, the δ ^{31}P value for $Ph_2(Me)PO$ is slightly downfield due to H-bonding effect.

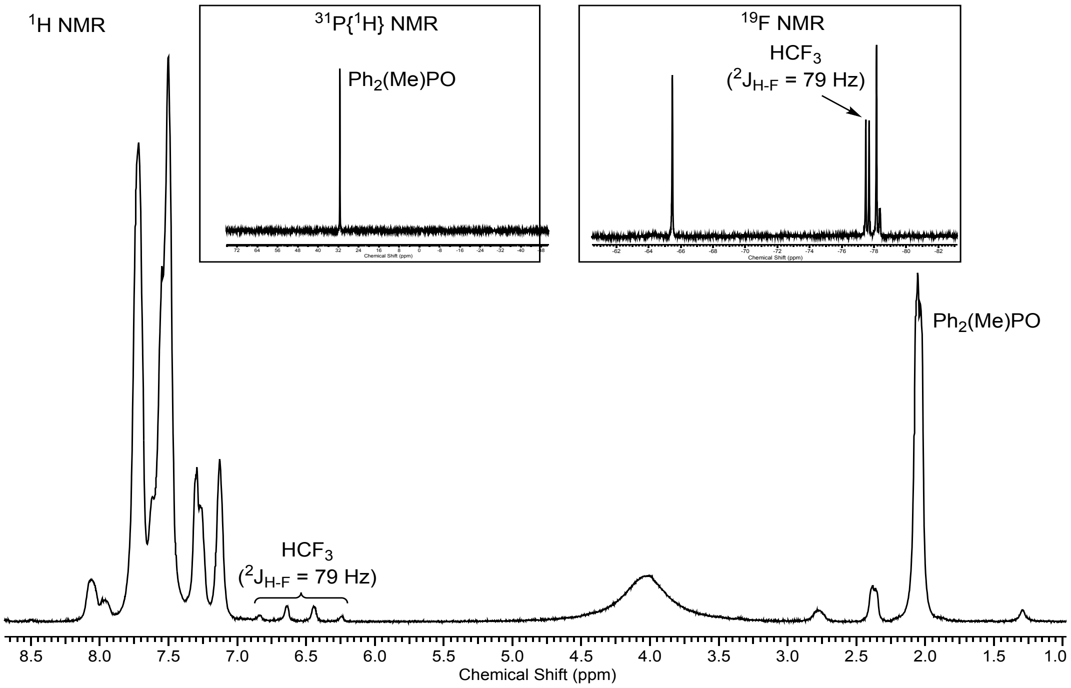


Figure S26. ^{1}H, ^{31}P{^{1}H} and ^{19}F-NMR spectra of **[2][OTf]** with H_2O / $PhNH_2$ in $CDCl_3$, after 5 min at R.T.

4.5 HCl addition

[1][OTf] (6 mg, 1 eq.) + **HCl $_{\textbf{(aq.)}}$ 37%** (2 µL, 2 eq.)

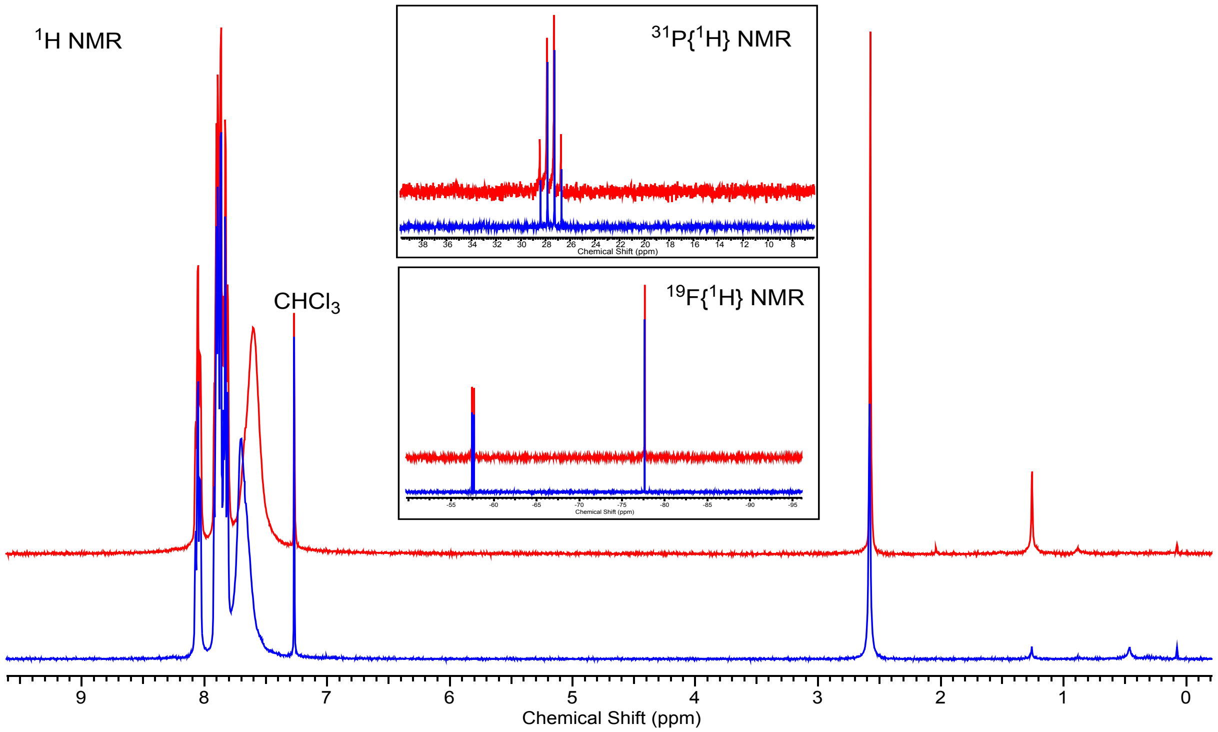
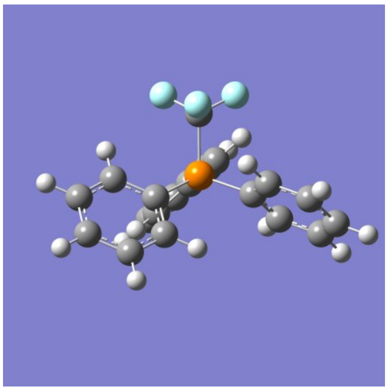


Figure S27. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of **[1][OTf]** with HCl in CDCl$_3$. Blue (after 5 min), red (after 6h at R.T.)

5. Hydride ion affinity calculations

Calculations were performed using the Gaussian09[8] suite of programmes. Structures were optimised at the M06-2X/6-311G(d,p) level with PCM(Dichloromethane) solvation.[9] In all cases, structures were confirmed as minima by frequency analysis and the absence of imaginary frequencies. Structures and energies for Et_3B and Et_3BH and were taken from previous work.[10,11] Full Cartesian coordinates for the optimised geometries for the HIA determinations are provided below.

Compound **[1]**$^+$

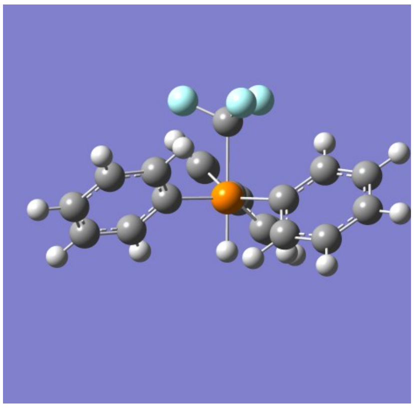


P	-0.582200	0.304900	0.138900
C	-0.012200	-1.387800	0.061800
C	-0.933600	-2.424500	0.225200
C	1.349400	-1.651700	-0.135200
C	-0.484200	-3.738700	0.188200
H	-1.985000	-2.212300	0.379000
C	1.779500	-2.969200	-0.173400
H	2.065300	-0.846900	-0.257300
C	0.865000	-4.008100	-0.011600
H	-1.190900	-4.548600	0.314400
H	2.828600	-3.184600	-0.329700
H	1.209600	-5.034500	-0.041800
C	-2.363400	0.434400	0.038600
C	-3.078700	0.879700	1.152600
C	-3.018900	0.047700	-1.137300
C	-4.465200	0.940800	1.083900
C	-4.402500	0.120700	-1.189900
C	-5.121800	0.565200	-0.082500
C	0.093700	1.205000	1.527800
C	0.786700	0.516900	2.526000
C	-0.100500	2.590400	1.601900
C	1.290700	1.227400	3.608600
H	0.930300	-0.555300	2.463400
C	0.412200	3.283700	2.687300
C	1.104800	2.602900	3.686800
H	1.827600	0.703800	4.389000

H	0.270600	4.354600	2.753700
H	1.501300	3.150900	4.532600
C	0.096400	1.156600	-1.406400
F	-0.472100	2.347500	-1.562200
F	1.410700	1.323200	-1.298600
F	-0.150300	0.421800	-2.486000
H	-0.642800	3.121900	0.828300
H	-2.464800	-0.305700	-1.999400
H	-4.919800	-0.169900	-2.095200
H	-6.202600	0.617200	-0.131100
H	-5.028800	1.282000	1.942700
H	-2.564300	1.171800	2.060400

Total Energy: - 1373.61255313 Hartrees

Compound **[1-H]**



P	1.206700	0.925200	-0.079300
H	1.074800	0.820800	1.369500
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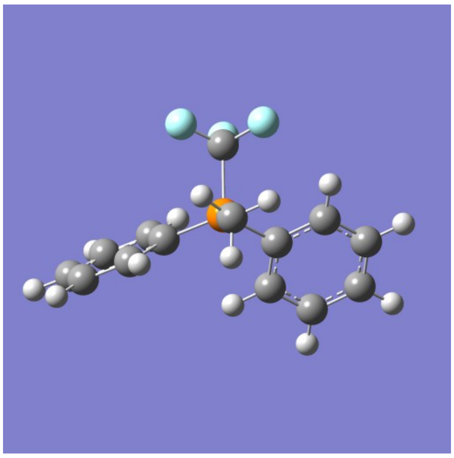
C	-0.874500	2.549100	0.724200
C	0.736400	3.670400	-0.684000
C	-1.609000	3.724200	0.825200
H	-1.204900	1.654700	1.244200
C	0.017500	4.853900	-0.549700
H	1.641300	3.657700	-1.279000
C	-1.158600	4.879500	0.192700
H	-2.522800	3.741000	1.406800
H	0.375400	5.755600	-1.031800
H	-1.721200	5.801100	0.282700
C	3.034900	0.919000	0.093200
C	3.881600	0.133100	-0.688500
C	3.565300	1.707900	1.114900
C	5.251300	0.142000	-0.445000
H	3.483300	-0.490000	-1.479300
C	4.937500	1.741700	1.330700

H	2.902900	2.298600	1.740700
C	5.780800	0.952000	0.554200
H	5.904400	-0.482300	-1.042700
H	5.345800	2.373500	2.110000
H	6.849500	0.964800	0.731300
C	0.283800	-0.650800	-0.269700
C	-0.773100	-0.815300	-1.164600
C	0.635200	-1.691600	0.590900
C	-1.470000	-2.018900	-1.195300
C	-0.040100	-2.904600	0.531400
C	-1.098700	-3.065600	-0.358000
C	1.392200	1.076200	-2.138800
F	1.638600	-0.108900	-2.758600
F	0.281900	1.566000	-2.752400
F	2.400200	1.896000	-2.540300
H	-1.062600	-0.012200	-1.830400
H	-2.301300	-2.138200	-1.879500
H	-1.637500	-4.004900	-0.394100
H	0.249800	-3.716800	1.186800
H	1.437700	-1.551200	1.308900

Total Energy: - 1374.33437839 Hartrees

Compound **[2]**$^+$

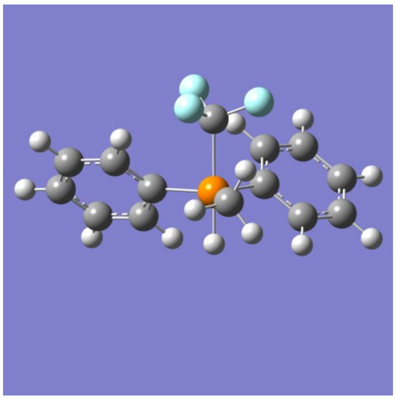


P	-0.605400	0.304500	0.125300
C	0.033600	-1.358900	-0.040400
C	-0.806900	-2.449400	0.197400
C	1.387800	-1.542500	-0.344200
C	-0.282900	-3.733900	0.123300
H	-1.852200	-2.301000	0.440500
C	1.893000	-2.831700	-0.419000
H	2.042300	-0.698400	-0.526500
C	1.059800	-3.922700	-0.185300
H	-0.926000	-4.584600	0.308400

H	2.937500	-2.984000	-0.658300
H	1.461800	-4.926700	-0.243200
C	-2.388000	0.363300	0.111900
C	-3.077200	0.976300	1.160600
C	-3.072400	-0.201900	-0.972100
C	-4.465100	1.022600	1.120300
C	-4.457300	-0.143600	-0.998100
C	-5.149800	0.466400	0.045600
C	-0.050400	1.265100	-1.397500
F	-0.622200	2.462700	-1.397400
F	1.272400	1.427100	-1.380600
F	-0.387600	0.624400	-2.509600
H	-2.536900	-0.683100	-1.783000
H	-4.995100	-0.576000	-1.831800
H	-6.231600	0.506800	0.019200
H	-5.007600	1.495400	1.928600
H	-2.548800	1.413300	1.999100
C	0.135600	1.192200	1.500200
H	-0.169900	2.238800	1.478300
H	-0.172800	0.720000	2.433400
H	1.219900	1.120300	1.402700

Total Energy: -1181.91022653 Hartrees

Compound **[2-H]**

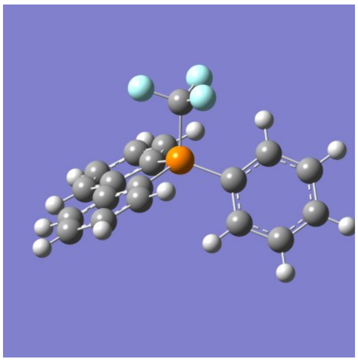


P	-1.977200	0.398200	-0.231100
H	-2.076700	0.131200	1.201300
C	-2.857200	1.993800	-0.011100
C	-3.988000	1.991900	0.806700
C	-2.404100	3.191300	-0.563600
C	-4.687400	3.170600	1.036000
H	-4.322500	1.068000	1.268500
C	-3.087600	4.375200	-0.304700
H	-1.519700	3.208700	-1.188200
C	-4.233600	4.364900	0.483500

H	-5.576500	3.159000	1.654900
H	-2.723800	5.306100	-0.722900
H	-4.768700	5.287500	0.674000
C	-0.142300	0.415700	-0.086100
C	0.729000	-0.189900	-0.991700
C	0.372800	1.063100	1.038800
C	2.101500	-0.150500	-0.764500
H	0.351400	-0.698800	-1.868600
C	1.745200	1.134200	1.242000
H	-0.306100	1.513000	1.757300
C	2.611200	0.518800	0.342500
H	2.772800	-0.638600	-1.460800
H	2.136900	1.656200	2.106700
H	3.681300	0.558200	0.506900
C	-1.851600	0.720500	-2.260900
F	-1.568500	-0.427000	-2.948000
F	-3.038100	1.136700	-2.770700
F	-0.931800	1.618000	-2.696100
C	-2.990300	-1.090300	-0.605500
H	-2.320600	-1.953100	-0.580000
H	-3.725200	-1.201400	0.190800
H	-3.476400	-1.041500	-1.576900

Total Energy: - 1182.63155661 Hartrees

Compound **[3]**$^{+}$

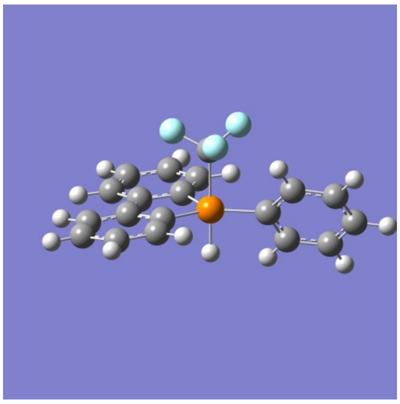


C	-1.017600	-6.161400	-0.095700
C	0.338200	-6.412800	-0.293300
C	1.247800	-5.360400	-0.328400
C	0.756500	-4.072300	-0.162500
C	-0.610300	-3.800500	0.033100
C	-1.500800	-4.864300	0.067000
H	-1.713200	-6.991000	-0.070100
H	0.688500	-7.428700	-0.419500
H	2.304300	-5.546100	-0.482100
H	-2.559800	-4.694100	0.216300

C	0.191200	-1.511500	0.090400
C	0.093300	-0.130800	0.185200
C	-1.170600	0.419600	0.377700
C	-2.289100	-0.405400	0.467000
C	-2.179900	-1.791100	0.365500
C	-0.928500	-2.359500	0.173300
H	0.967900	0.504000	0.111000
H	-1.282000	1.493300	0.455600
H	-3.266000	0.038000	0.615500
H	-3.064500	-2.412000	0.433800
C	2.665800	-2.414200	1.441300
C	2.739200	-2.216400	-1.511100
C	2.490600	-2.877200	-2.718300
C	3.787500	-1.298300	-1.386800
C	3.305400	-2.611100	-3.810100
H	1.678500	-3.590100	-2.804200
C	4.590900	-1.045500	-2.489100
H	3.982100	-0.787400	-0.451900
C	4.349300	-1.698300	-3.694700
H	3.125100	-3.118800	-4.748800
H	5.406600	-0.339300	-2.404500
H	4.981700	-1.494900	-4.550100
F	1.970600	-2.899200	2.457600
F	2.968100	-1.142100	1.699200
F	3.792600	-3.101800	1.312000
P	1.642600	-2.527100	-0.139100

Total Energy: - 1372.41673467 Hartrees

Compound **[3-H]**



C	-0.903000	-0.138300	0.686600
C	0.427900	-0.278900	1.075200
C	1.321000	0.777400	0.914700
C	0.861800	1.965300	0.366100
C	-0.482300	2.124000	-0.023300

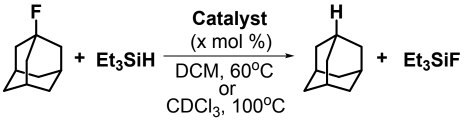
C	-1.362200	1.054900	0.140500
H	-1.590400	-0.965600	0.814600
H	0.770300	-1.212800	1.504200
H	2.355900	0.670600	1.218000
H	-2.402000	1.151000	-0.149800
C	0.256900	4.361300	-0.607500
C	0.102100	5.660700	-1.065000
C	-1.158200	6.073400	-1.491000
C	-2.233700	5.187800	-1.459000
C	-2.073200	3.885200	-0.998500
C	-0.819800	3.457500	-0.563700
H	0.944200	6.343400	-1.087900
H	-1.301800	7.085700	-1.848300
H	-3.209400	5.518600	-1.793900
H	-2.923100	3.213000	-0.974600
P	1.760900	3.496100	-0.077400
C	3.470100	4.214500	-0.131500
C	4.323100	4.395800	0.959900
C	3.905200	4.578900	-1.408600
C	5.590400	4.934900	0.766600
H	4.022500	4.115800	1.959000
C	5.154800	5.158700	-1.590700
H	3.261600	4.409800	-2.265900
C	6.003500	5.328100	-0.502100
H	6.254700	5.051800	1.614200
H	5.469300	5.461400	-2.582000
H	6.987100	5.760400	-0.642400
H	1.985100	2.966700	-1.420600
C	1.480800	4.146000	1.830700
F	2.140000	3.401700	2.763900
F	1.862200	5.429000	2.038900
F	0.182700	4.092100	2.203000

Total Energy: -1373.13599265 Hartrees

6. Hydrodefluorination reactions

General procedure: under inert atmosphere, in a J. Young NMR tube the catalyst was dissolved in dried solvent (0.05 mL), followed by the addition of the 1-fluoro-adamantane and Et_3SiH. The system was then sealed and heated at 60°C or 100 °C in an oil bath for 18 hours. Subsequent addition of fluorobenzene (10 μL) to the reaction mixture allowed the determination of the ^{19}F-NMR yields based on the relative integral of the fluorine of Et_3SiF.

Table 1. Hydrodefluorination with **[1][OTf]** and **[1][BArF]**.



Entry	Catalyst	Eq. Silane	Catalyst loading	Temp. (°C)	Conv. (%)	Et_3SiF (%)
1	[1][OTf]	1.2	5 mol %	60	31	29
2	[1][BArF]	1.2	5 mol %	60	39	35
3	[1][OTf]	2.2	10 mol %	100	70	60
4	[1][BArF]	2.2	10 mol %	100	99	97

To avoid showing similar spectra multiple times, for each catalyst one result is reported.

Entry 3: 1-fluoro-adamantane (20 mg, 0.13 mmol, 1.0 eq.), Et_3SiH (46 µL, 0.28 mmol, 2.2 eq.), **[1][OTf]** (6 mg, 0.01 mmol, 0.05 eq.). After 18 hours at 100°C, Et_3SiF was found as main product (catalyst decomposition noted as well). Et_3SiF NMR yield = 60%. $^{19}F\{^1H\}$ NMR (376 MHz, $CHCl_3$): δ -177 ppm (s, 1F). ^1H NMR and $^{19}F\{^1H\}$ NMR spectra are in agreement with those reported in the literature.[1]

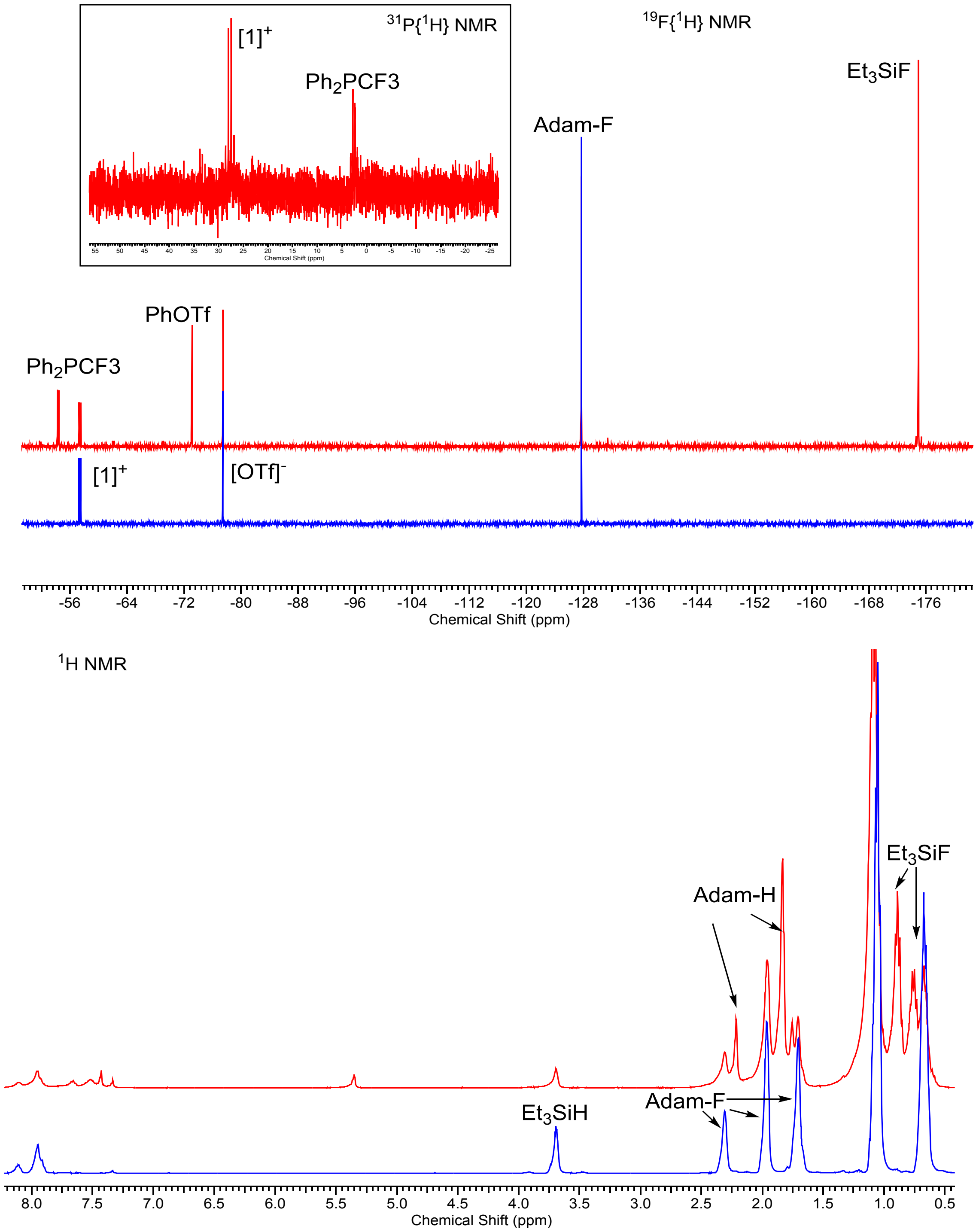


Figure S28. $^{19}F\{^1H\}$-NMR, $^{31}P\{^1H\}$ and ^1H NMR spectra of the reduction of 1-fluoroadamantane with Et_3SiH with **[1][OTf]** in dried $CDCl_3$. Blue (after 5 min), red (after 18 h at 100°C).

Entry 4: 1-fluoro-adamantane (20 mg, 0.13 mmol, 1.0 eq.), Et_3SiH (46 µL, 0.28 mmol, 2.2 eq.), **[1][BArF]** (13 mg, 0.01 mmol, 0.05 eq.). After 18 hours at 100°C, full conversion to Et_3SiF was observed (catalyst decomposition noted as well). Et_3SiF NMR yield = 97%. $^{19}F\{^1H\}$ NMR (376 MHz, $CHCl_3$): δ -177 ppm (s, 1F). The results are in agreement with those reported in the literature.[1]

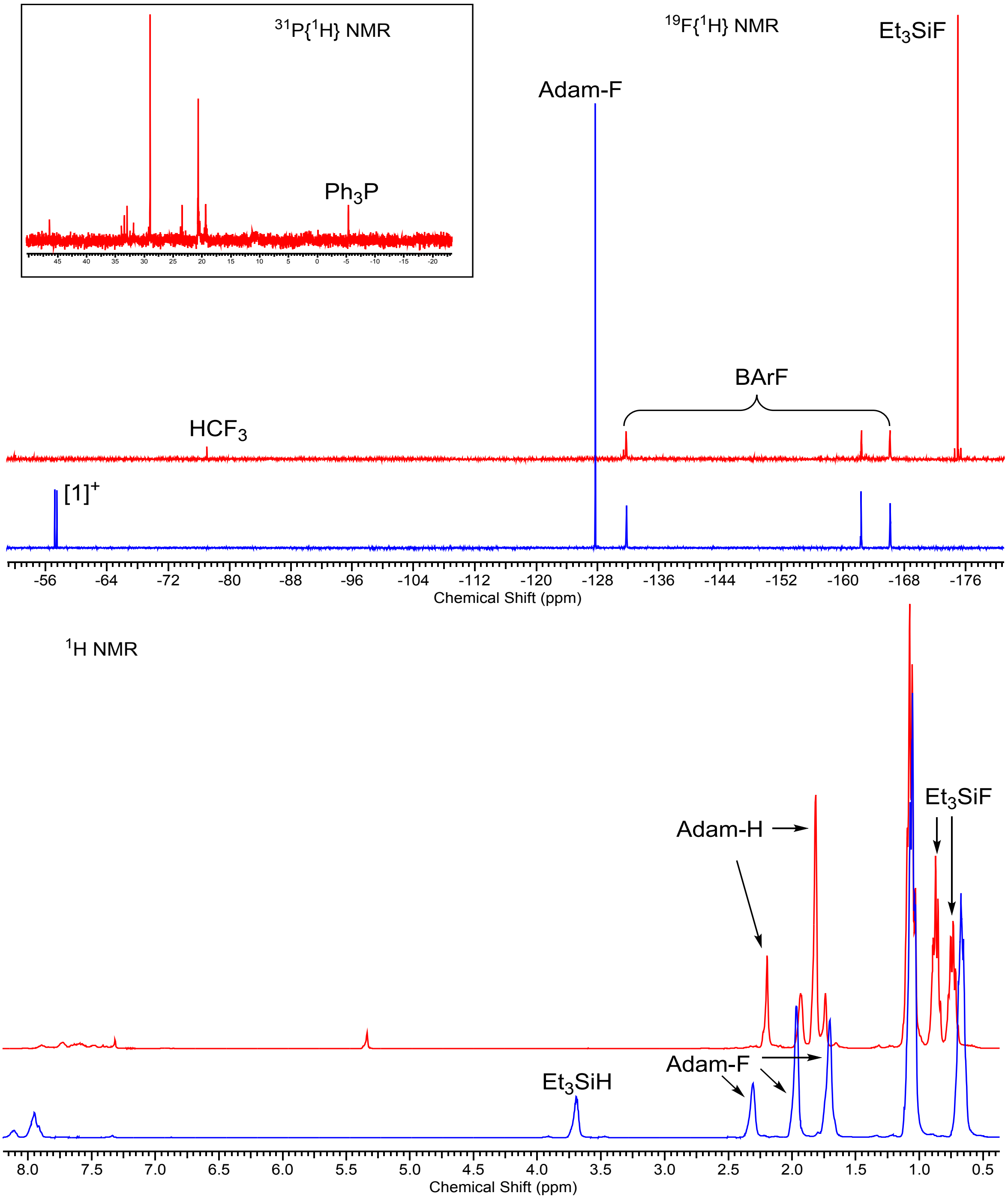


Figure S29. $^{19}F\{^1H\}$-NMR, $^{31}P\{^1H\}$ and ^1H NMR spectra of the reduction of 1-fluoro-adamantane with Et_3SiH with **[1][BArF]** in dried $CDCl_3$. Blue (after 5 min), red (after 18 h at 100°C).

Reaction under ambient conditions: the reaction in entry 4 was repeated under ambient conditions using $CDCl_3$ straight from the Winchester. After 18 hours at 100°C, good conversion to Et_3SiF was observed. As for the reaction under anhydrous conditions, catalyst decomposition was noted as well. Et_3SiF NMR yield = 76%.

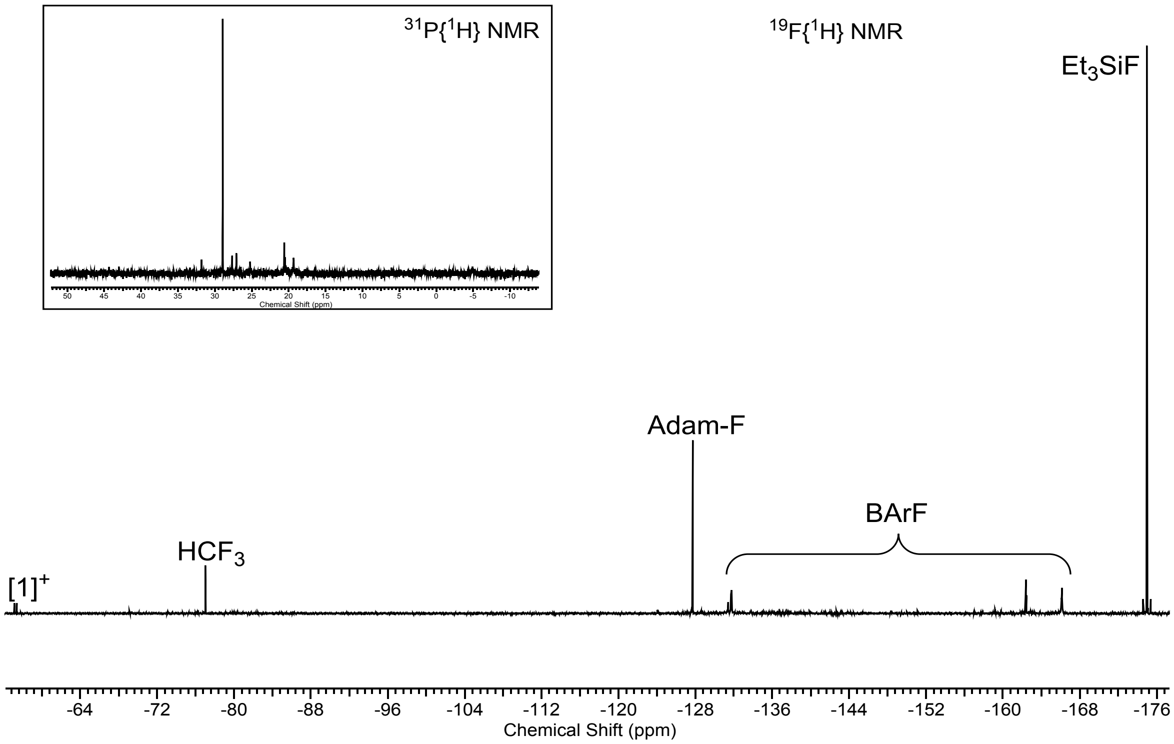
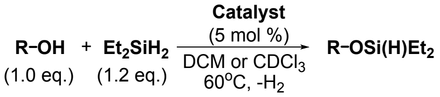


Figure S30. $^{19}F\{^1H\}$-NMR and $^{31}P\{^1H\}$ spectra of the reduction of 1-fluoroadamantane with Et_3SiH with **[1][BArF]** in wet $CDCl_3$ under ambient conditions, after 18 h at 100°C.

7. Dehydrosilylation of alcohols

General procedure: under inert atmosphere, in a J. Young NMR tube the catalyst (5 mol %) was dissolved in dried solvent (0.05 mL), followed by the addition of the alcohol and the silane. The system was then sealed and heated at 60°C in an oil bath. Subsequent addition of mesitylene to the reaction mixture allowed the determination of the ^{1}H-NMR yields based on the relative integral of the benzylic protons of the product (when BnOH was used) or of the silicon-attached proton (in case of $PhOSi(H)Et_2$).

Table 2. Alcohol dehydrosilylation with **[2][OTf]**, **[1][OTf]** and **[1][BArF]**.



$$\underset{(1.0\text{ eq.})}{\mathbf{R{-}OH}} + \underset{(1.2\text{ eq.})}{\mathbf{Et_2SiH_2}} \xrightarrow[\text{DCM or CDCl}_3\text{, }60^{o}\text{C, -H}_2]{\textbf{Catalyst}\ (5\text{ mol }\%)} \mathbf{R{-}OSi(H)Et_2}$$

Entry	**Catalyst**	**R**	**Solvent**	**Time (h)**	**Conv. (%)**
1	[2][OTf]	Bn	DCM	18	0
2	[1][OTf]	Bn	DCM	2	90
3	[1][BArF]	Bn	DCM	2	90[a]
4	[2][OTf]	Ph	$CDCl_3$	18	19
5	[1][OTf]	Ph	$CDCl_3$	2	94
6	[1][BArF]	Ph	$CDCl_3$	4	78

[a] Product further reacted to give Bn_2O and siloxane.

To avoid showing similar spectra multiple times, for each substrate one result is reported.

Entry 2: BnOH (25 µL, 0.24 mmol, 1.0 eq.), Et_2SiH_2 (45 µL, 0.28 mmol, 1.2 eq.), **[1][OTf]** (6 mg, 0.02 mmol, 0.05 eq.). After 2 hours at 60°C, BnOSi(H)Et_2 was found as the main product (NMR yield = 90%). Diagnostic peaks: ^1H NMR (400 MHz, $CHCl_2$): δ 4.75 (s, 2H, Bn$_{-}$), 4.50 (quint, *J* = 2.1 Hz, Si-H) ppm. $^{29}Si\{^1H\}$ NMR (79 MHz, $CHCl_2$): δ 12.8 ppm. The results are in agreement with those reported in the literature.[12]

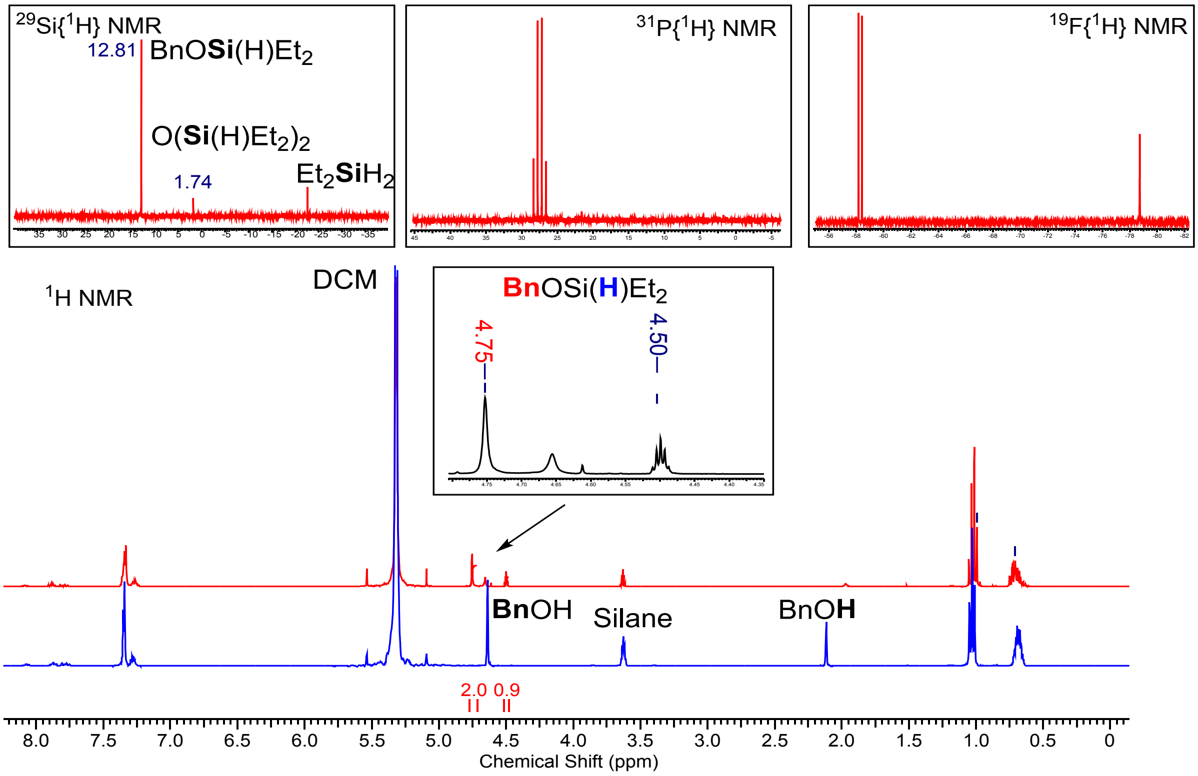


Figure S31. ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the dehydrosilylation of BnOH with Et_2SiH_2 with **[1][OTf]** in dried DCM. Blue (after 5 min), red (after 2 h at 60°C).

Entry 6: PhOH (20 mg, 0.20 mmol, 1.0 eq.), Et_2SiH_2 (32 µL, 0.25 mmol, 1.2 eq.), **[1][BArF]** (10 mg, 0.01 mmol, 0.05 eq.). After 4 hours at 60°C, $PhOSi(H)Et_2$ was found as the main product (NMR yield = 78%). Diagnostic peaks: ^1H NMR (400 MHz, $CHCl_3$): δ 4.68 (quint, *J* = 2.1 Hz, Si-H) ppm. $^{29}Si\{^1H\}$ NMR (79 MHz, $CHCl_3$): δ 10.3 ppm. The results are in agreement with those reported in the literature.[13]

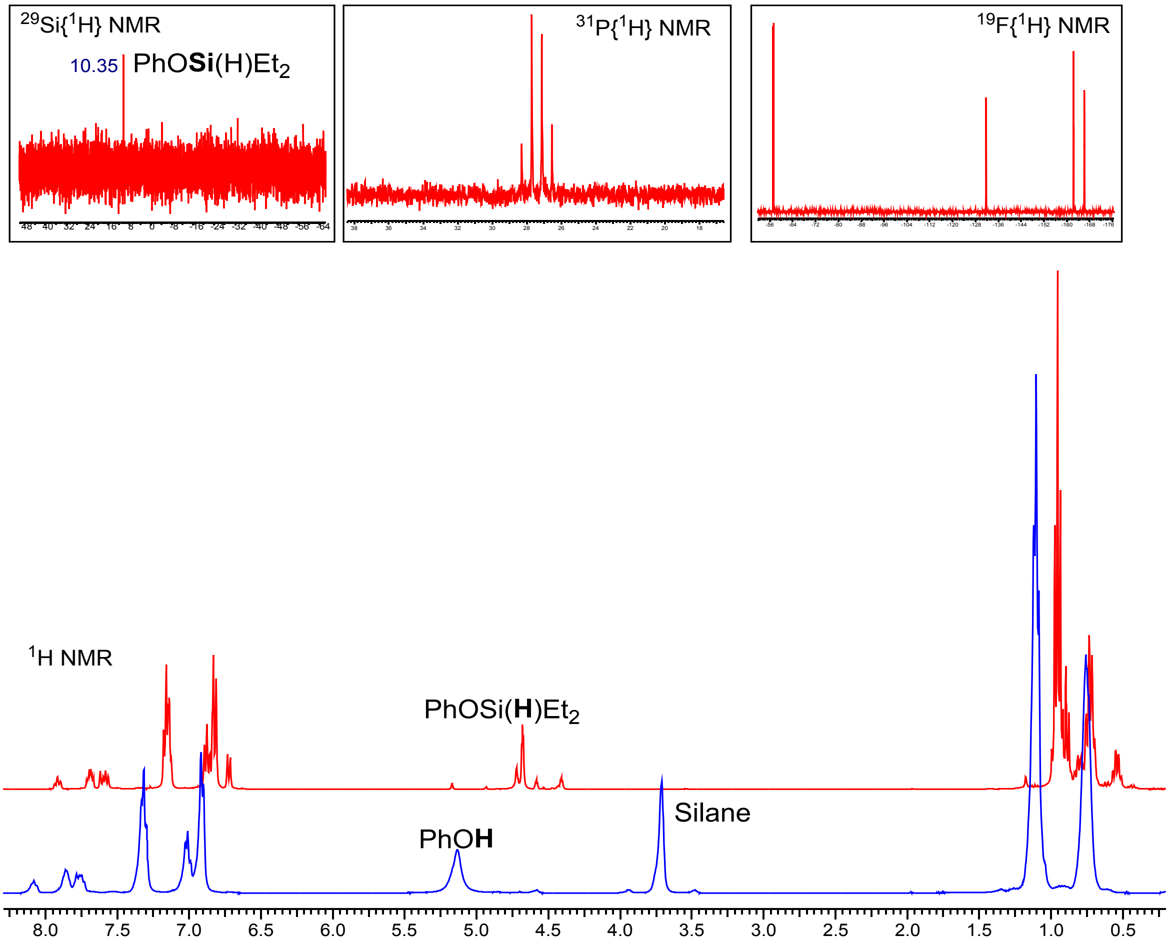


Figure S32. ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the dehydrosilylation of PhOH with Et_2SiH_2 with **[1][BArF]** in dried $CDCl_3$. Blue (after 5 min), red (after 2 h at 60°C).

Reaction under ambient conditions (PhOH): the reaction in entry 5 was repeated under ambient conditions using $CDCl_3$ straight from the Winchester. No decomposition was observed after 2 h at 60°C, with $PhOSi(H)Et_2$ found as the main product (NMR yield = 78%). Note: water from the unpurified solvent reacts to produce the corresponding siloxane.

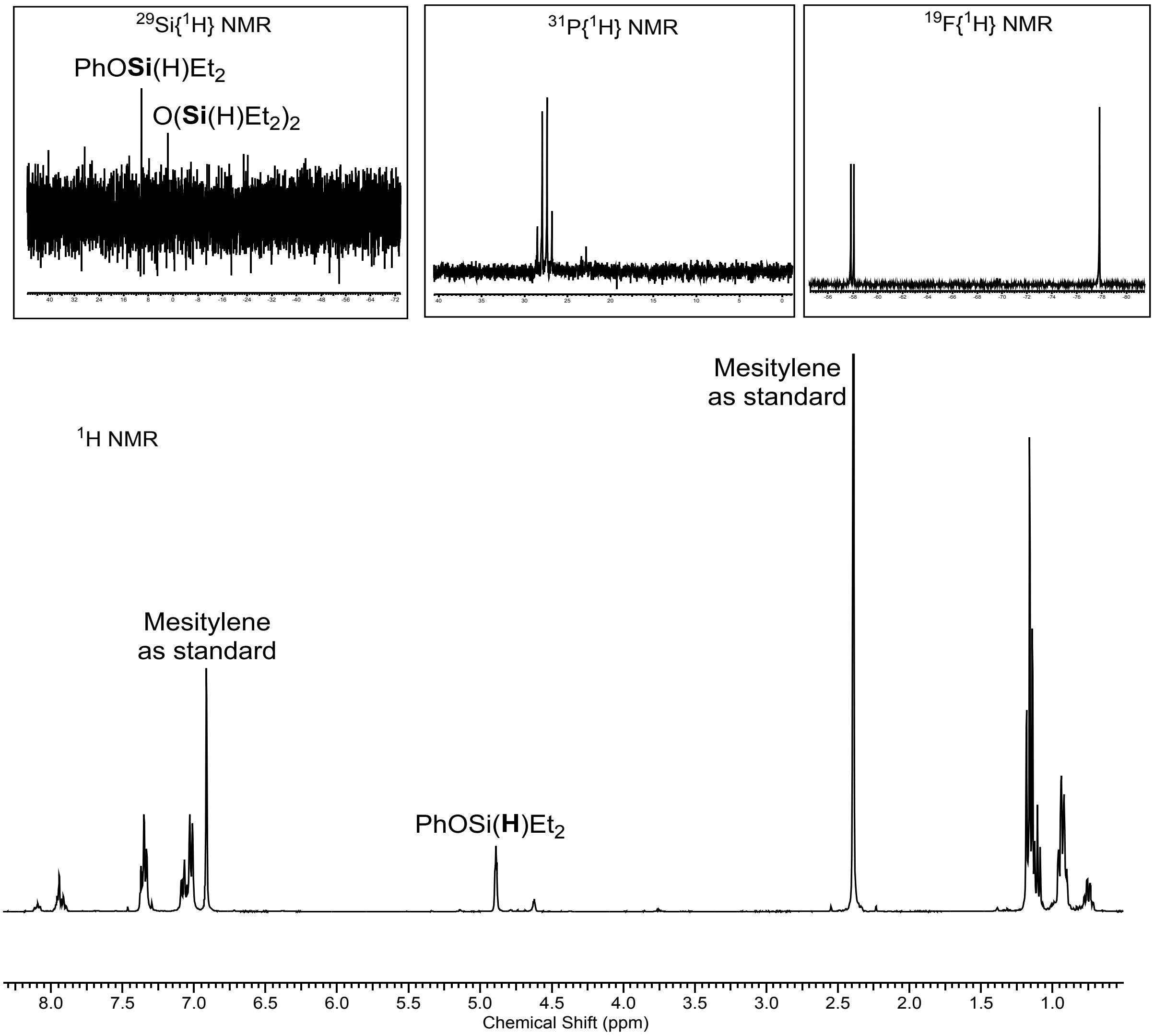
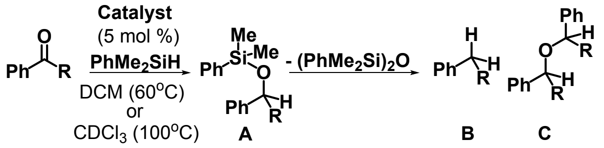


Figure S33. ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the dehydrosilylation of PhOH with Et_2SiH_2 with **[1][OTf]** in wet $CDCl_3$ under ambient conditions, after 2 h at 60°C.

8. C=O reductions

General procedure: under inert atmosphere, in a J. Young NMR tube the catalyst (5 mol %) was dissolved in dried solvent (0.05 mL), followed by the addition of the carbonyl and the silane. The system was then sealed and heated at 60^{o}C or 100 ^{o}C in an oil bath. Subsequent addition of mesitylene to the reaction mixture allowed the determination of the ^{1}H-NMR yields based on the relative integral of the benzylic protons of the product.

Table 3. C=O reductions with **[1][OTf]** and **[1][BArF]**.



Entry	Catalyst	R	Eq. Silane	Temp./Time (^{o}C / h)	Conv. (%)	A : B : C (%)
1	[1][OTf]	H	1.2	60 / 1	92	0 : 0 : 45
2	[1][BArF]	H	1.2	60 / 3	89	0 : 0 : 44
3	[1][OTf]	Me	1.2	100 / 2	0	-
4	[1][BArF]	Me	1.2	100 / 2	83[a]	21 : 13 : 0
5	[1][BArF]	Me	2.2	100 / 4	91	59 : 15 : 0
6	[1][OTf]	Ph	2.2	100 / 4	0	-
7	[1][BArF]	Ph	2.2	100 / 4	89	50 : 39 : 0

[a] Mixture of byproducts including styrene and 1-phenylethanol.

To avoid showing similar spectra multiple times, for each substrate one result is reported.

Entry 2: PhCHO (25 µL, 0.24 mmol, 1.0 eq.), $PhMe_2SiH$ (45 µL, 0.29 mmol, 1.2 eq.), **[1][BArF]** (12 mg, 0.01 mmol, 0.05 eq.). After 3 hours at 60°C, Bn_2O was found as the main product upon siloxane loss. Bn_2O NMR yield = 44% (max 50%). ^1H NMR (400 MHz, CH_2Cl_2): δ 4.58 ppm (s, 4H, Bn-). $^{29}Si\{^1H\}$ NMR (79 MHz, CH_2Cl_2): δ –1.13 ppm (siloxane). The results are in agreement with those reported in the literature.[12]

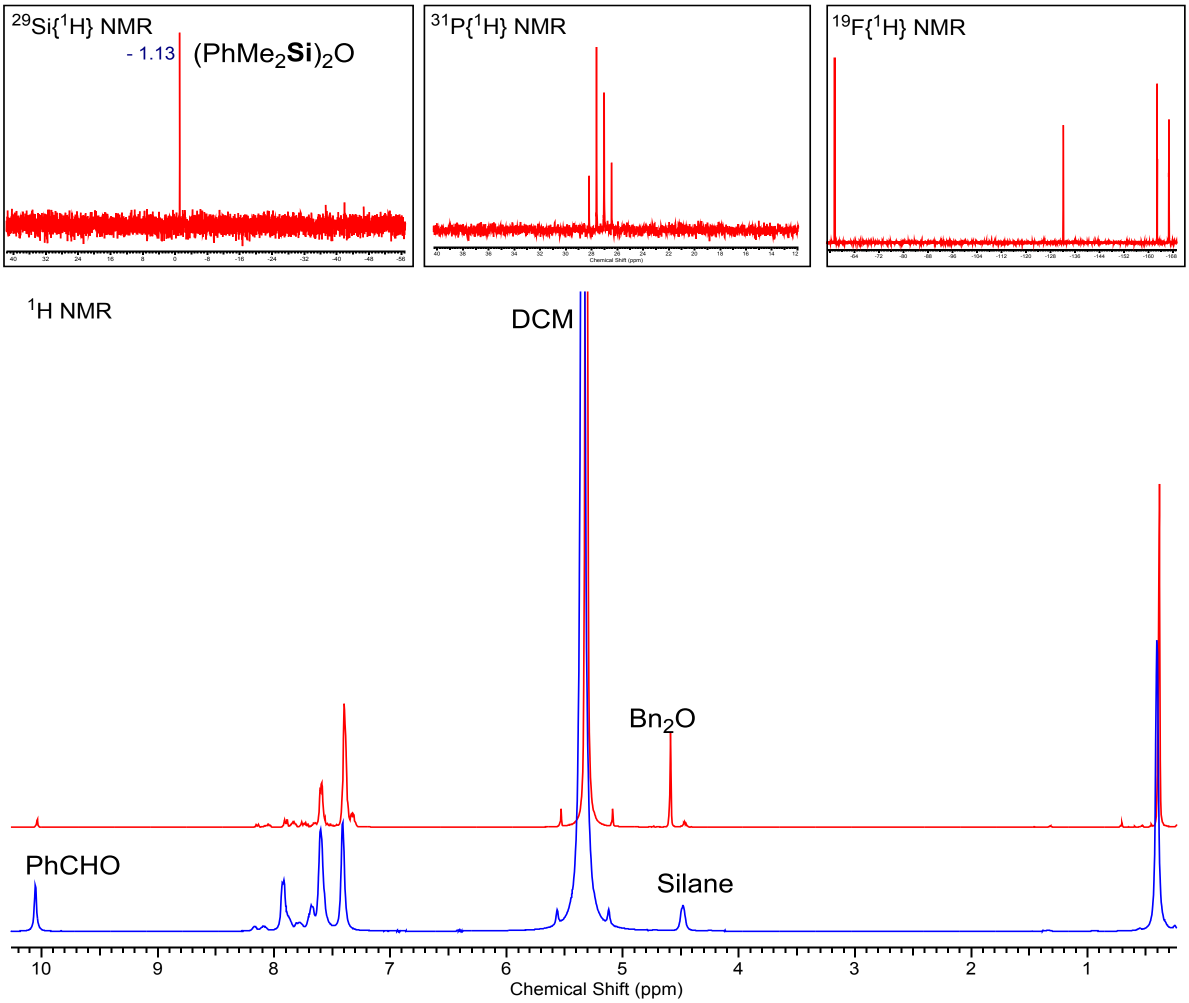


Figure S34. ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of PhCHO with $PhMe_2SiH$ with **[1][BArF]** in dried DCM. Blue (after 5 min), red (after 3 h at 60°C).

Entry 3: PhC(O)Me (25 µL, 0.21 mmol, 1.0 eq.), $PhMe_2SiH$ (39 µL, 0.25 mmol, 1.2 eq.), **[1][OTf]** (5 mg, 0.01 mmol, 0.05 eq.). After 2 hours at 100°C, minimal reduction was observed, while the catalyst had partially decomposed.

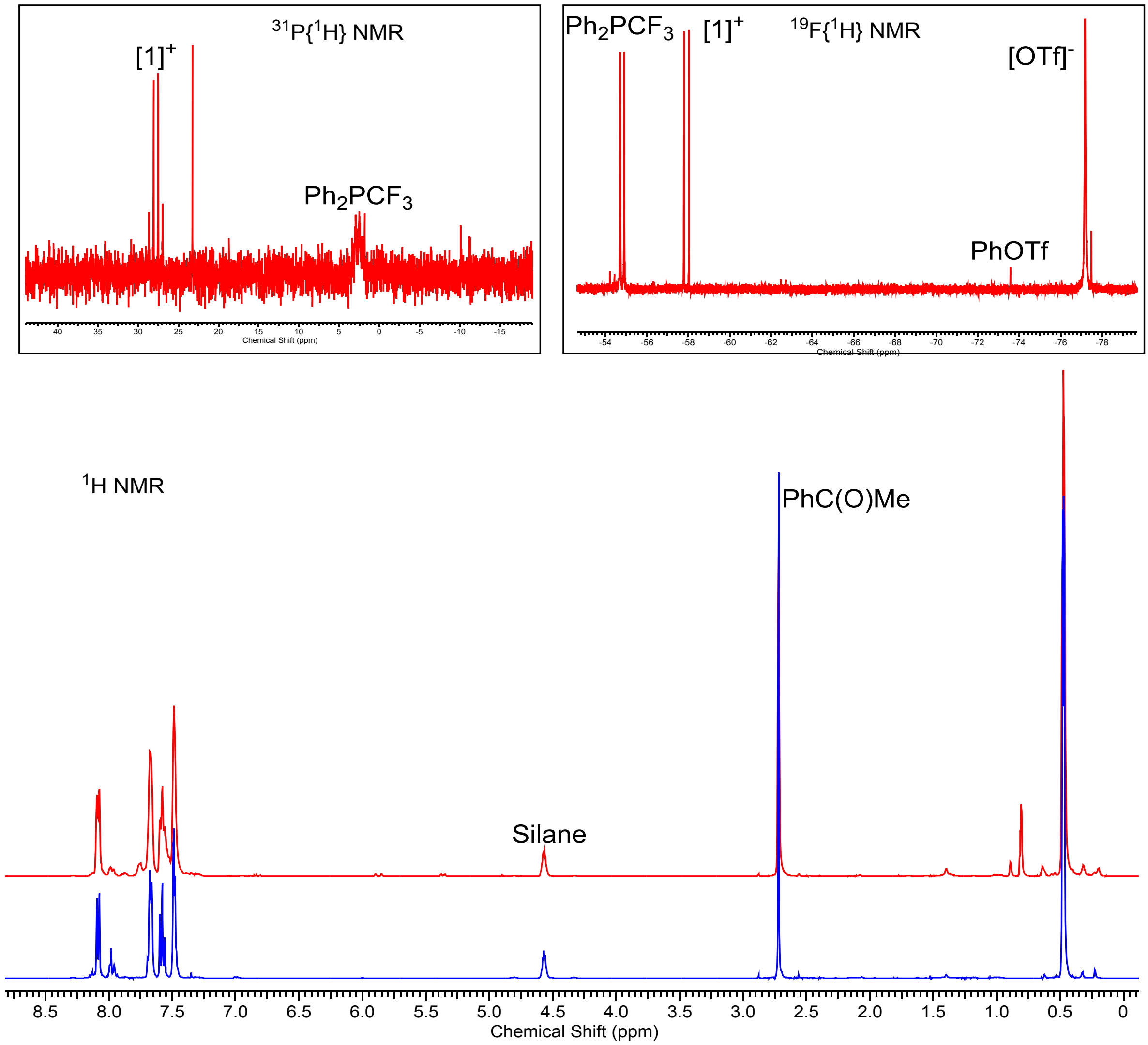


Figure S35. ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of PhC(O)Me with $PhMe_2SiH$ with **[1][OTf]** in dried $CHCl_3$. Blue (after 5 min), red (after 2 h at 100°C).

Entry 5: PhC(O)Me (12 µL, 0.10 mmol, 1.0 eq.), PhMe$_2$SiH (35 µL, 0.22 mmol, 2.2 eq.), **[1][BArF]** (5 mg, 0.005 mmol, 0.05 eq.). After 4 hours at 100ºC, PhCH(Me)OSiPhMe$_2$ (NMR yield = 59%) and PhCH$_2$Me (NMR yield = 13%) were found as main products. PhCH(Me)OSiPhMe$_2$ ^{1}H NMR (400 MHz, CHCl$_3$): δ 4.87 (q, *J* = 6.4 Hz, 1H, -C*H*Me), 1.44 (d, *J* = 6.4 Hz, 3H, -CH*Me*), 0.35 (s, 3H, -Si*Me*), 0.33 (s, 3H, -Si*Me'*) ppm. PhCH$_2$Me ^{1}H NMR (400 MHz, CHCl$_3$): δ 2.66 (q, *J* = 7.6 Hz, 2H, -C*H*$_2$Me), 1.26 (t, *J* = 7.6 Hz, 3H, -CH$_2$*Me*) ppm. The results are in agreement with those reported in the literature.[12a,14]

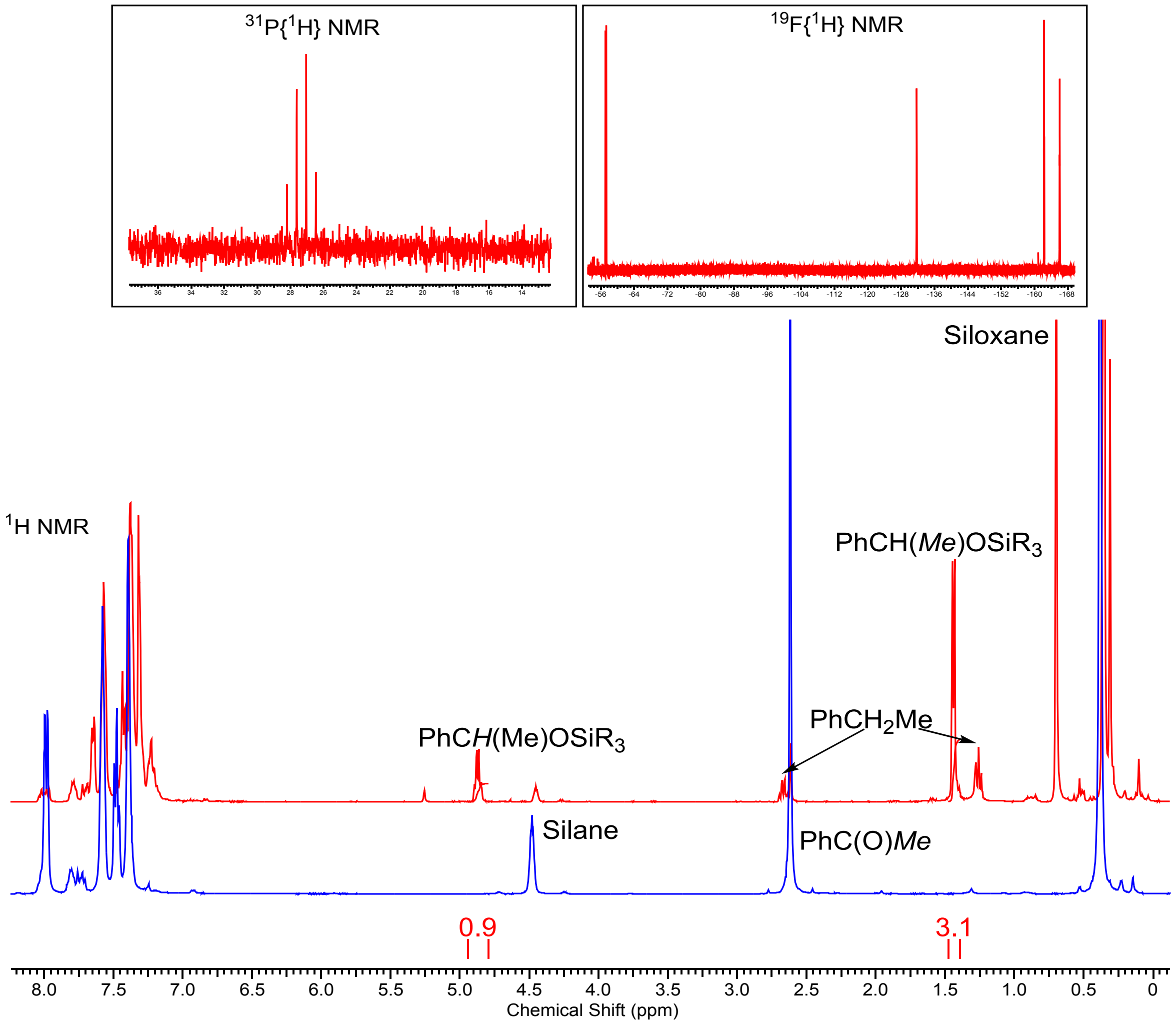


Figure S36. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of the reduction of PhC(O)Me with PhMe$_2$SiH with **[1][BArF]** in dried CHCl$_3$. Blue (after 5 min), red (after 2 h at 100ºC).

Entry 6: Ph_2CO (39 mg, 0.21 mmol, 1.0 eq.), $PhMe_2SiH$ (72 µL, 0.46 mmol, 2.2 eq.), **[1][OTf]** (5 mg, 0.01 mmol, 0.05 eq.). After 4 hours at 100°C, minimal reduction was observed, while the catalyst had partially decomposed.

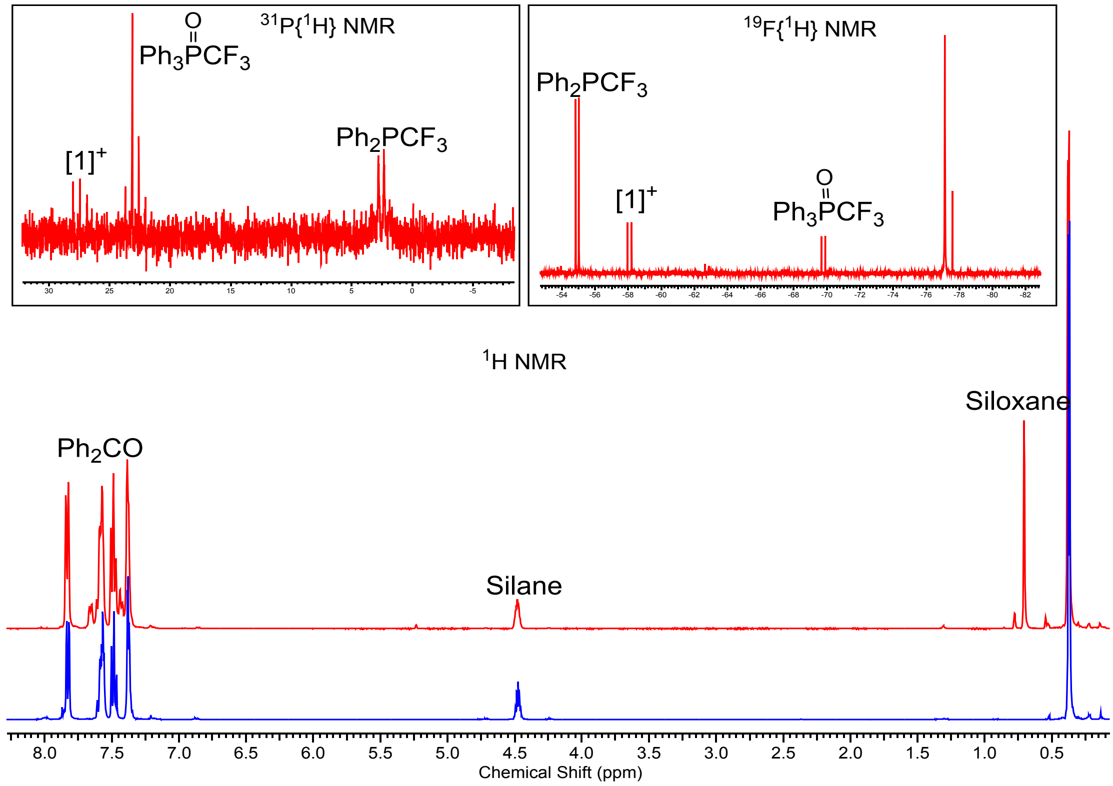


Figure S37. ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of Ph_2CO with $PhMe_2SiH$ with **[1][OTf]** in dried $CHCl_3$. Blue (after 5 min), red (after 4 h at 100°C).

Entry 7: Ph_2CO (39 mg, 0.21 mmol, 1.0 eq.), $PhMe_2SiH$ (72 µL, 0.46 mmol, 2.2 eq.), **[1][BArF]** (11 mg, 0.005 mmol, 0.05 eq.). After 4 hours at 100ºC, $Ph_2C(H)OSiPhMe_2$ (NMR yield = 50%) and Ph_2CH_2 (NMR yield = 39%) were found as the main products. $Ph_2C(H)OSiPhMe_2$ ^1H NMR (400 MHz, $CHCl_3$): δ 5.76 (s, 1H, -C*H*-), 0.30 (s, 6H, -Si*Me*$_2$) ppm. Ph_2CH_2 ^1H NMR (400 MHz, $CHCl_3$): δ 3.97 ppm (s, 2H, -C*H*$_2$-). The results are in agreements with those reported in the literature.[12a,14]

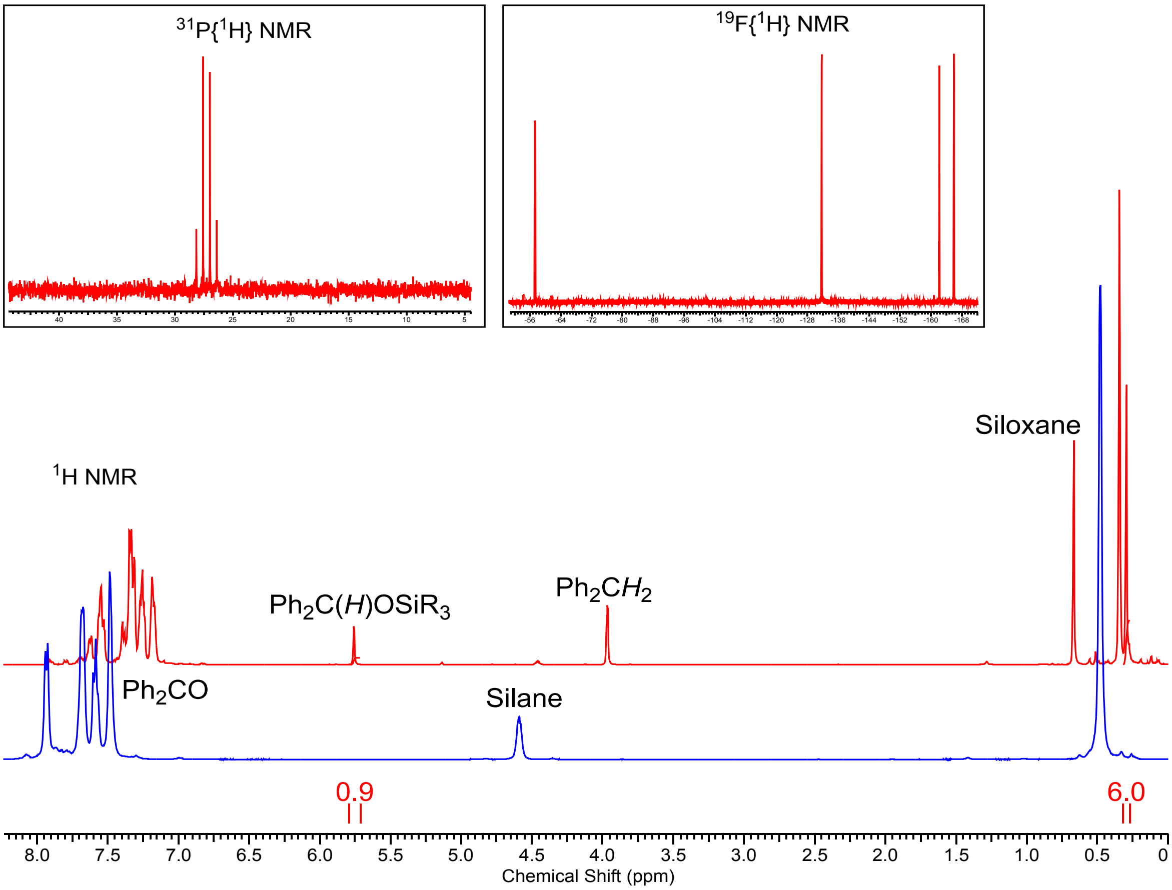


Figure S38. ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of Ph_2CO with $PhMe_2SiH$ with **[1][BArF]** in dried $CHCl_3$. Blue (after 5 min), red (after 4 h at 100ºC).

Reaction under ambient conditions (PhCHO): the reaction in entry 2 was repeated under ambient conditions using $CDCl_3$ straight from the Winchester. No decomposition was observed after 3 h at 60°C, with Bn_2O and siloxane found as main products (NMR conversion PhCHO 92%). Note: water from the unpurified solvent reacts to produce the corresponding siloxane.

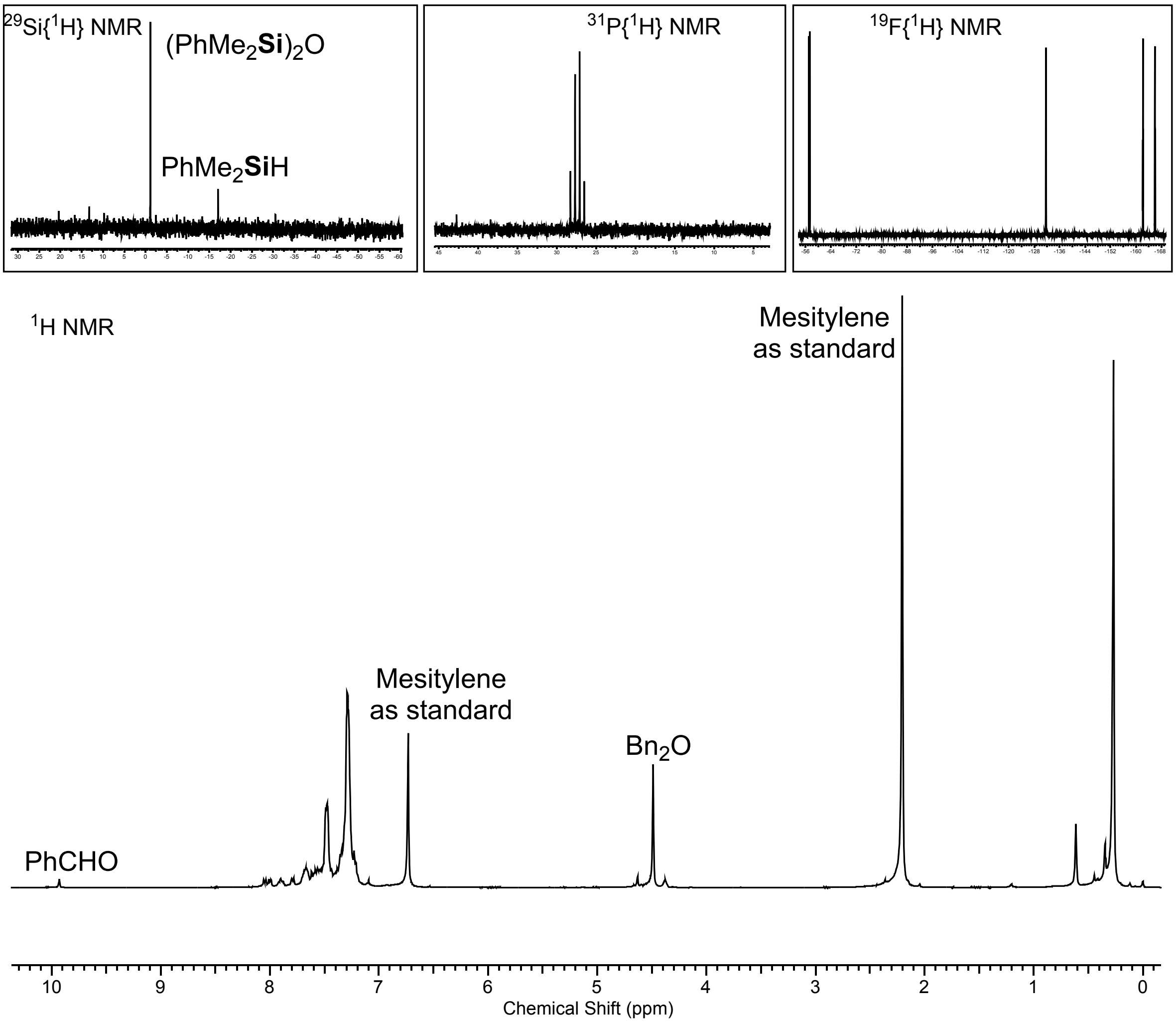


Figure S39. ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of PhCHO with $PhMe_2SiH$ and **[1][BArF]** in wet DCM under ambient conditions, after 3 h at 60°C.

Reaction under ambient conditions (PhC(O)Me): the reaction in entry 5 was repeated under ambient conditions using $CDCl_3$ straight from the Winchester. No decomposition was observed after 8 h at 100°C, with the silane completely consumed (NMR conversion PhC(O)Me 80%). Note: water may have caused hydrolysis of the product (e.g. other set of –CH(Me)- could be detected).

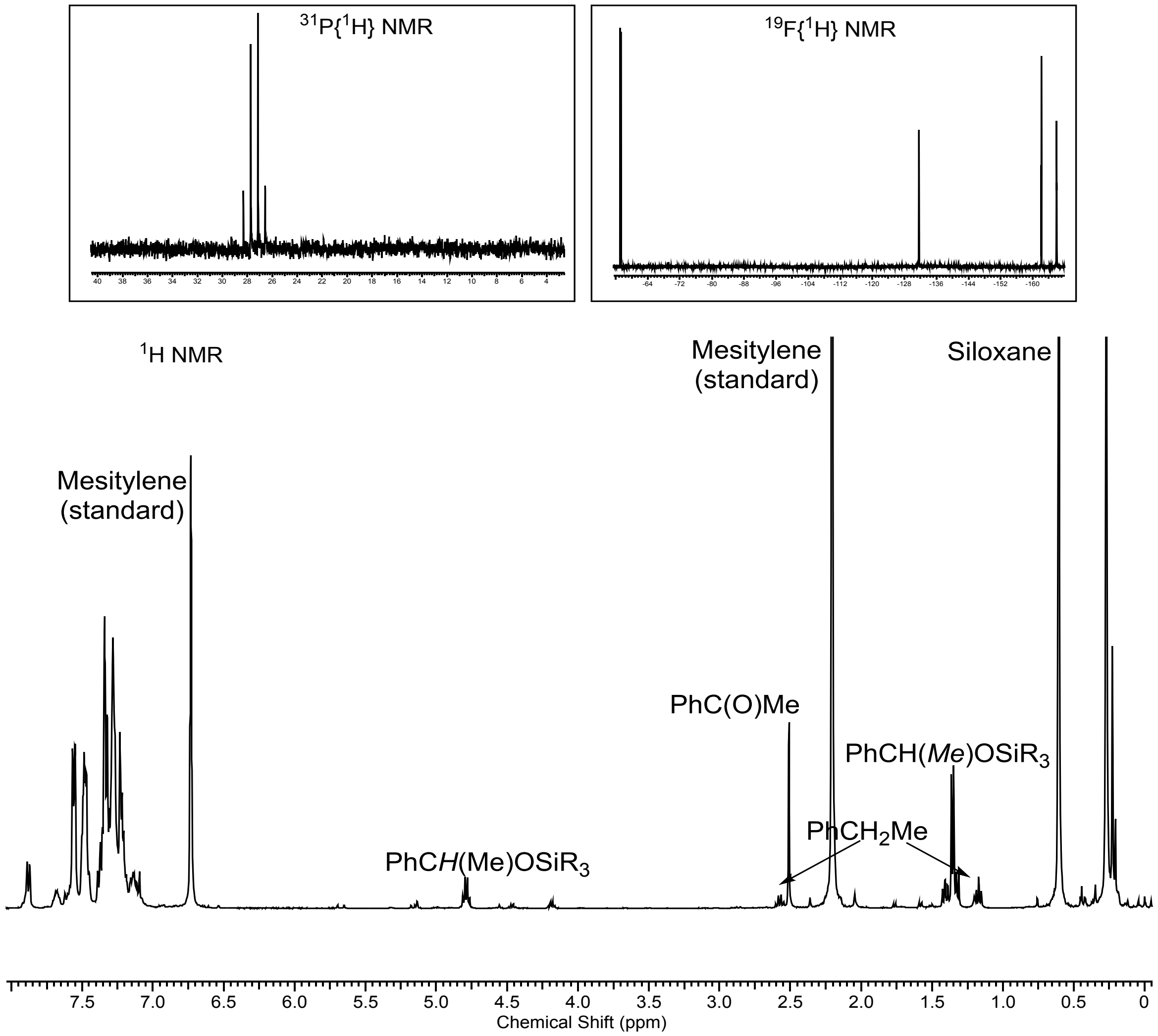


Figure S40. ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of PhC(O)Me with $PhMe_2SiH$ and **[1][BArF]** in wet $CDCl_3$ under ambient conditions, after 8 h at 100°C.

Reaction under ambient conditions (Ph_2CO): the reaction in entry 7 was repeated under ambient conditions using $CDCl_3$ straight from the Winchester. No decomposition was observed after 8 h at 100°C, with the silane completely consumed (NMR conversion Ph_2CO 70%).

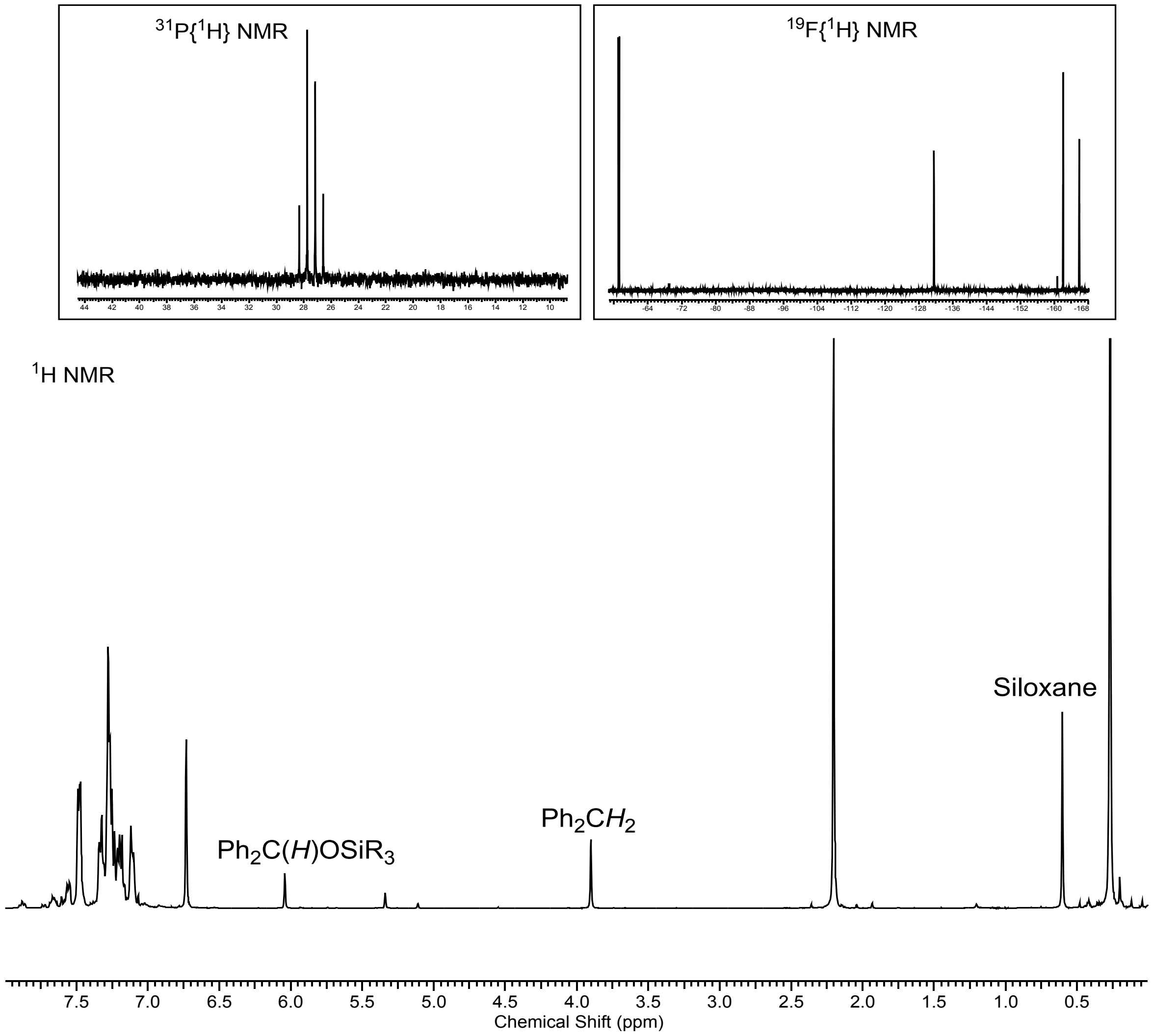
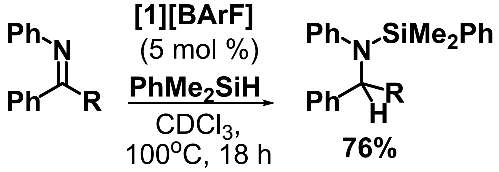


Figure S41. ^1H, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of Ph_2CO with $PhMe_2SiH$ and **[1][BArF]** in wet $CDCl_3$ under ambient conditions, after 8 h at 100°C.

9. Imine reductions

Under inert atmosphere, in a J. Young NMR tube the **[1][BArF]** (5 mg, 0.005 mmol, 0.05 eq.) was dissolved in dried $CDCl_3$ (0.05 mL), followed by the addition of the *N*-benzylidene aniline (18 mg, 0.10 mmol, 1.0 eq.) and $PhMe_2SiH$ (19 µL, 0.12 mmol, 1.2 eq.). The system was then sealed and heated at 100 ºC in an oil bath. After 18 hours at 100ºC, full imine reduction was observed and $PhCH_2N(Ph)SiPhMe_2$ was found as the main product (NMR yield = 76% based on the relative integral of the benzylic protons of the product). ^1H NMR (400 MHz, $CHCl_3$): δ 4.67 (s, 2H, $-CH_2-$), 0.52 (s, 6H, $-SiMe_2$) ppm. $^{29}Si\{^1H\}$ NMR (79 MHz, CH_2Cl_2): δ 1.22 ppm. The results are in agreements with those reported in the literature.[15]



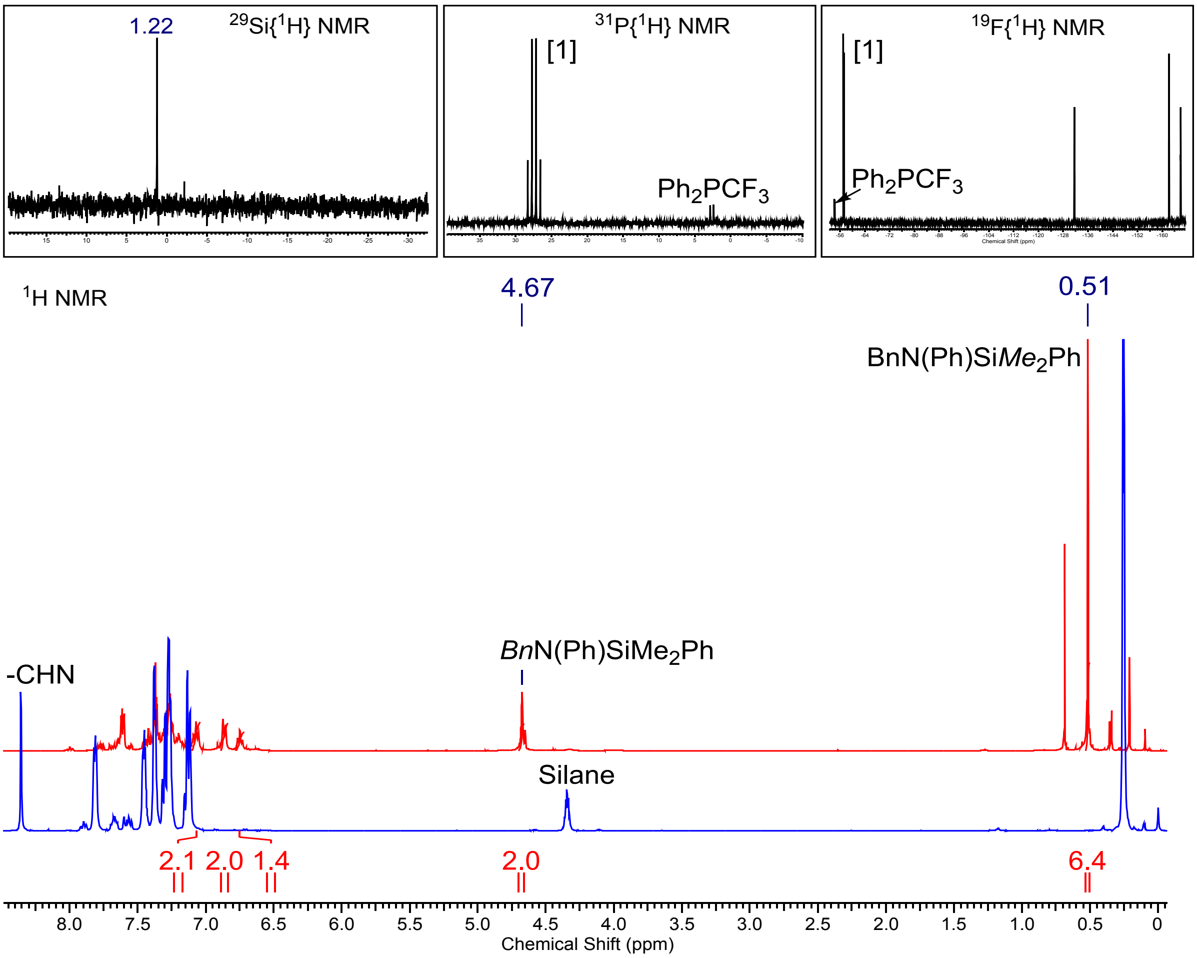


Figure S42. ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of PhC(H)NPh with $PhMe_2SiH$ with **[1][BArF]** in dried $CHCl_3$. Blue (after 5 min), red (after 18 h at 100ºC).

Reaction under ambient conditions (PhC(H)NPh): the reaction was repeated under ambient conditions using $CDCl_3$ straight from the Winchester. No decomposition was observed after 8 h at 100°C, with the imine completely consumed (NMR conversion $PhCH_2N(Ph)SiPhMe_2$ 56%). Note: water may have caused hydrolysis of the silyl amine product to the NH congener.

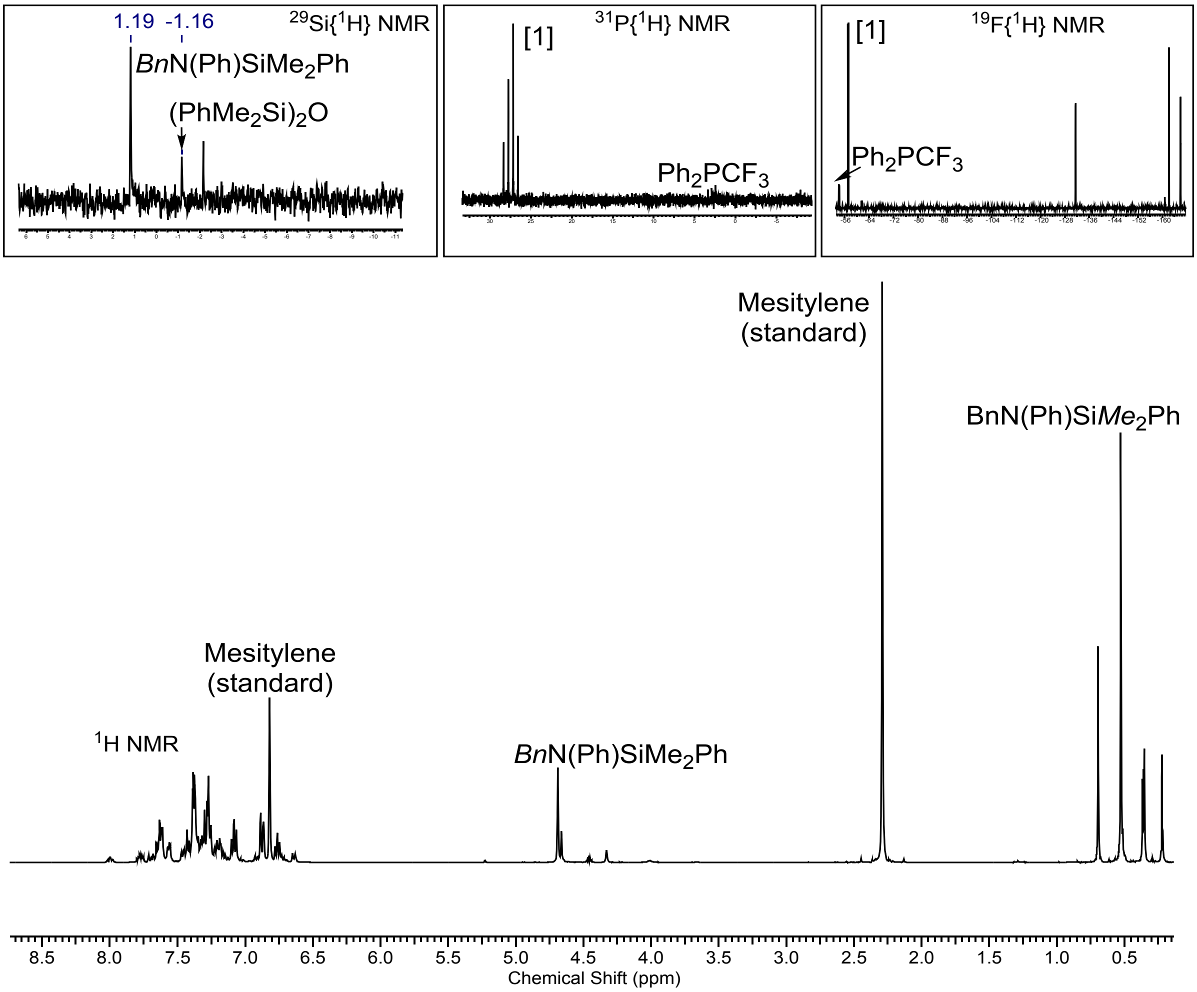


Figure S43. ^1H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$-NMR spectra of the reduction of PhC(H)NPh with $PhMe_2SiH$ with **[1][BArF]** in wet $CDCl_3$ under ambient conditions, after 8 h at 100°C.

10. H/D silane scrambling

$$\mathbf{PhMe_2SiH} + \mathbf{Et_3SiD} \xrightarrow[\text{DCM, 18h 60}^{o}\text{C}]{\mathbf{[1][OTf]}\ (5\ \text{mol}\ \%)} \mathbf{PhMe_2SiD} + \mathbf{Et_3SiH}$$

Under inert atmosphere, in a J. Young NMR tube **[1][OTf]** was dissolved in dried DCM (0.05 mL), followed by the addition of the fresh distilled $PhMe_2SiH$ (34 µL, 0.21 mmol, 1.0 eq.) and Et_3SiD (35 µL, 0.21 mmol, 1.0 eq.). The system was then sealed and heated at 60°C in an oil bath for 18 hours, revealing formation of $PhMe_2SiD$ and Et_3SiH, although at small extent (~ 6%).

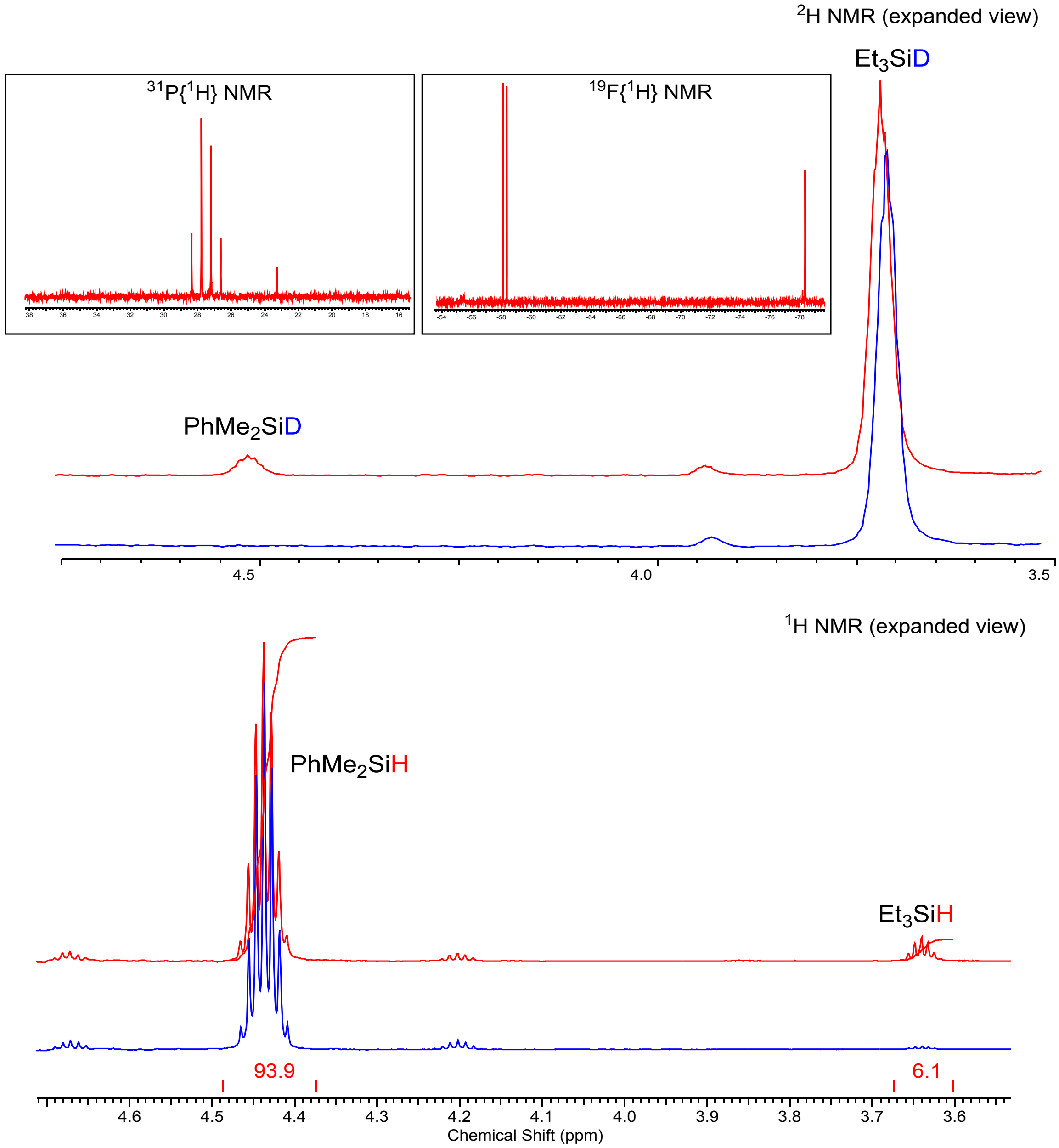
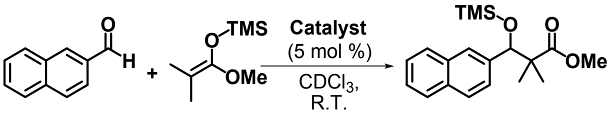


Figure S44. ^{1}H, ^{2}H, ^{29}Si{^{1}H}, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of the H/D silane scrambling with **[1][OTf]** in dried CH_2Cl_2. Blue (after 5 min), red (after 18 h at 60°C).

11. Mukaiyama aldol reaction

General procedure: under inert atmosphere, in a J. Young NMR tube the catalyst and 2-naphthaldehyde were dissolved in dried $CDCl_3$ (0.05 mL), followed by the addition of the 1-methoxy-2-methyl-1-trimethylsiloxypropene and toluene (32 μL) as internal standard. The system was then sealed, inverted for 19 hours at room temperature and subsequently analyzed by multinuclear NMR spectroscopy.



Catalyst	Time (h)	Conv. (%)
[2][OTf]	19	99
[1][OTf]	19	95
[1][BArF]	5	93

To avoid showing similar spectra multiple times, one example is reported.

Entry 1: 2-Naphthadehyde (47 mg, 0.30 mmol, 1.0 eq.), 1-methoxy-2-methyl-1-trimethylsiloxypropene (73 μL, 0.36 mmol, 1.2 eq.), **[2][OTf]** (6 mg, 0.02 mmol, 0.05 eq.). After 19 hours at R.T., the corresponding Mukaiyama aldol product was found as main product (NMR yield = 99%). Diagnostic peaks: ^{1}H NMR (400 MHz, $CHCl_2$): δ 5.18 (s, 1H, -C(*H*)-), 3.70 (s, 3H, -OMe), 1.21 (s, 3H, Me), 1.07 (s, 3H, Me'), 0.00 (s, 9H, -OTMS) ppm. The results are in agreements with those reported in the literature.[16]

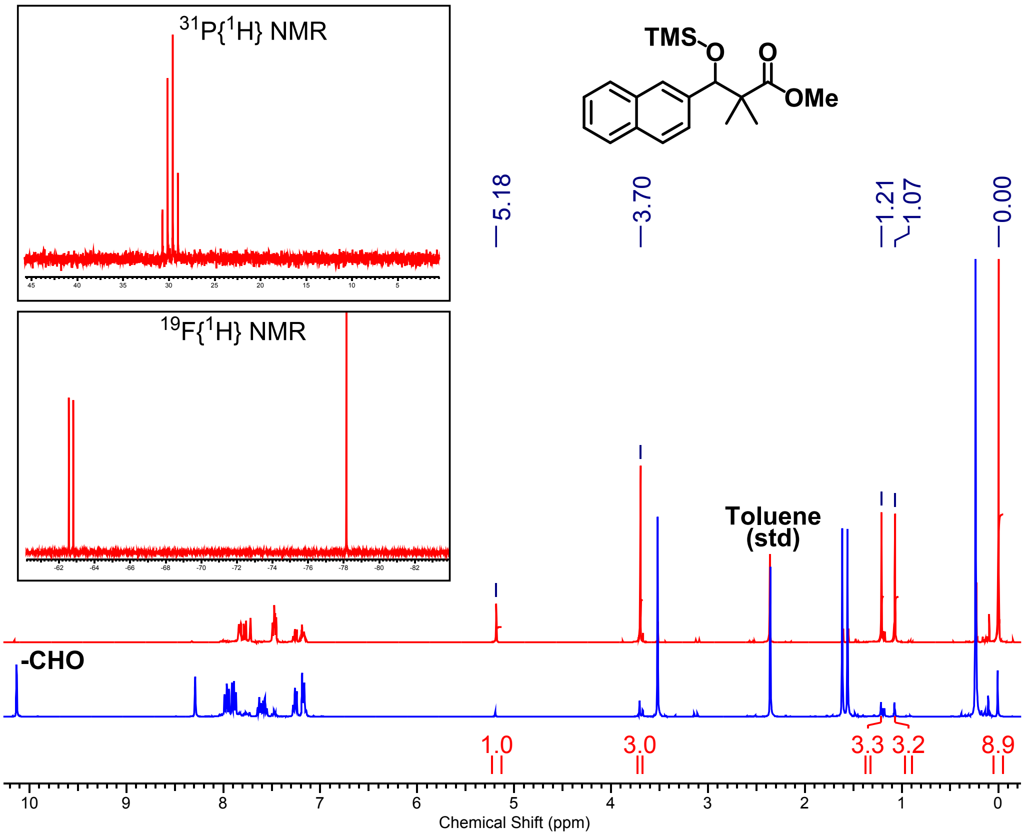


Figure S45. ^{1}H, ^{31}P{^{1}H} and ^{19}F{^{1}H}-NMR spectra of the Mukaiyama reaction with **[2][OTf]** in dried $CHCl_3$. Blue (after 20 min), red (after 19 h at R.T.).

12. Crystallographic analysis of [1][OTf], [1][BArF], [2][OTf]

Crystallographic data for compounds **[1][OTf]** and **[2][OTf]** were recorded on a Bruker X8 Prospector diffractometer, at 293 K with Cu Kα radiation (mirror monochromator, λ = 1.54184). Data for compound for **[1][BArF]** were recorded on a Bruker Apex2 X-ray diffractometer, at 150 K with Mo Kα radiation (mirror monochromator, λ =0.71073). The CrysAlisPro[17] software package was used for data collection, cell refinement and data reduction. For all data sets the CrysAlisPro software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All further data processing was undertaking within the Olex2 software.[18] The structures were solved using the ShelXT[19] structure solution program using Intrinsic Phasing. All structures were refined with the SHELXL[20] refinement package using Least Squares minimisation against F2. Non-hydrogen atoms were refined anisotropically.

Compound	**[1][OTf]**	**[1][BArF]**	**[2][OTf]**
CCDC code	1586279	1586281	1586280
Empirical formula	$C_{20}H_{15}F_6O_3PS$	$C_{43}H_{15}BF_{23}P$	$C_{15}H_{13}F_6O_3PS$
Formula weight	480.35	1010.33	418.28
Temperature / K	293(2)	150(2)	293(2)
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	Pbca	Pbca	P-1
a / Å	21.9081(6)	14.9846(19)	11.4013(6)
b / Å	8.3531(2)	19.108(2)	11.4161(6)
c / Å	22.4426(7)	27.311(3)	13.9435(7)
α / °	90	90	81.712(4)
β / °	90	90	76.486(4)
γ / °	90	90	89.978(4)
Volume / Å^3	4107.0(2)	7819.9(16)	1745.14(16)
Z	8	8	4
ρ_{calc} gcm^{-3}	1.554	1.716	1.592
M / mm^{-1}	2.836	0.215	3.233
F(000)	1952.0	4000.0	848.0
Crystal size / mm^3	0.4 × 0.3 × 0.1	0.1 × 0.1 × 0.1	0.3 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection / °	7.878 to 148.53	2.982 to 55.318	6.592 to 149.622
Index ranges	$-26 \le h \le 24$, $-9 \le k \le 9$, $-24 \le l \le 24$	$-19 \le h \le 19$, $-24 \le k \le 24$, $-35 \le l \le 35$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-17 \le l \le 15$
Reflections collected	17128	127741	18932
Independent reflections	3836 [R_{int} = 0.0425, R_{sigma} = 0.0195]	9054 [R_{int} = 0.0730, R_{sigma} = 0.0388]	6797 [R_{int} = 0.0195, R_{sigma} = 0.0164]
Data/restraints/parameters	3836/0/280	9054/0/613	6797/0/499
Goodness-of-fit on F^2	1.062	1.036	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.1201	R_1 = 0.0422, wR_2 = 0.1193	R_1 = 0.0327, wR_2 = 0.0865
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.1219	R_1 = 0.0881, wR_2 = 0.1612	R_1 = 0.0339, wR_2 = 0.0874
Largest diff. peak/hole / e Å^{-3}	0.52/-0.49	0.41/-0.43	0.35/-0.48

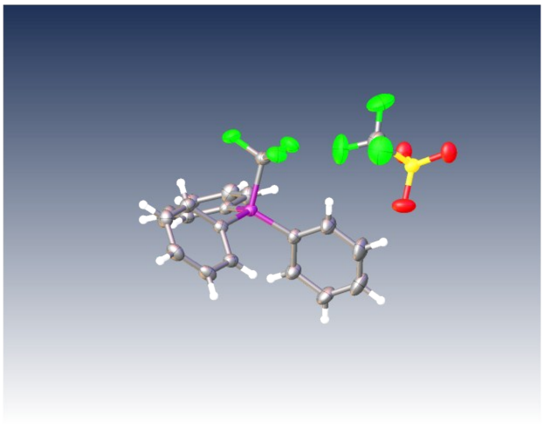


Figure S46. ORTEP representation of the molecular structure of compound **[1][OTf]**, with thermal ellipsoids set at the 50 % level.

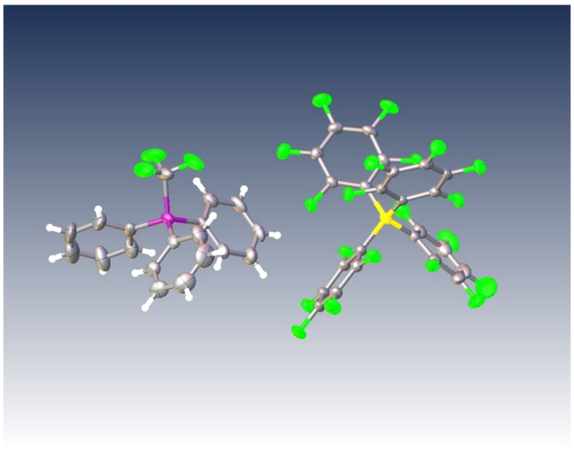


Figure S47. ORTEP representation of the molecular structure of compound **[1][BArF]**, with thermal ellipsoids set at the 50 % level.

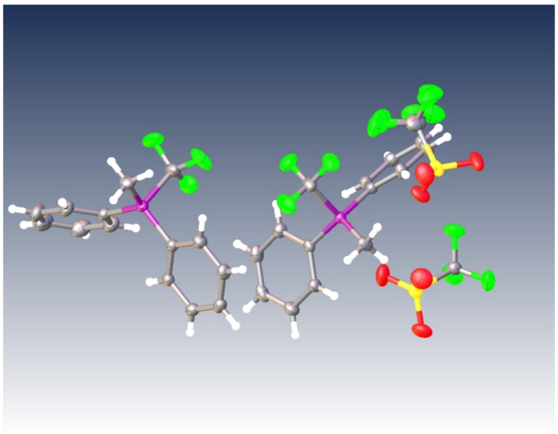


Figure S48. ORTEP representation of the molecular structure of compound **[2][OTf]**, with thermal ellipsoids set at the 50 % level. **[2][OTf]** displays disorder on one triflate anion.

13. References

1 C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science,* 2013*,* **341**, 1374.

2 Z. Moussa, S. A. Ahmed, A. S. ElDouhaibi, S. Y. Al-Raqa, *Tetrahedron Lett.,* 2010*,* **51**, 1826.

3 P. Romanato, S. Duttwyler, A. Linden, K. K. Baldridge, J. S. Siege, *J. Am. Chem. Soc*., 2010, **132**, 7828.

4 T. Umemoto, S. Ishihara, *J. Am. Chem. Soc*., 1993, **115***,* 2156.

5 C. B. Caputo, D. Winkelhaus, R.Dobrovetsky, L. J. Hounjet, D. W. Stephan, *Dalton Trans.,* 2015*,* **44**, 12256.

6 M. B. Murphy-Jolly, L. C. Lewis, A. J. M. Caffyn, *Chem. Commun*., 2005, 4479.

7 N. Nebra, V. V. Grushin, *J. Am. Chem. Soc.,* 2014*,* **136**, 16998.

8 Gaussian 09, Revision C1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

9 http://comp.chem.umn.edu/info/DFT.htm.

10 E. R. Clark and M. J. Ingleson, *Angew. Chem. Int. Ed*., 2014, **53**, 11306.

11 E. R. Clark, A. Del Grosso and M. J. Ingleson, *Chem. Eur. J.,* 2013*,* **19**, 2462.

12 (a) V. Fasano, J. E. Radcliffe, L. D. Curless, M. J. Ingleson, *Chem. Eur. J.* 2017, **23**, 187. (b) B. Chatterjeea, C. Gunanathan, *Chem. Commun.,* 2014*,* **50**, 888.

13 T. A. Boebel, J. F. Hartwig, *J. Am. Chem. Soc*., 2008, **130**, 7534.

14 For selectivity in ketone reductions see: M. Mehta, M. H. Holthausen, I. Mallov, M. Pérez, Z.-W. Qu, S.Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.,* 2015, **54**, 8250.

15 D. V. Gutsulyak, A. van der Est, G. I. Nikonov, *Angew. Chem. Int. Ed.,* 2011, **50**, 1384.

16 A. G. Barrado, J. M. Bayne, T. C. Johnstone, C. W. Lehmann, D. W. Stephan, M. Alcarazo, *Dalton Trans.* 2017, DOI: 10.1039/c7dt03197a

17 CrysAlisPro, Agil. Technol. Version 1.1 71.35.19 (release 27-10-2011 CrysAlis171.NET) (compiled Oct 27 2011,150211)

18 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339.

19 G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3.

20 G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3.