Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Electronic supplementary information (ESI) for:

Aryl dechlorination and defluorination with an organic super-photoreductant

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1) General experimental details

All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. Most reagents were bought from Fluorochem, Alfar Aesar, Acros Organics or Sigma-Aldrich (now Merck) in normal "reagent grade" purity and used as received. TDAE was purchased from TCI and Sigma-Aldrich with > 95 % purity and stored under argon in a glove box.

All NMR spectra were recorded on a Bruker Avance III instrument operating at 400 MHz proton frequency. All samples were recorded at 295 K in 5 mm diameter tubes. Chemical shifts were referenced internally to residual solvent peak using δ values as reported by GOTTLIEB *et al.*[1] Starting material consumption and product formation were determined from ^{1}H or ^{19}F-NMR measurements (^{1}H: 400 MHz, ^{19}F: 376 MHz, 16 scans) in sealed NMR tubes against 1-fluoropentane as internal standard. Representative measurements based on weighted samples revealed very good recovery rates in the ^{19}F-NMR spectrum.

Sample preparation for photoreduction reactions and spectrophotometric measurements were done in a LabStar Eco glove box from MBrown with an argon atmosphere. The samples were kept under an argon atmosphere prior to the respective measurements. HPLC-grade solvents were used for these spectrophotometric measurements.

Absorption spectra were recorded as solutions on a Cary 5000 UV-Vis-NIR spectrometer from Varian. Photoluminescence spectra were recorded as solutions and in frozen matrix on a Fluorolog-322 instrument from Horiba Jobin-Yvon. Photoluminescence lifetimes in different solvents and quenching experiments were determined on a LifeSpec II spectrometer (time-correlated single photon counting technique) from Edinburgh Instruments.

For photoreduction reactions, reaction mixtures in sealed NMR tubes (closed with 'Precision Seal® rubber septa cap for 5-6 mm O.D. tubes and ampules' purchased from Sigma-Aldrich and Parafilm) were irradiated with a LED light source in a self-made passive water-cooled system (details in next section). As light sources, Kessil PR160 LEDs with 390 nm and 440 nm output were used.

2) Irradiation setup

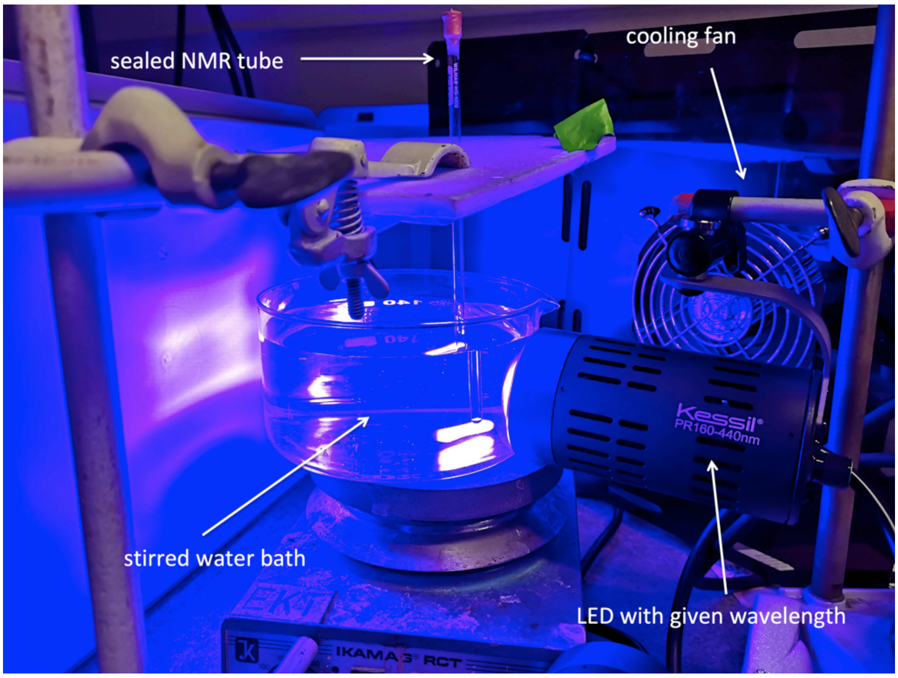

Figure S1 Irradiation setup for photoreductions. The samples were cooled with a passive water-cooling setup. A fan is used to minimize heating of the water bath by the LEDs.

3) Synthetic procedures

Photoreduction with TDAE – General Procedure

A vial was charged with substrate (1 eq., e.g. 100 μmol), the corresponding amount of TDAE (e.g. 1.25 eq.), internal standard (1 eq.) and deuterated solvent (1 mL) under an argon atmosphere in a glove box. 0.6 mL of the resulting solution were transferred to an NMR tube, capped with a rubber cap, wrapped with Parafilm and irradiated outside of the glove box under passive water-cooling for specified lengths of time with an LED lamp (Kessil PR160, λ_{em} = 390 nm or 440 nm) and the product formation was monitored by ^{1}H-NMR (400 MHz, 16 scans) and ^{19}F-NMR (376 MHz, 16 scans).

Dimerization of 4-fluorobenzyl chloride (13) and isolation of the product

A Schlenk tube was charged with a magnetic stir bar, 4-fluorobenzyl chloride (**13**, 59.9 μL, 500 μmol, 1.0 eq.), TDAE (145 μL, 623 μmol, 1.25 eq.) and dry benzene (4 mL) under an argon atmosphere and irradiated under passive water-cooling for 30 min with an LED lamp (Kessil PR160, λ_{em} = 440 nm). Aqueous HCl (1 M, 20 mL) was added to the solution and extracted with DCM (3 · 30 mL). The combined organic phases were dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the residue was purified by sublimation to obtain the pure product as white solid (**14**, 42.9 mg, 79 %).

^{1}H{^{19}F }-NMR (500 MHz, $CDCl_3$): δ 7.10 – 7.05 (d, J = 8.5 Hz, 4H), 6.97 – 6.93 (d, J = 8.5 Hz, 4H), 2.86 (s, 4H) ppm.
^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ 117.49 (s, 1F) ppm.
^{13}C-NMR (126 MHz, $CDCl_3$): δ161.49 (d, J = 243.6 Hz, 2C), 137.09 (d, J = 3.2 Hz, 2C), 129.97 (d, J = 7.7 Hz, 4C), 115.20 (d, J = 21.1 Hz, 4C), 37.29 (s, 2C) ppm.

4) Spectroscopic measurements

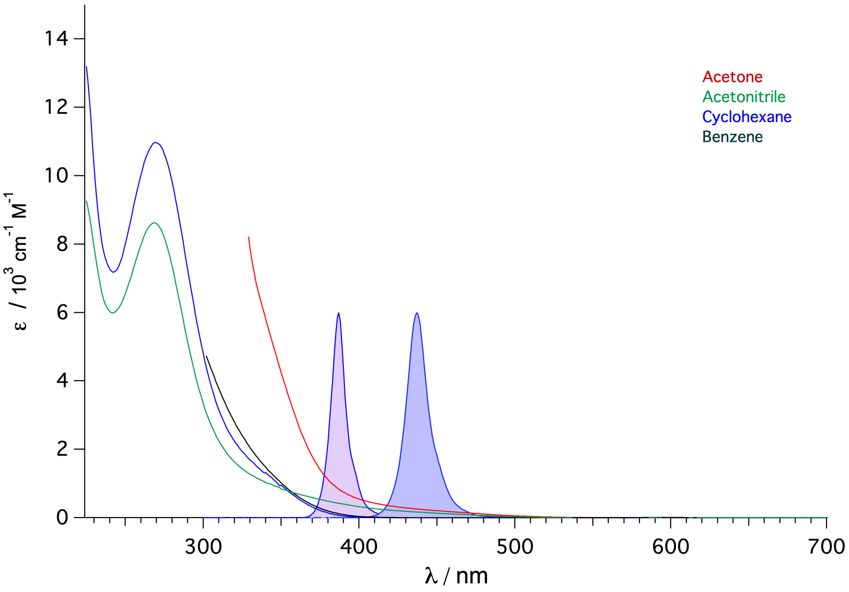

Figure S2 UV-Vis absorption spectra of TDAE (100 μM) in de-aerated acetone (red), acetonitrile (green), cyclohexane (blue) and benzene (black) at room temperature. Solvent absorptions preclude detection of the TDAE spectra at equally short wavelengths in acetone and benzene as in acetonitrile and cyclohexane. Emission spectra of Kessil LED Lamps are shown for the 390 nm (violet) and 440 nm (blue) lamps.

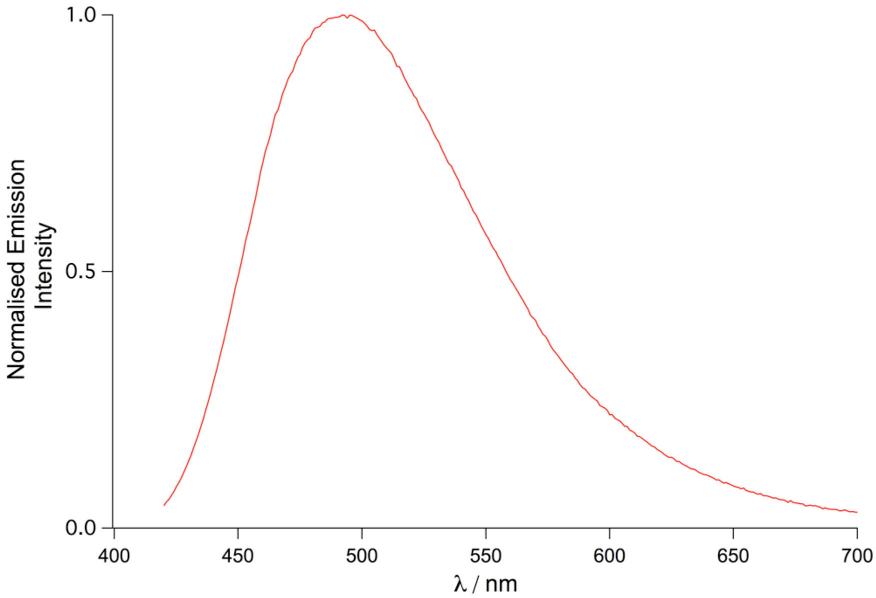

Figure S3 Emission spectrum of TDAE (1 mM) in de-aerated cyclohexane at room temperature (λ_{ex} = 405 nm).

Emission spectra at room temperature (**Figure S3**) and at 77 K (**Figure S4**) are very similar, compatible with fluorescence from a singlet excited state in both cases.

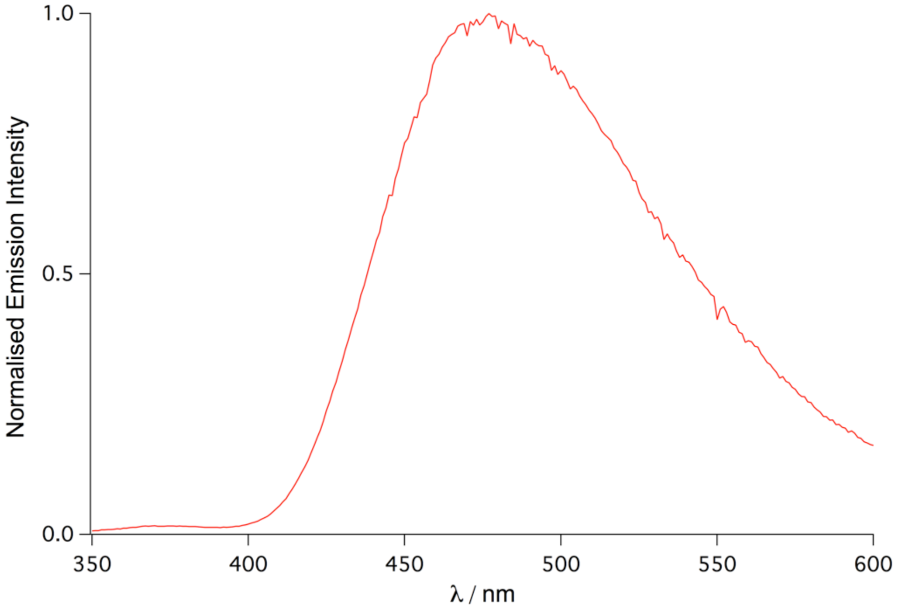

Figure S4 Emission spectrum of TDAE (100 µM) in de-aerated 2-methyltetrahydrofuran at 77 K (λ_{ex} = 320 nm).

In the following figures the scale of all Stern-Volmer plots (inset of respective figure) is kept constant to simplify a graphic comparison between the different measurements.

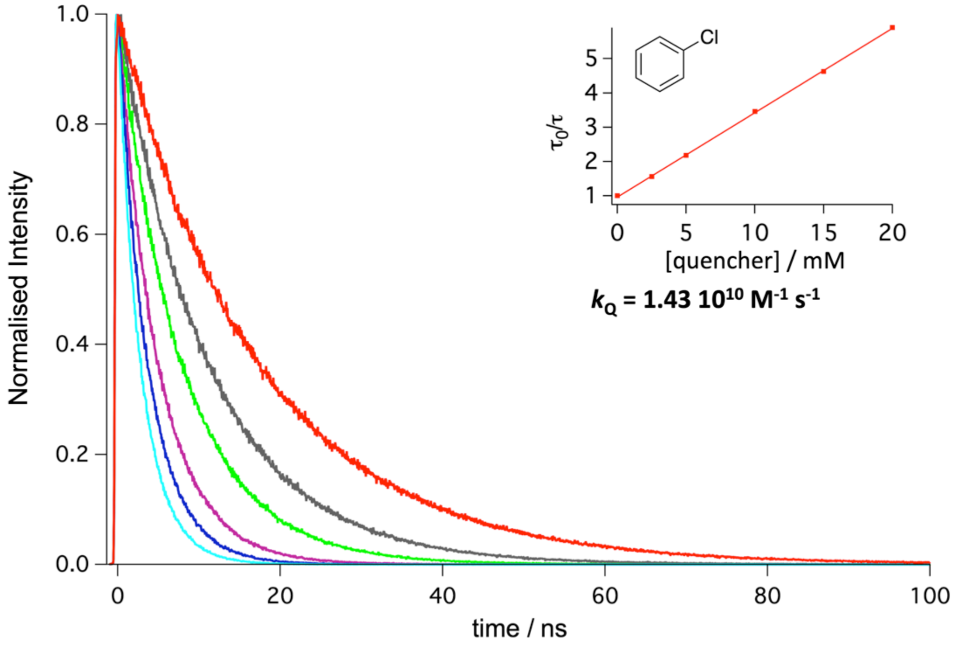

Figure S5 Emission decay of TDAE (10 mM) in neat de-aerated cyclohexane (grey trace) and in de-aerated cyclohexane with different concentrations of chlorobenzene (2.5, 5, 10, 15, 20 mM) observed at 470 nm (λ_{ex} = 405 nm). The inset displays the resulting Stern-Volmer plot.

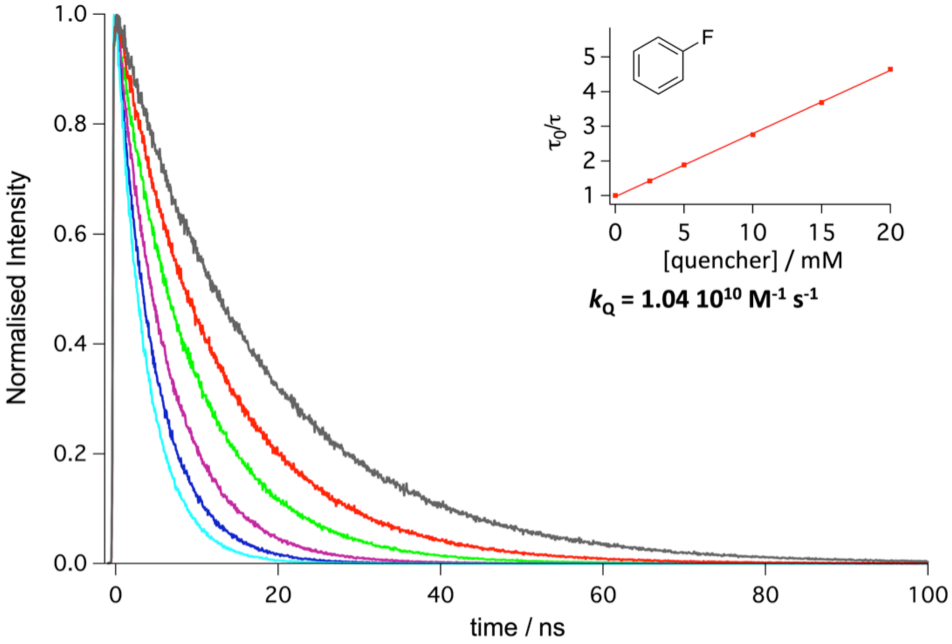

Figure S6 Emission decay of TDAE (10 mM) in neat de-aerated cyclohexane (grey trace) and in de-aerated cyclohexane with different concentrations of fluorobenzene (2.5, 5, 10, 15, 20 mM) observed at 470 nm (λ_{ex} = 405 nm). The inset displays the resulting Stern-Volmer plot.

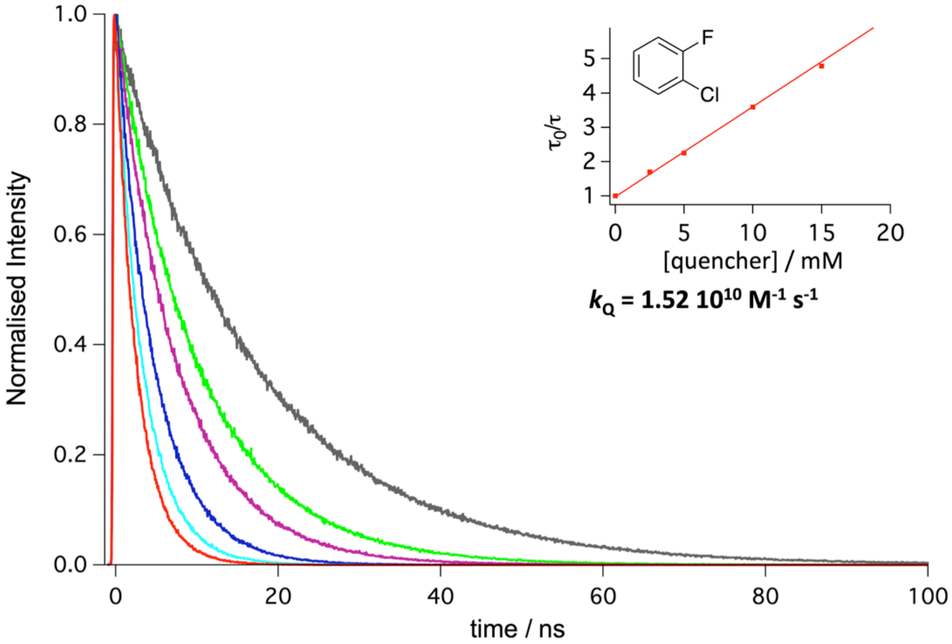

Figure S7 Emission decay of TDAE (10 mM) in neat de-aerated cyclohexane (grey trace) and in de-aerated cyclohexane with different concentrations of 1-chloro-2-fluorobenzene **3** (2.5, 5, 10, 15, 20 mM) observed at 470 nm (λ_{ex} = 405 nm). The inset displays the resulting Stern-Volmer plot.

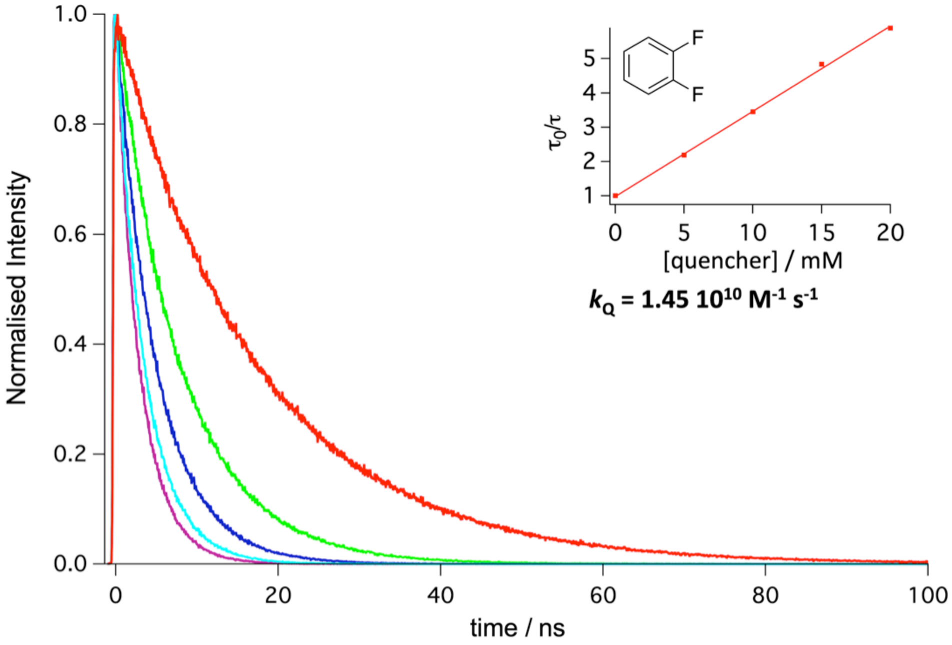

Figure S8 Emission decay of TDAE (10 mM) in neat de-aerated cyclohexane (grey trace) and in de-aerated cyclohexane with different concentrations of 1.2-fluorobenzene **9** (5, 10, 15, 20 mM) observed at 470 nm (λ_{ex} = 405 nm). The inset displays the resulting Stern-Volmer plot.

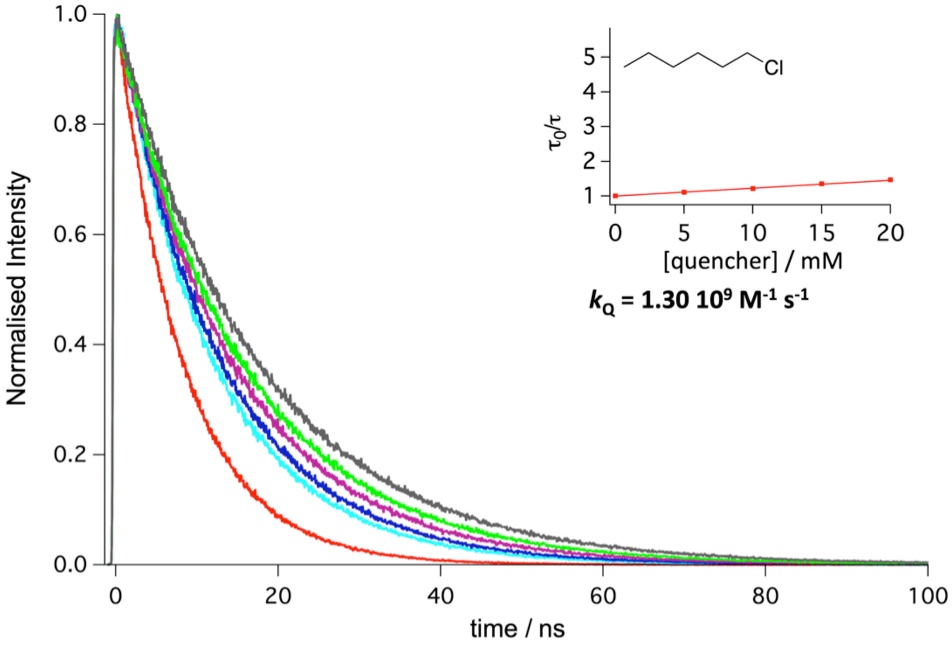

Figure S9 Emission decay of TDAE (10 mM) in neat de-aerated cyclohexane (grey trace) and in de-aerated cyclohexane with different concentrations of 1-chlorohexane (5, 10, 15, 20, 50 mM) observed at 470 nm (λ_{ex} = 405 nm). The inset displays the resulting Stern-Volmer plot.

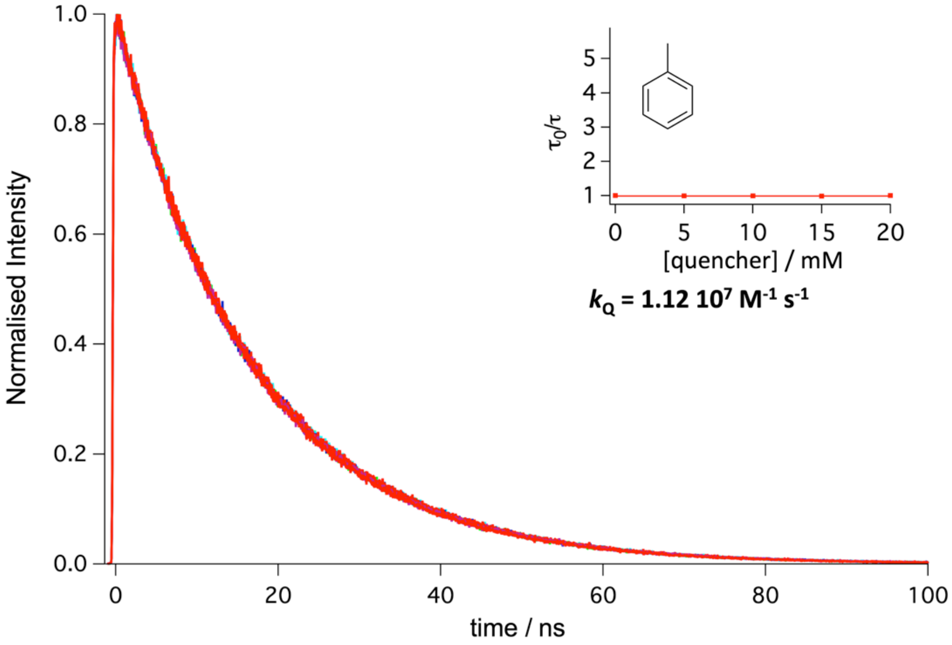

Figure S10 Emission decay of TDAE (10 mM) in neat de-aerated cyclohexane (red trace) and in de-aerated cyclohexane with different concentrations of toluene (5, 10, 15, 20 mM) observed at 470 nm (λ_{ex} = 405 nm). The inset displays the resulting Stern-Volmer plot.

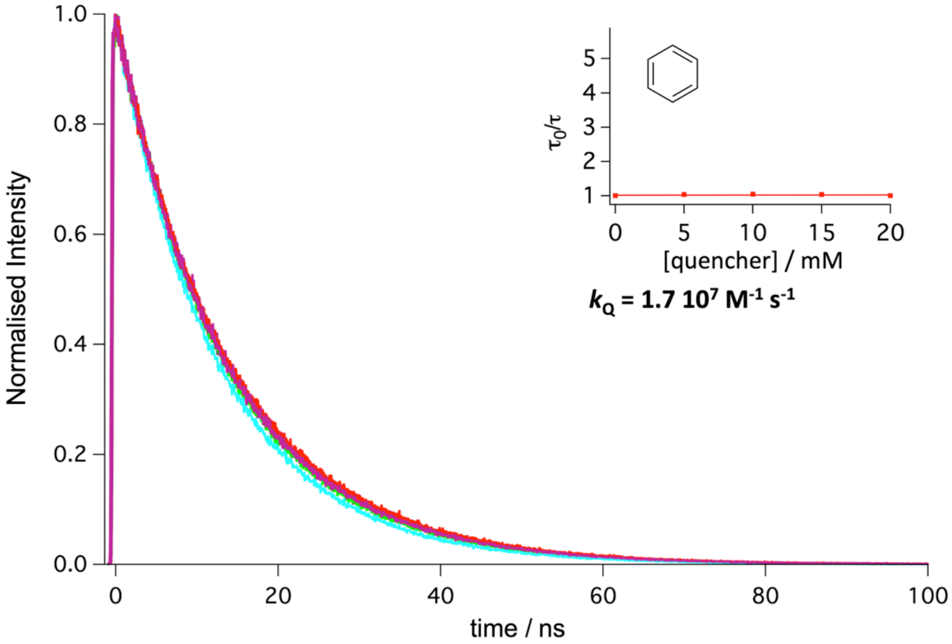

Figure S11 Emission decay of TDAE (10 mM) in neat de-aerated cyclohexane (red trace) and in de-aerated cyclohexane with different concentrations of benzene (5, 10, 15, 20 mM) observed at 470 nm (λ_{ex} = 405 nm). The inset displays the resulting Stern-Volmer plot.

5) NMR data

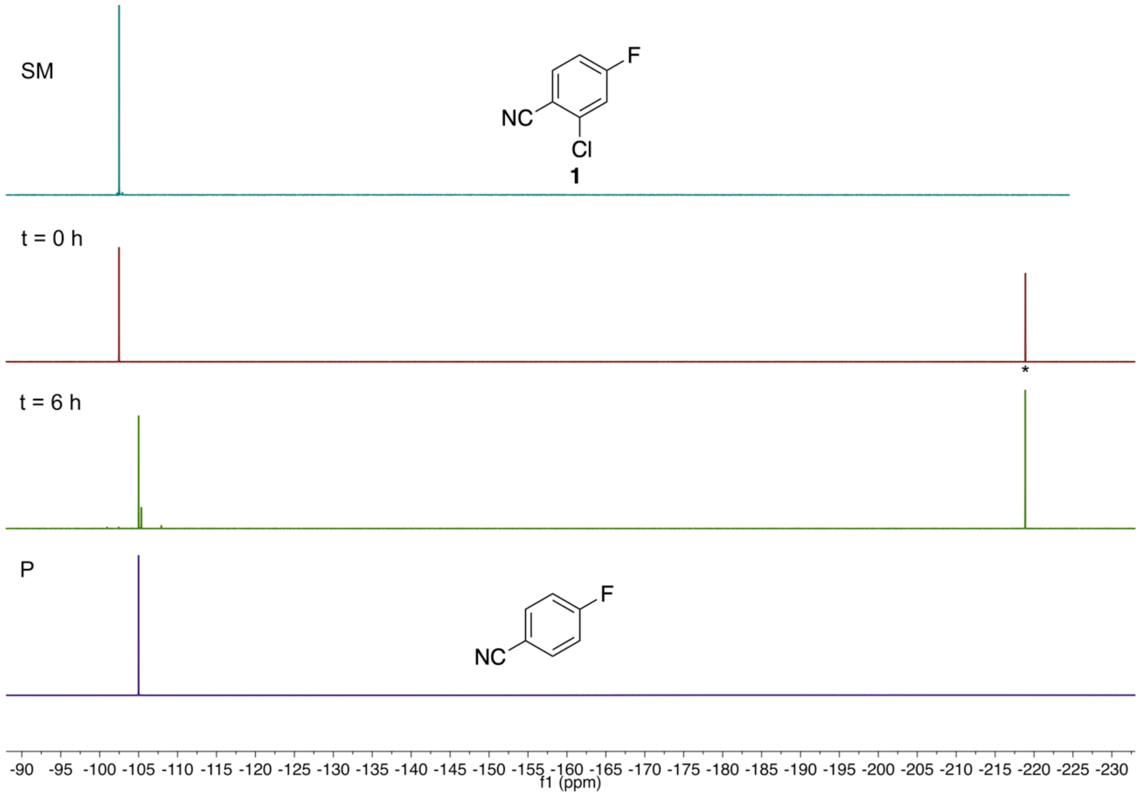

Figure S12 ^{19}F-NMR spectra monitoring dechlorination of substrate **1** over time. Reaction conditions: 100 mM **1**, 1.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

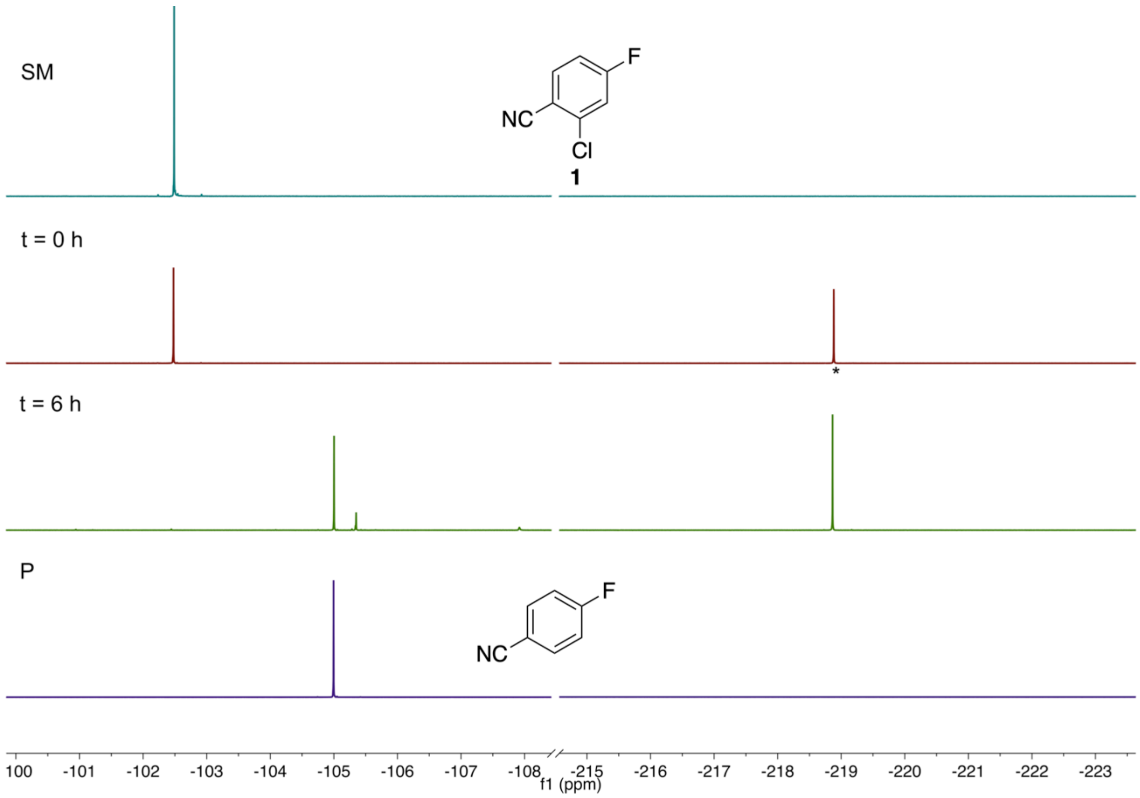

Figure S13 Expansions of the ^{19}F-NMR spectra from **Figure S12**.

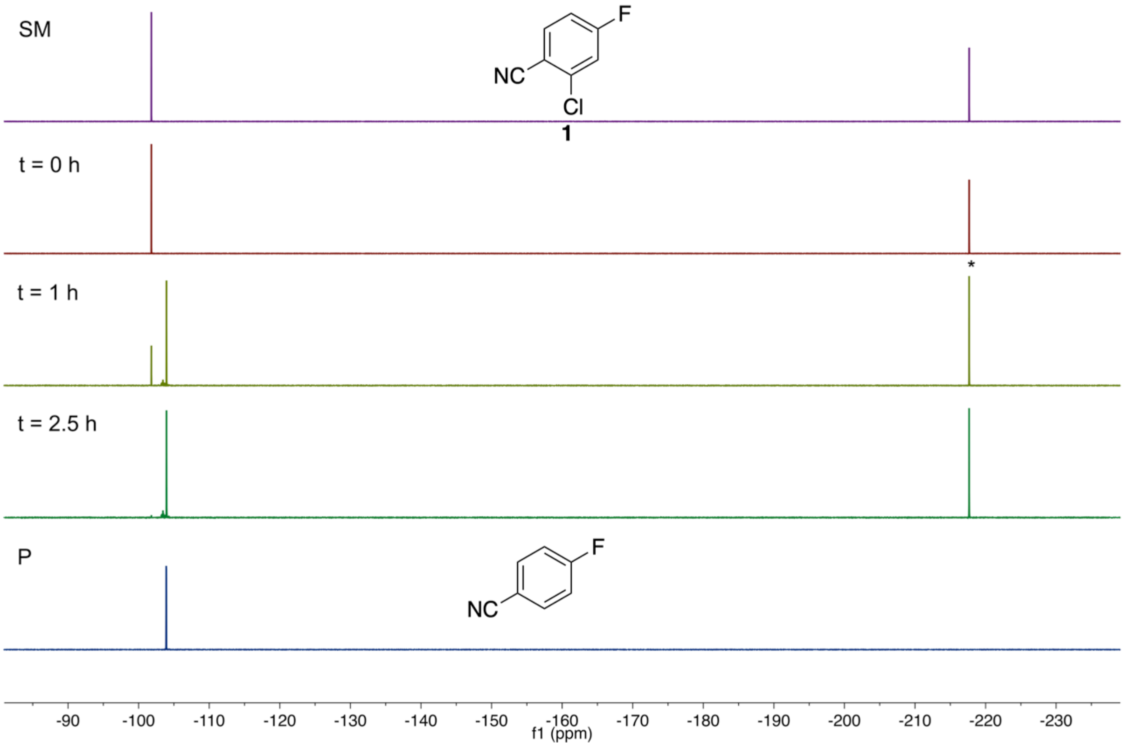

Figure S14 ^{19}F-NMR spectra monitoring dechlorination of substrate **1** over time. Reaction conditions: 50 mM **1**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

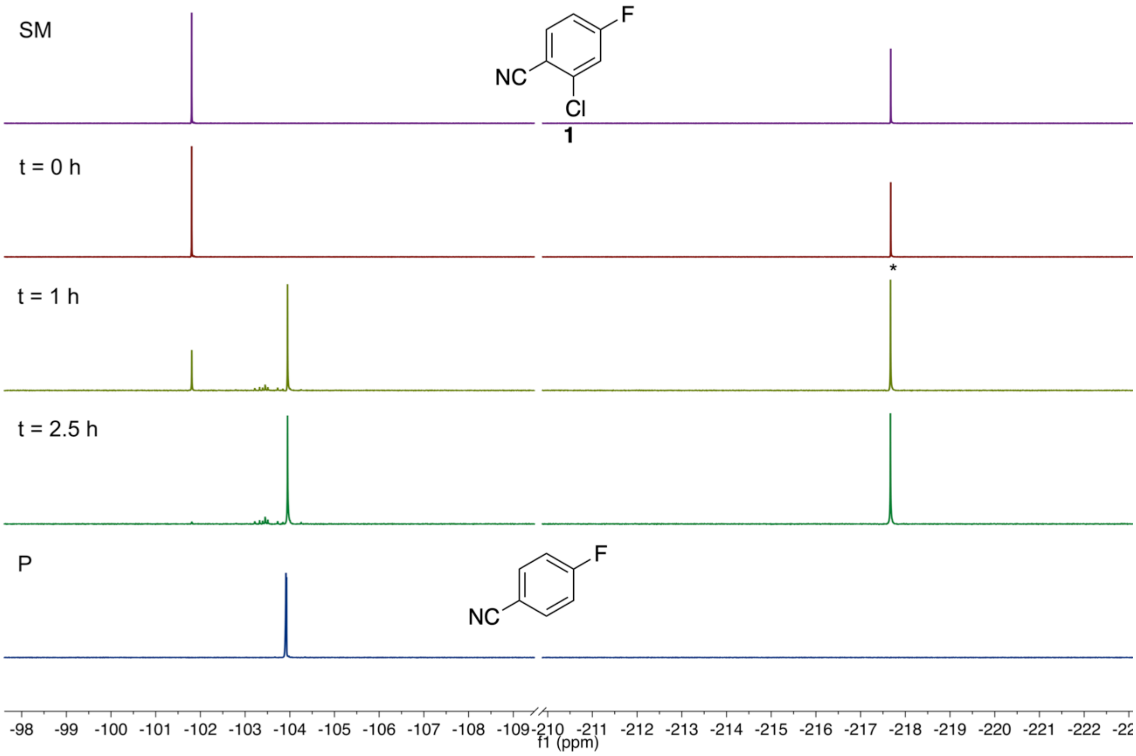

Figure S15 Expansions of the ^{19}F-NMR spectra from **Figure S14**.

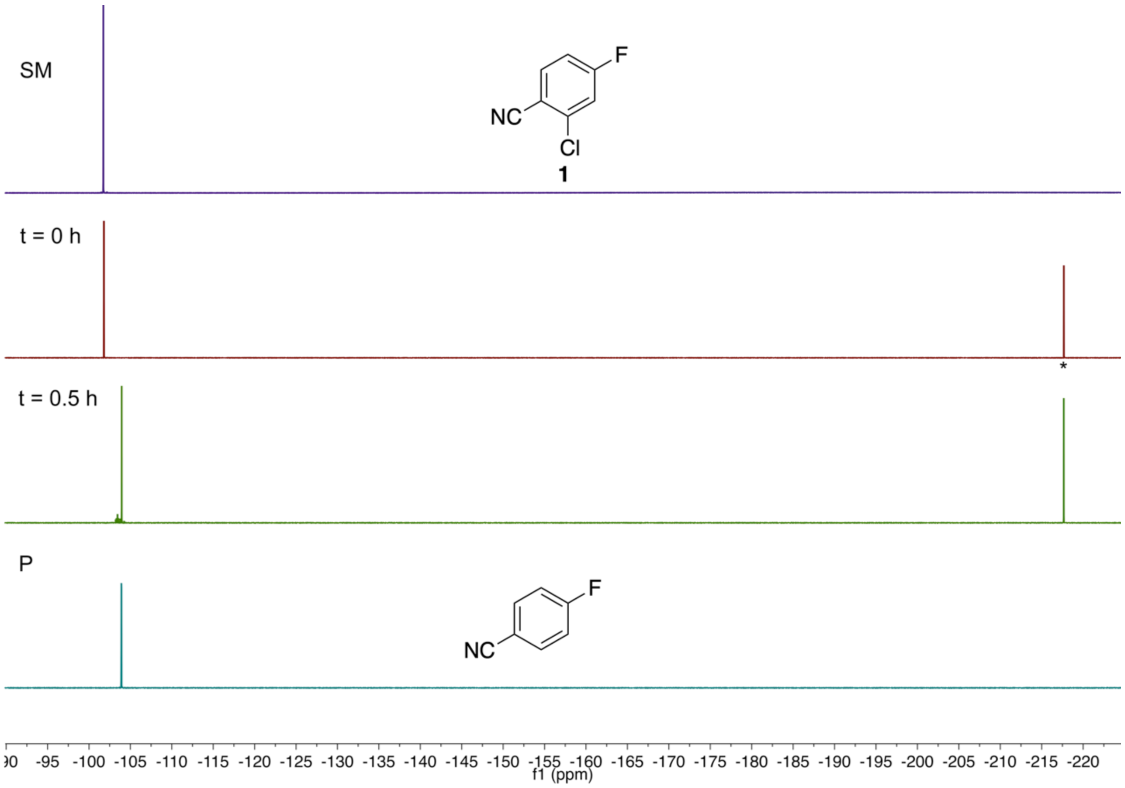

Figure S16 ^{19}F-NMR spectra monitoring dechlorination of substrate **1** over time. Reaction conditions: 50 mM **1**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

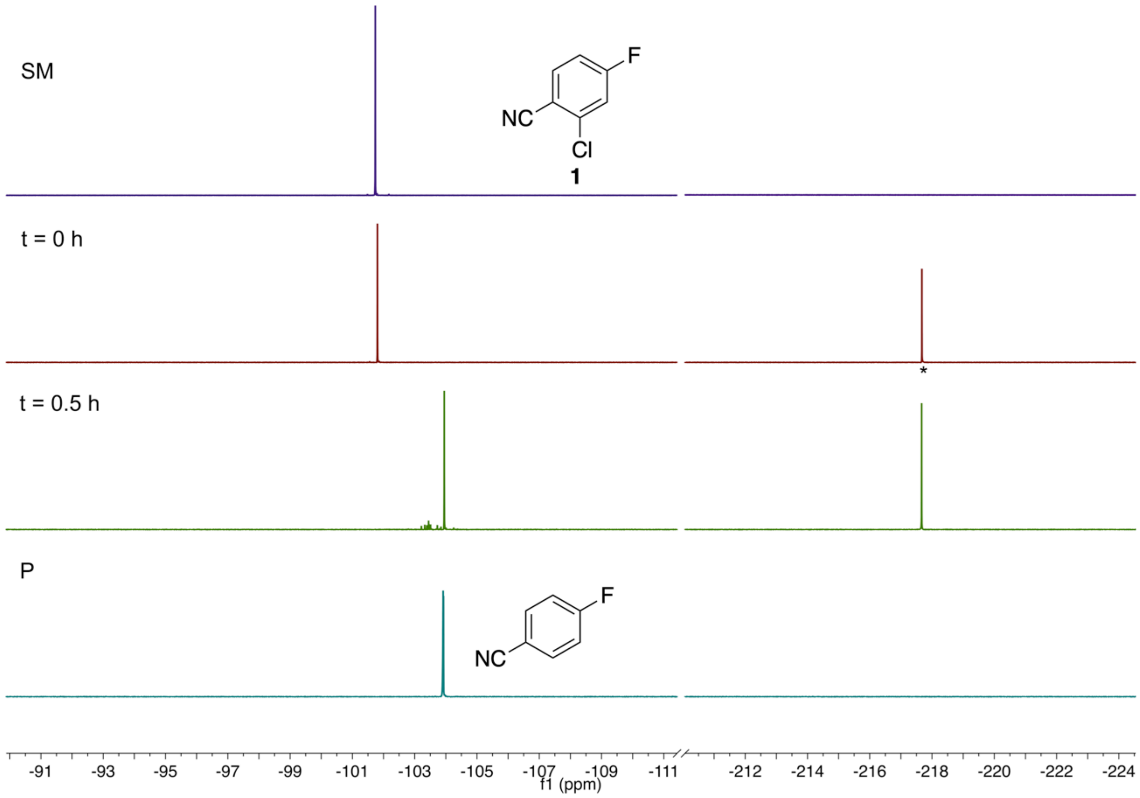

Figure S17 Expansions of the ^{19}F-NMR spectra from **Figure S16**.

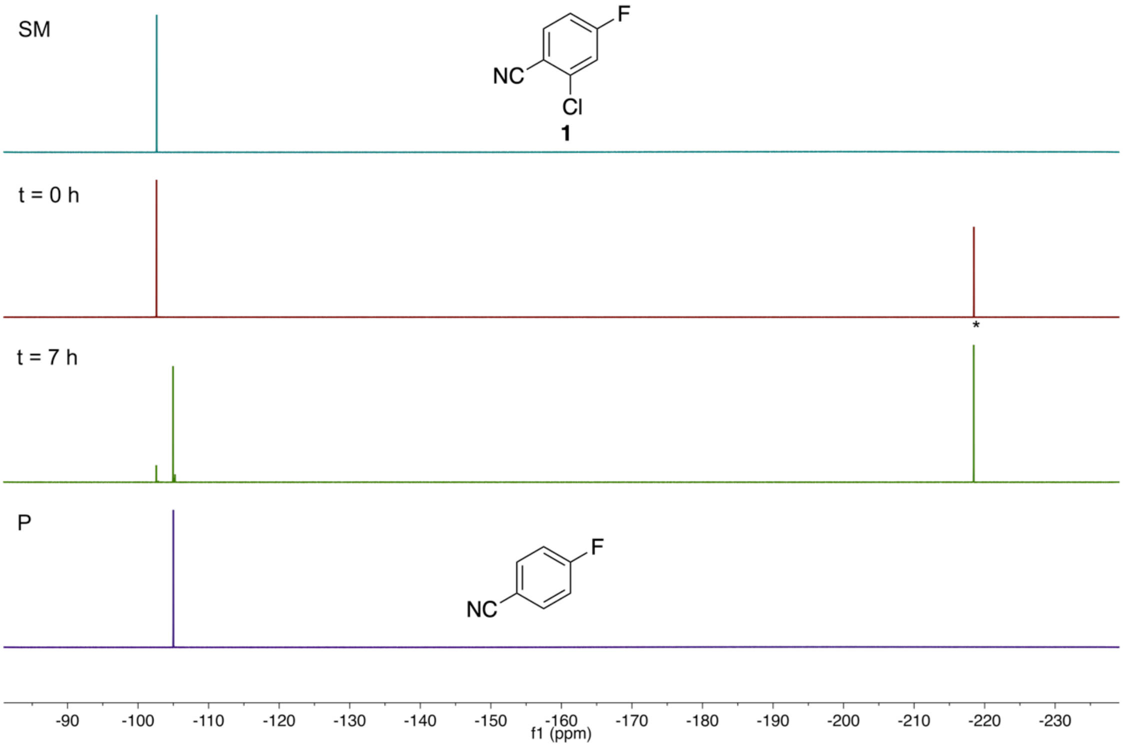

Figure S18 ^{19}F-NMR spectra monitoring dechlorination of substrate **1** over time. Reaction conditions: 100 mM **1**, 1.25 eq. TDAE, MeCN-d$_3$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

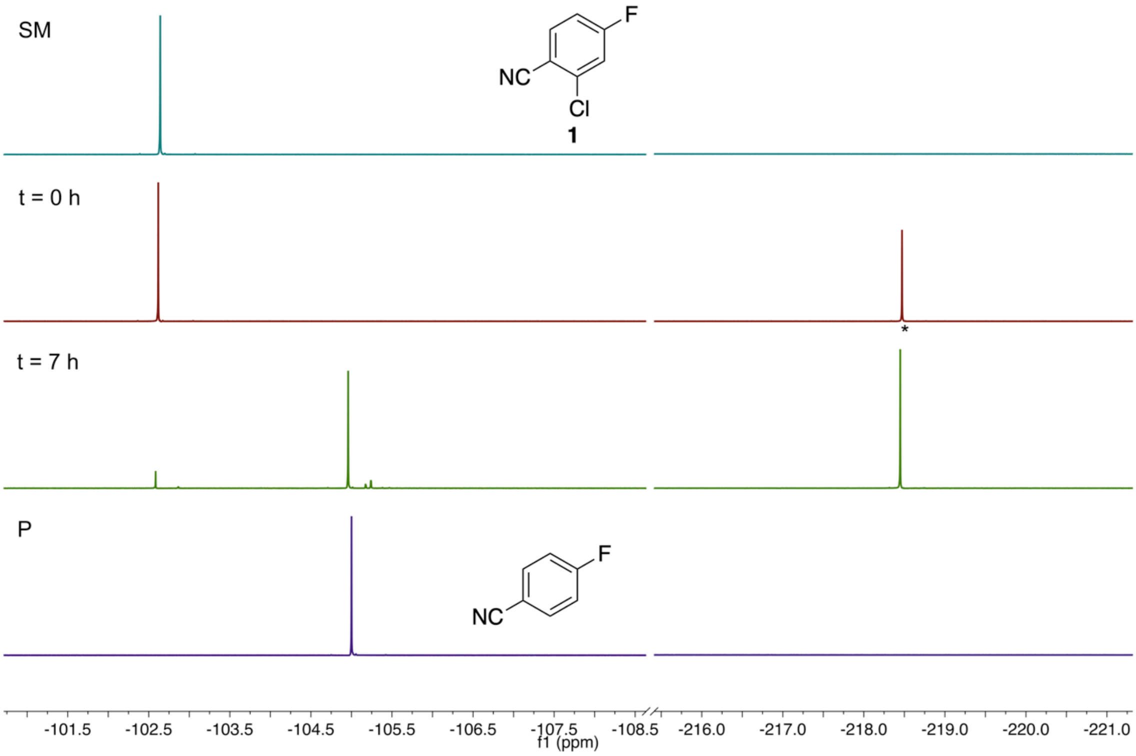

Figure S19 Expansions of the ^{19}F-NMR spectra from **Figure S18**.

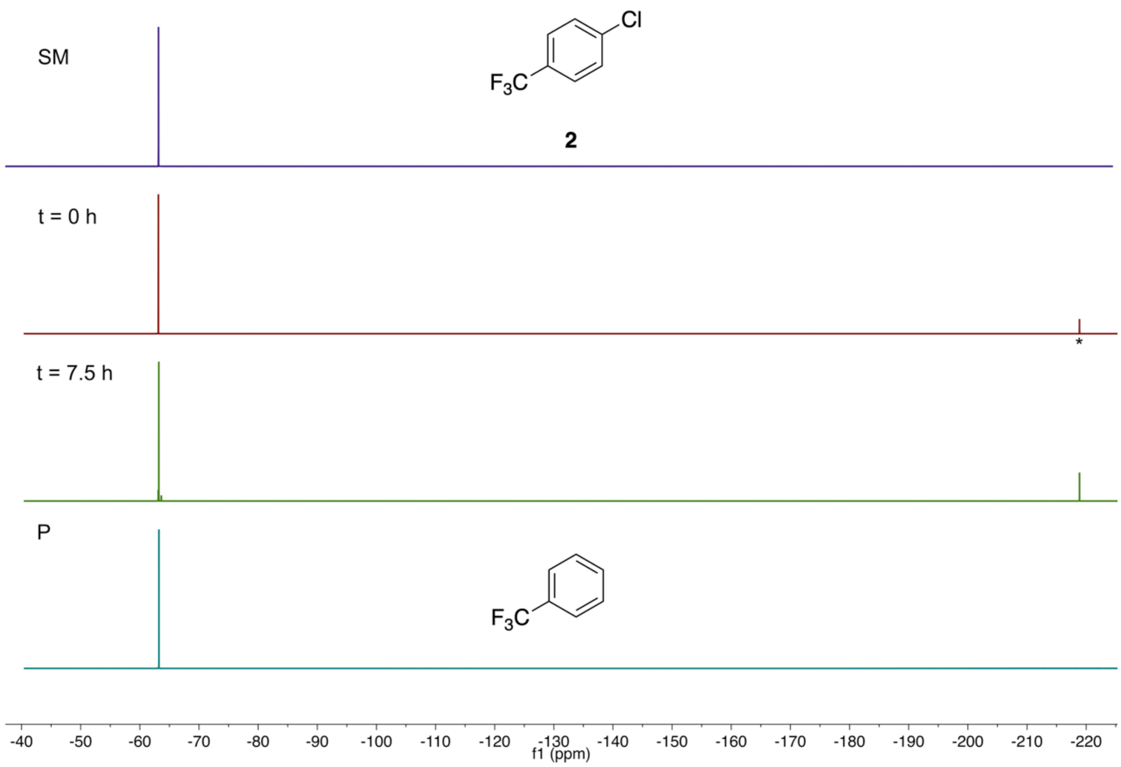

Figure S20 ^{19}F-NMR spectra monitoring dechlorination of substrate **2** over time. Reaction conditions: 100 mM **2**, 1.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

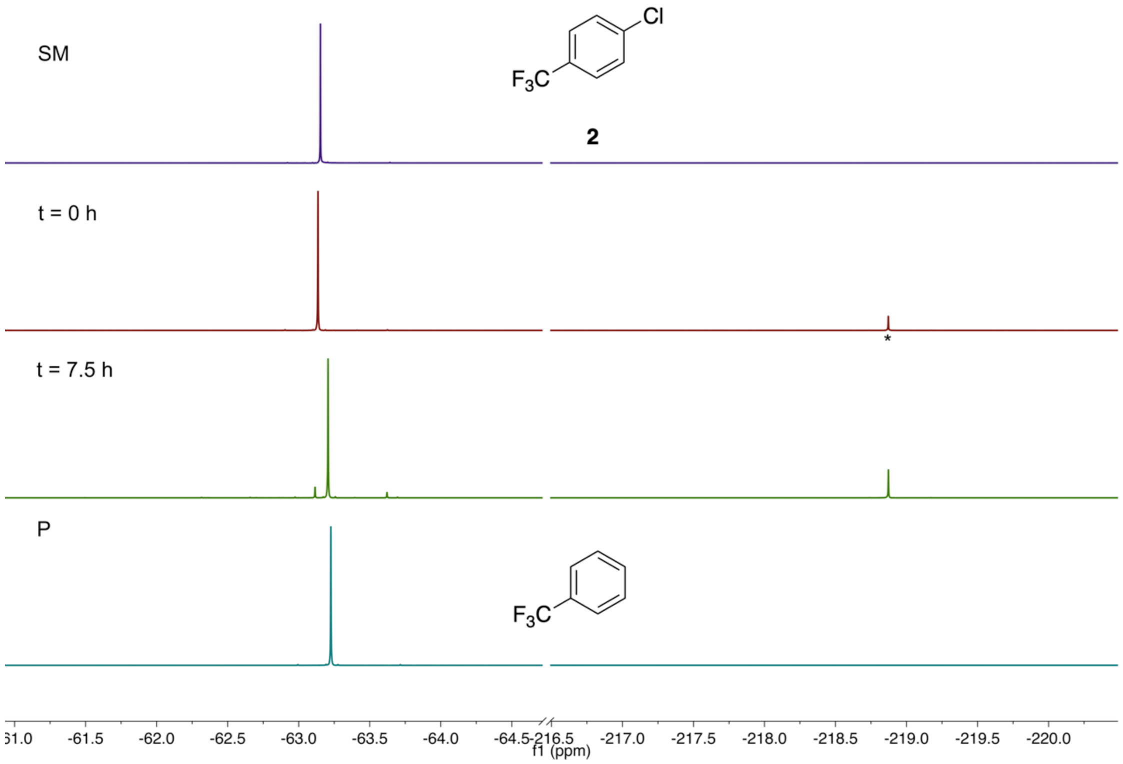

Figure S21 Expansions of the ^{19}F-NMR spectra from **Figure S20**.

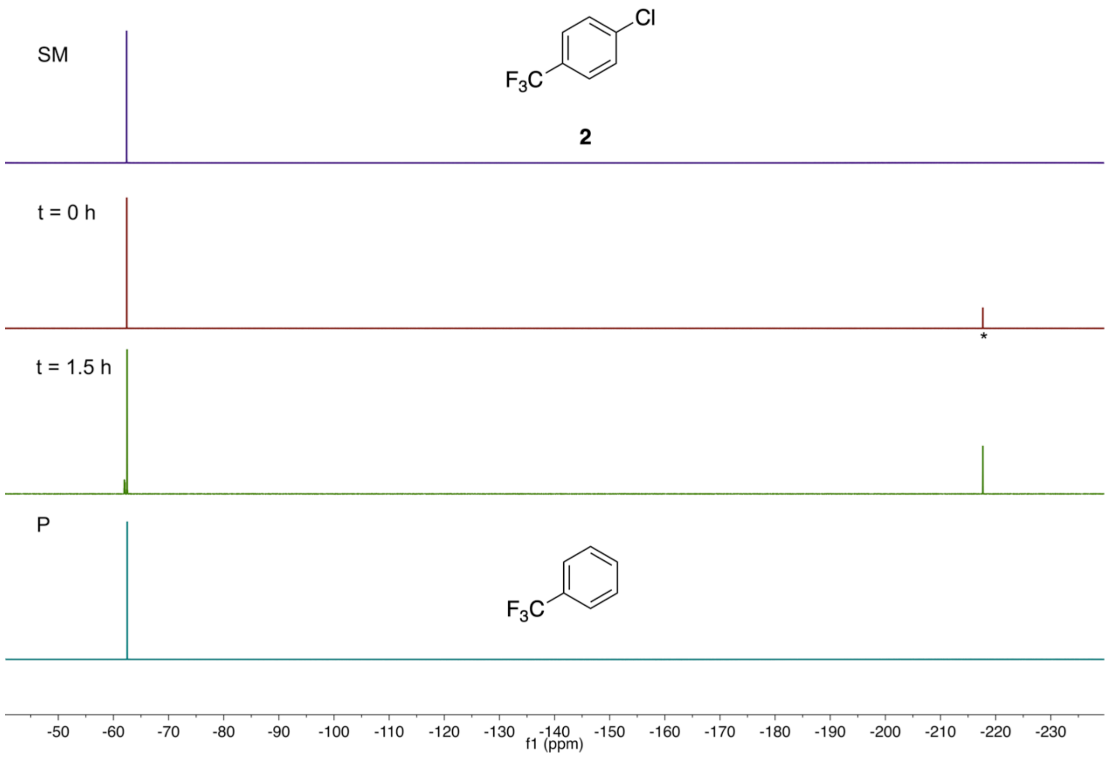

Figure S22 ^{19}F-NMR spectra monitoring dechlorination of substrate **2** over time. Reaction conditions: 50 mM **2**, 1.25 eq. TDAE, benzene-d_6, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

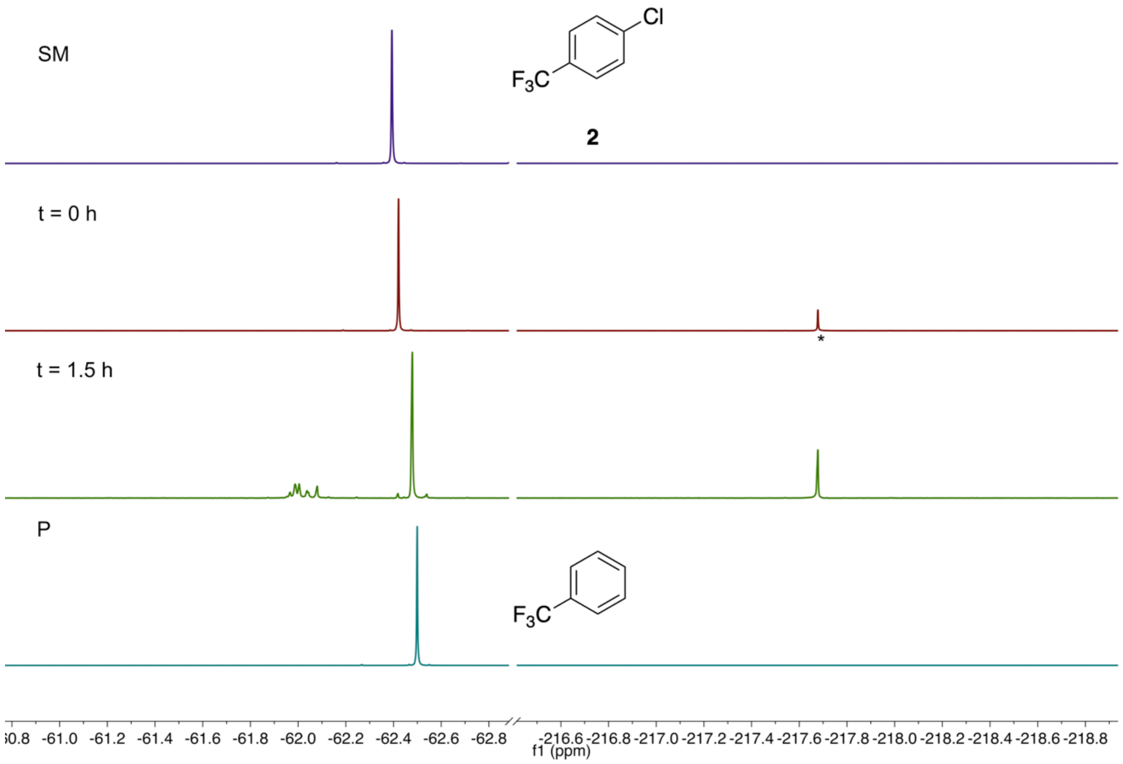

Figure S23 Expansions of the ^{19}F-NMR spectra from **Figure S22**.

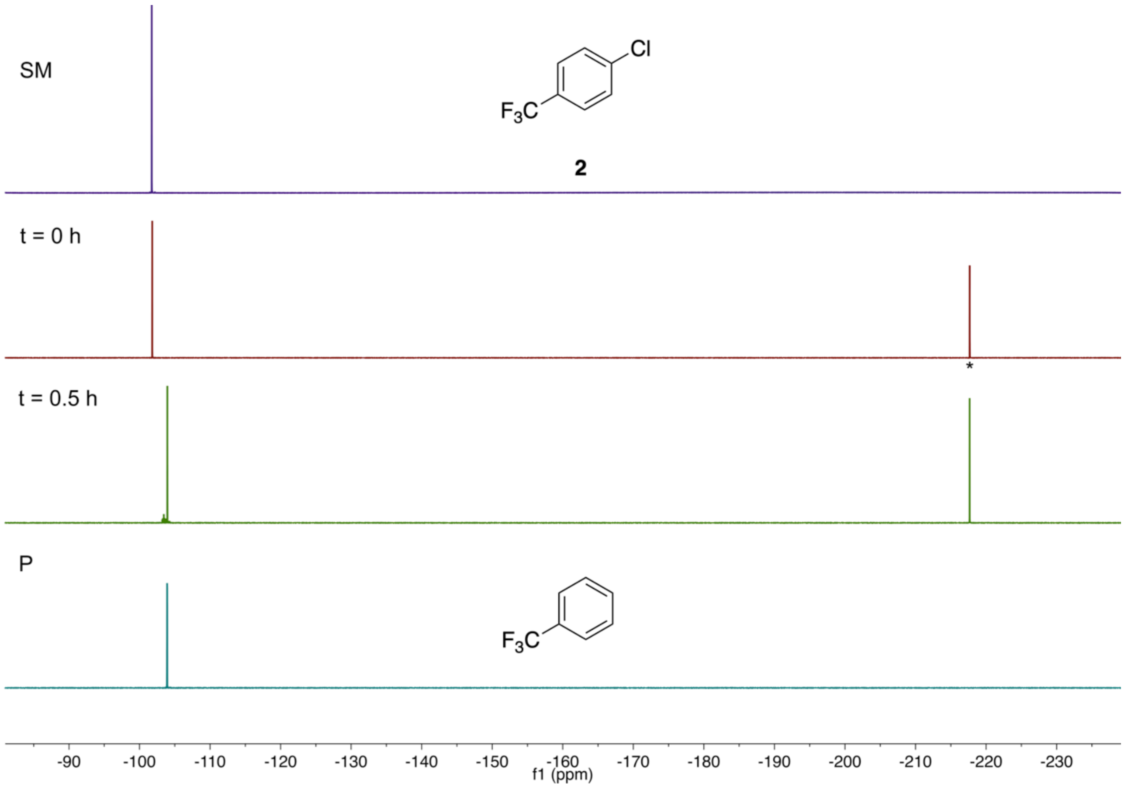

Figure S24 ^{19}F-NMR spectra monitoring dechlorination of substrate **2** over time. Reaction conditions: 50 mM **2**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

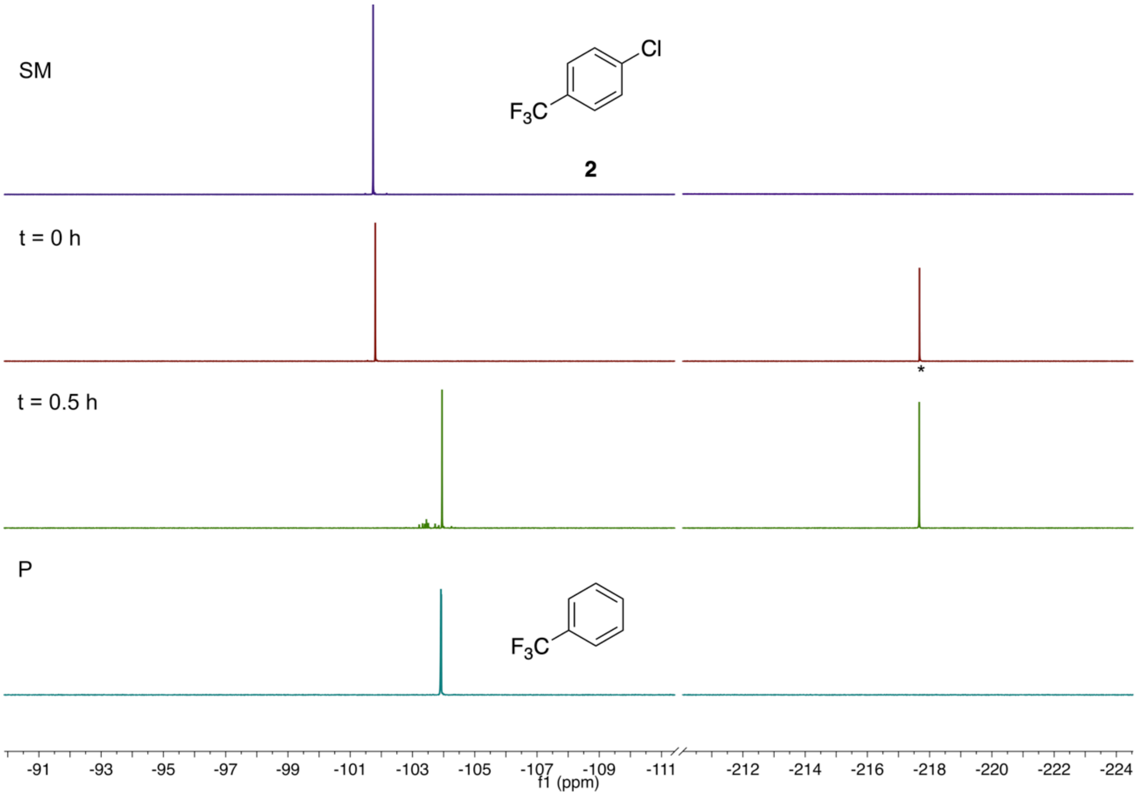

Figure S25 Expansions of the ^{19}F-NMR spectra from **Figure S24**.

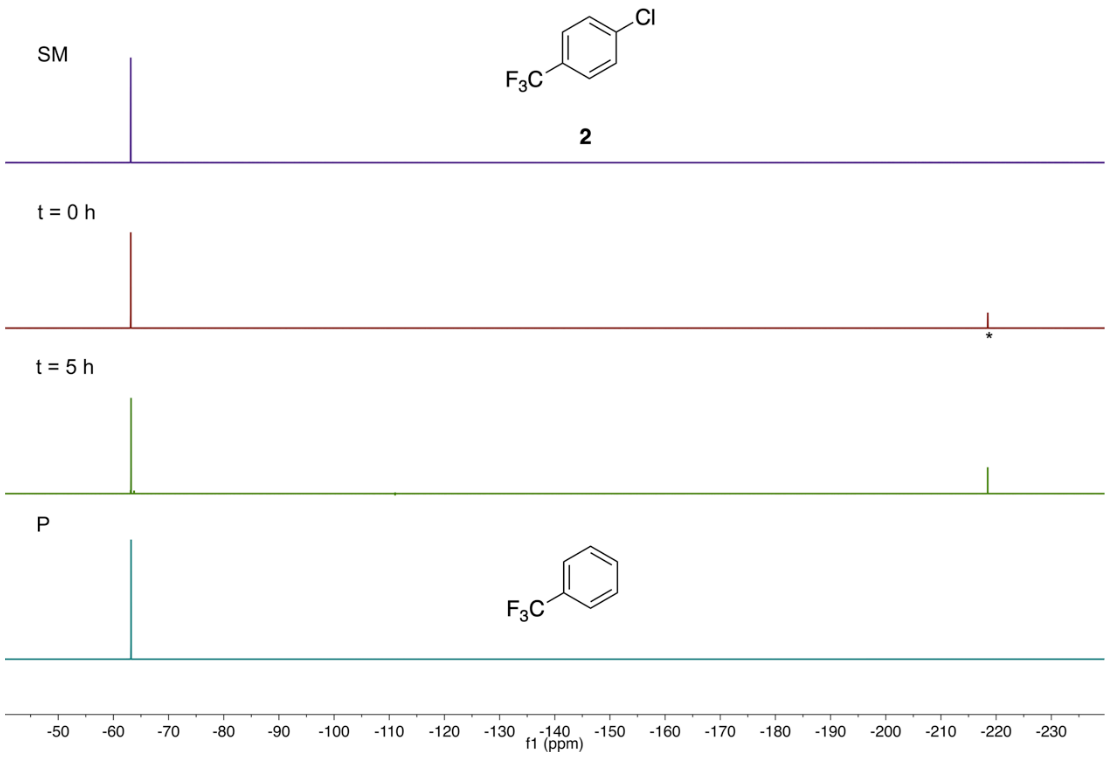

Figure S26 ^{19}F-NMR spectra monitoring dechlorination of substrate **2** over time. Reaction conditions: 100 mM **2**, 1.25 eq. TDAE, MeCN-d$_3$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

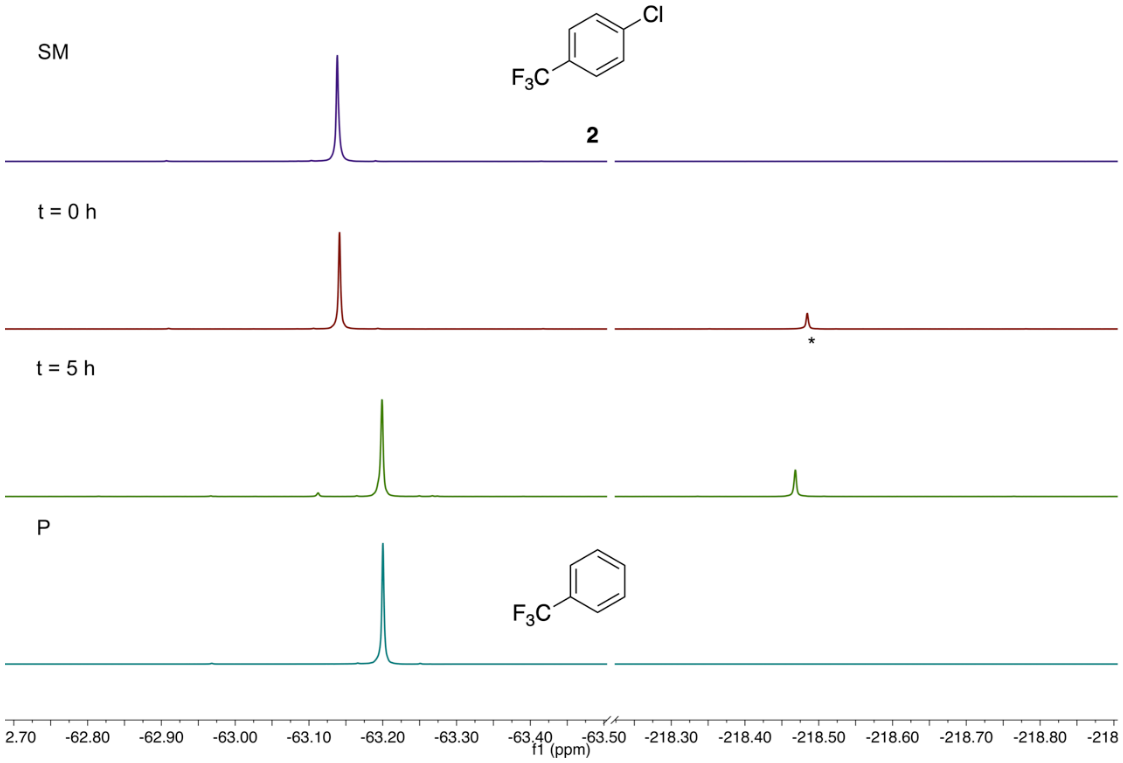

Figure S27 Expansions of the ^{19}F-NMR spectra from **Figure S26**.

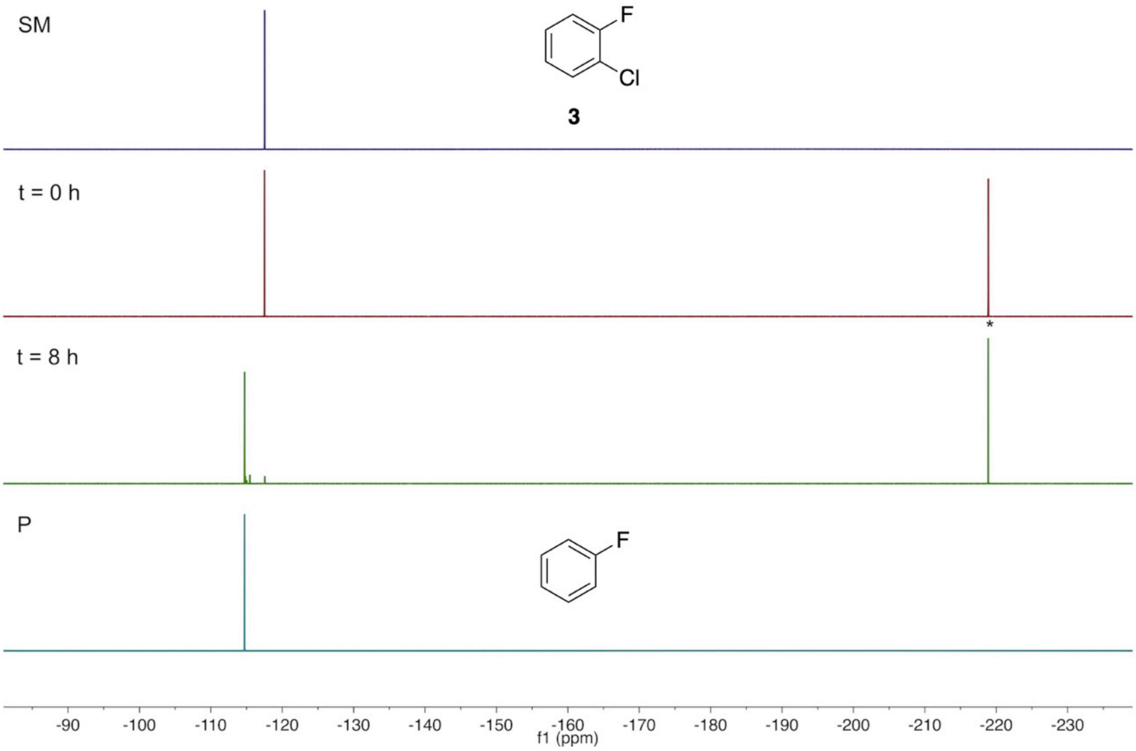

Figure S28 ^{19}F-NMR spectra monitoring dechlorination of substrate **3** over time. Reaction conditions: 100 mM **3**, 1.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

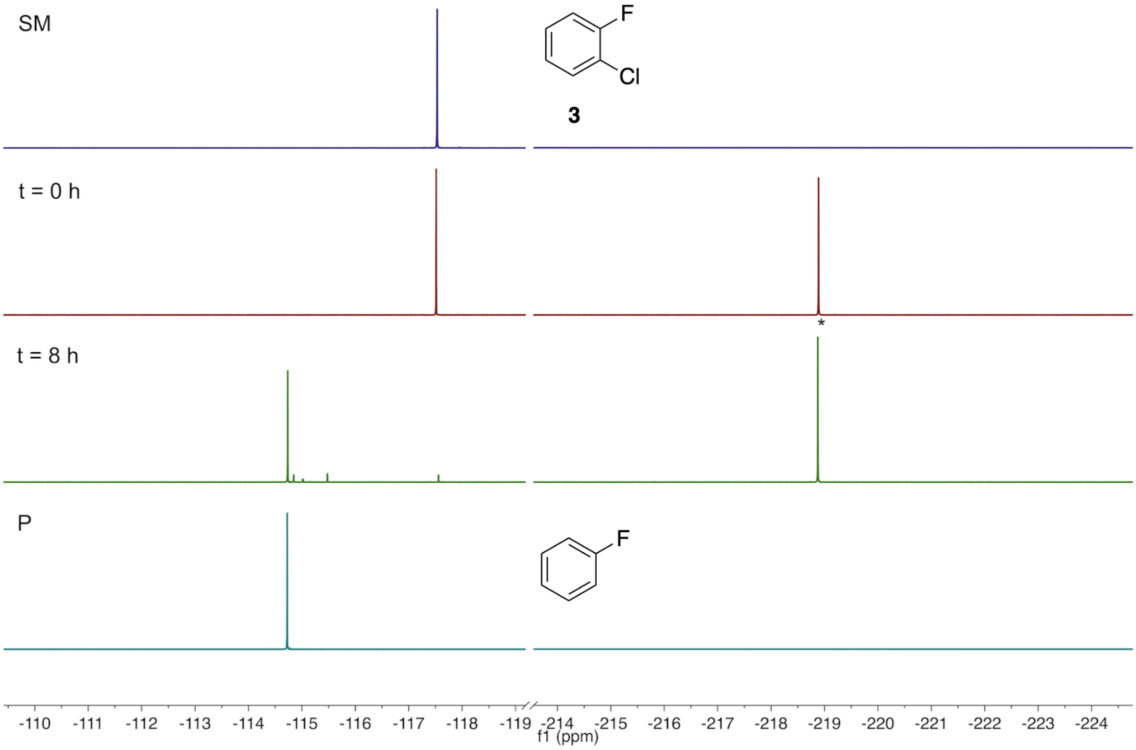

Figure S29 Expansions of the ^{19}F-NMR spectra from **Figure S28**.

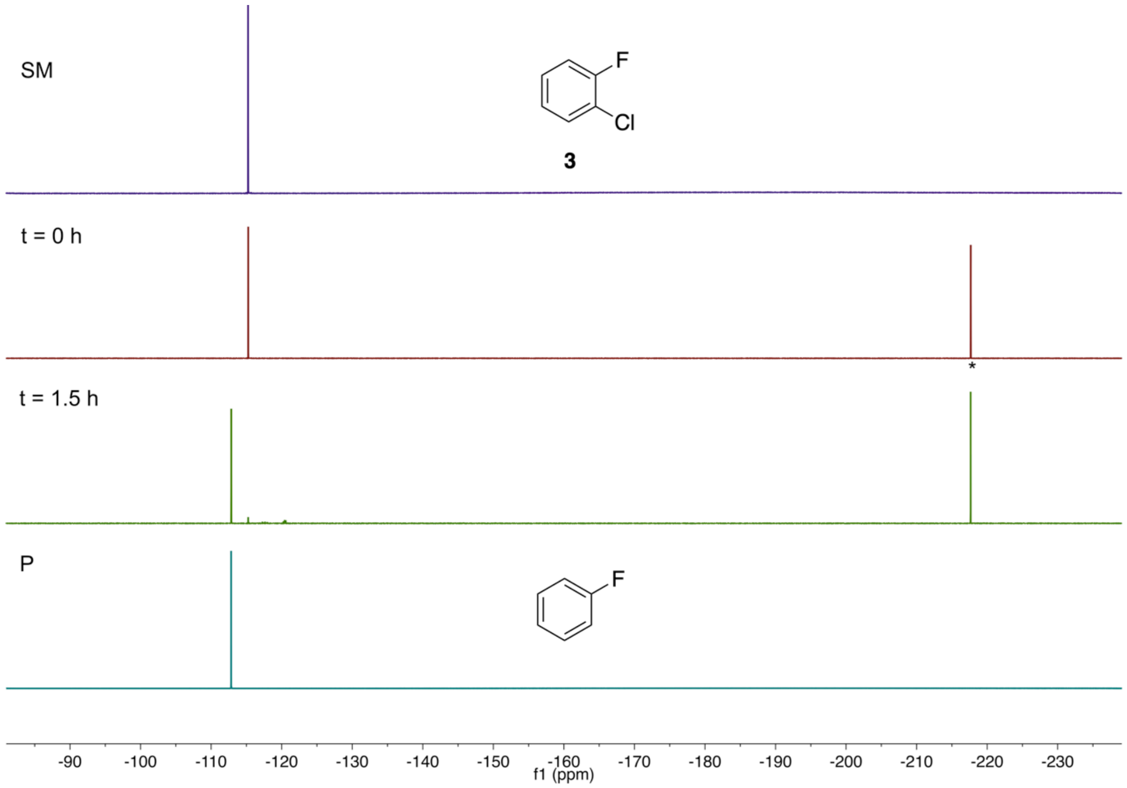

Figure S30 ^{19}F-NMR spectra monitoring dechlorination of substrate **3** over time. Reaction conditions: 50 mM **3**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

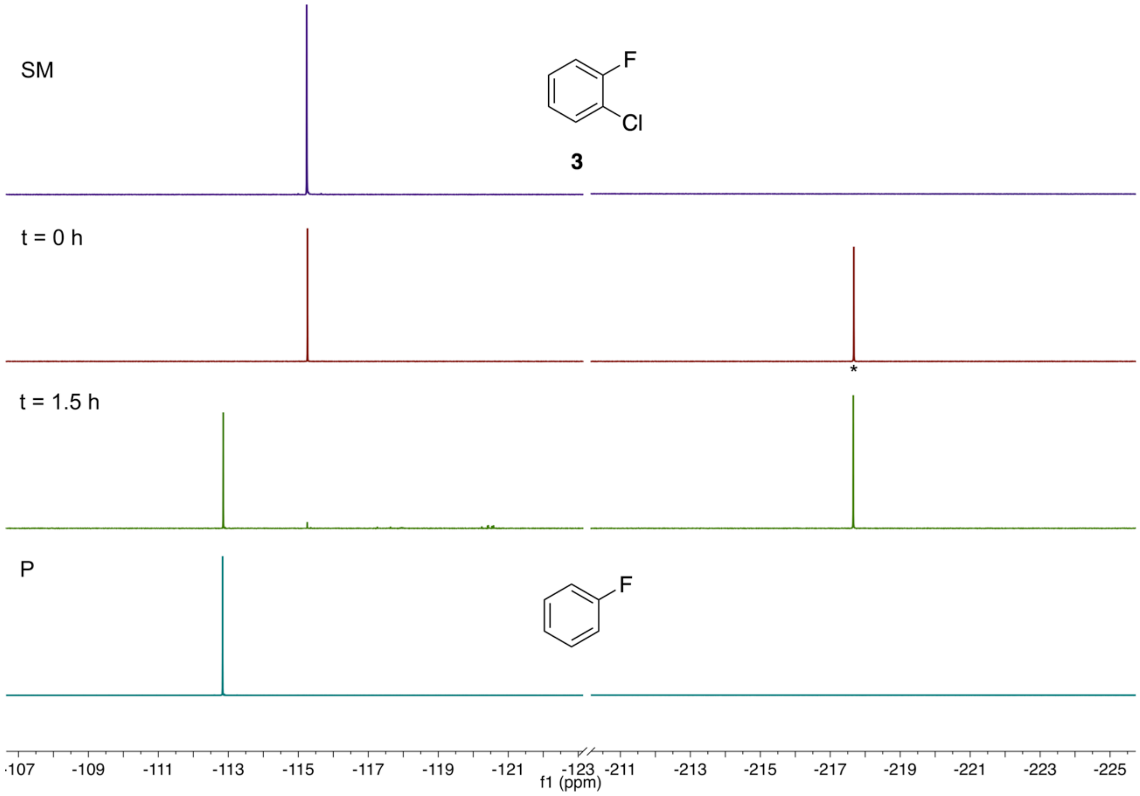

Figure S31 Expansions of the ^{19}F-NMR spectra from **Figure S30**.

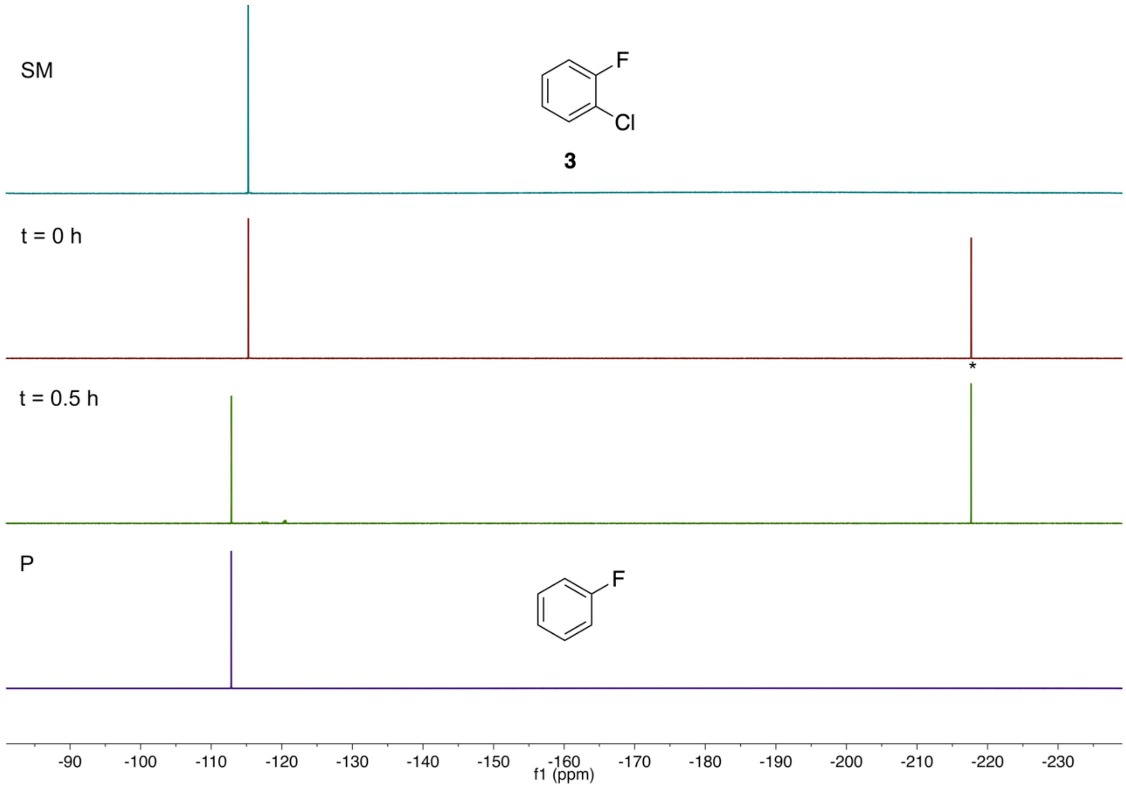

Figure S32 ^{19}F-NMR spectra monitoring dechlorination of substrate **3** over time. Reaction conditions: 50 mM **3**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

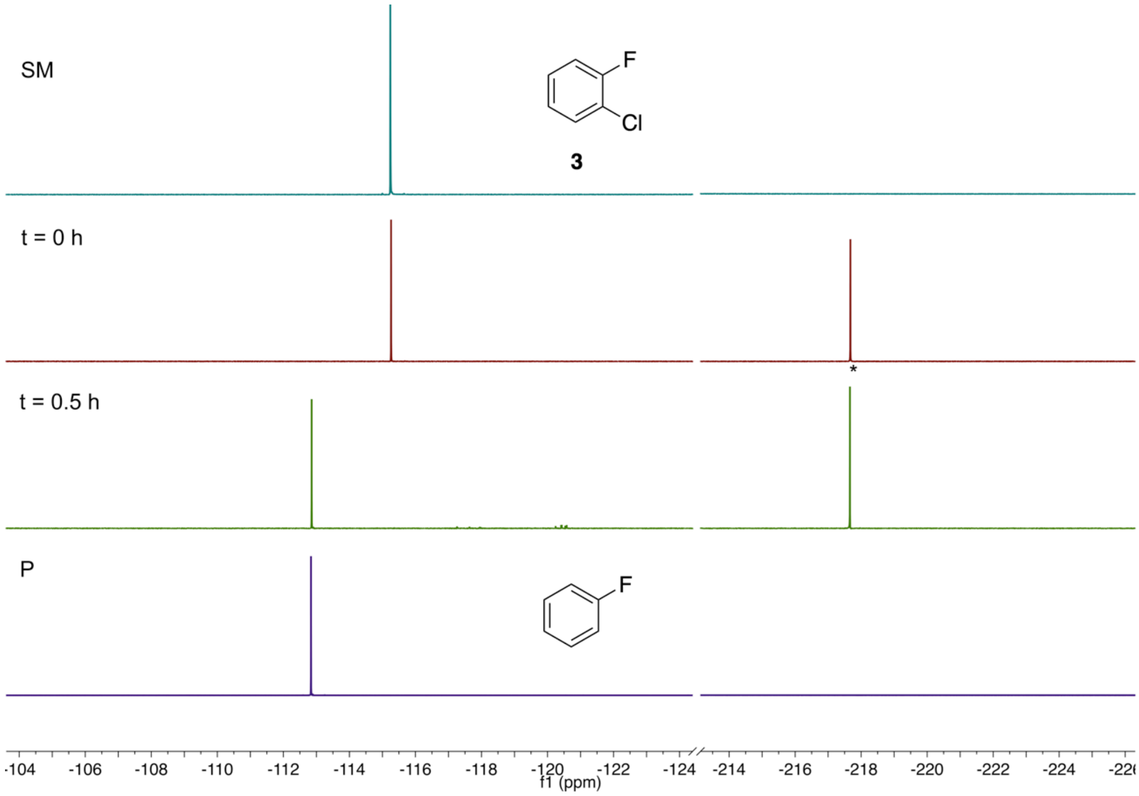

Figure S33 Expansions of the ^{19}F-NMR spectra from **Figure S32**.

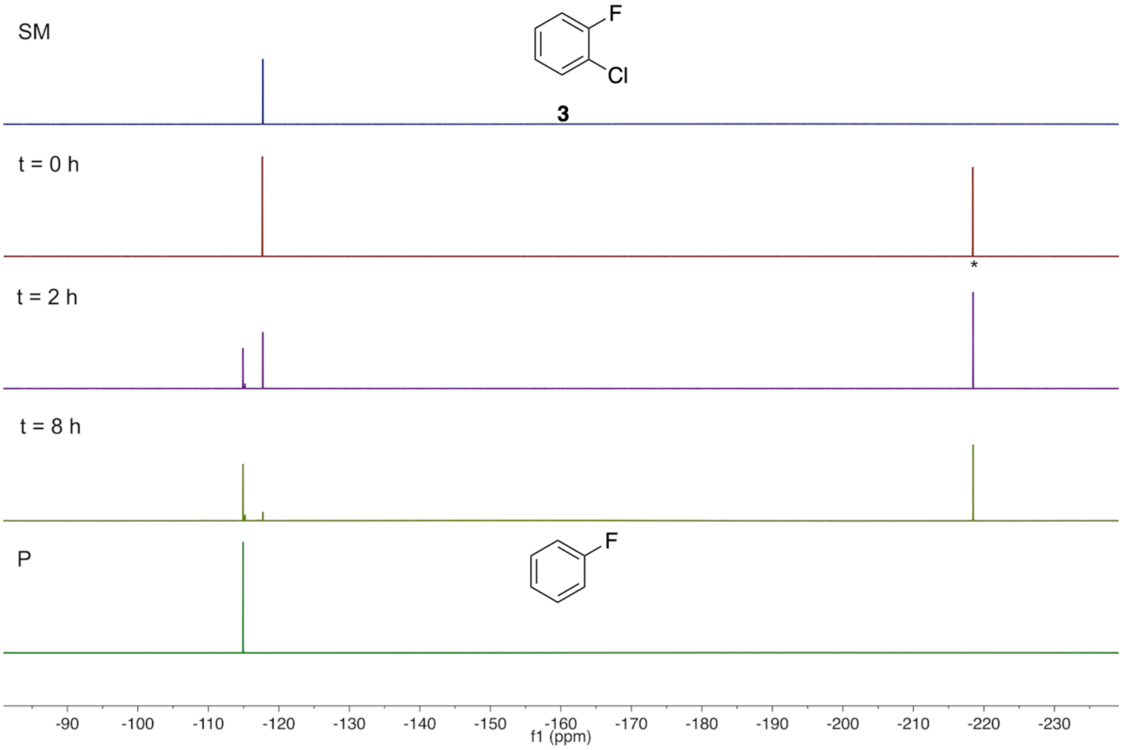

Figure S34 ^{19}F-NMR spectra monitoring dechlorination of substrate **3** over time. Reaction conditions: 100 mM **3**, 1.25 eq. TDAE, MeCN-d_3, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

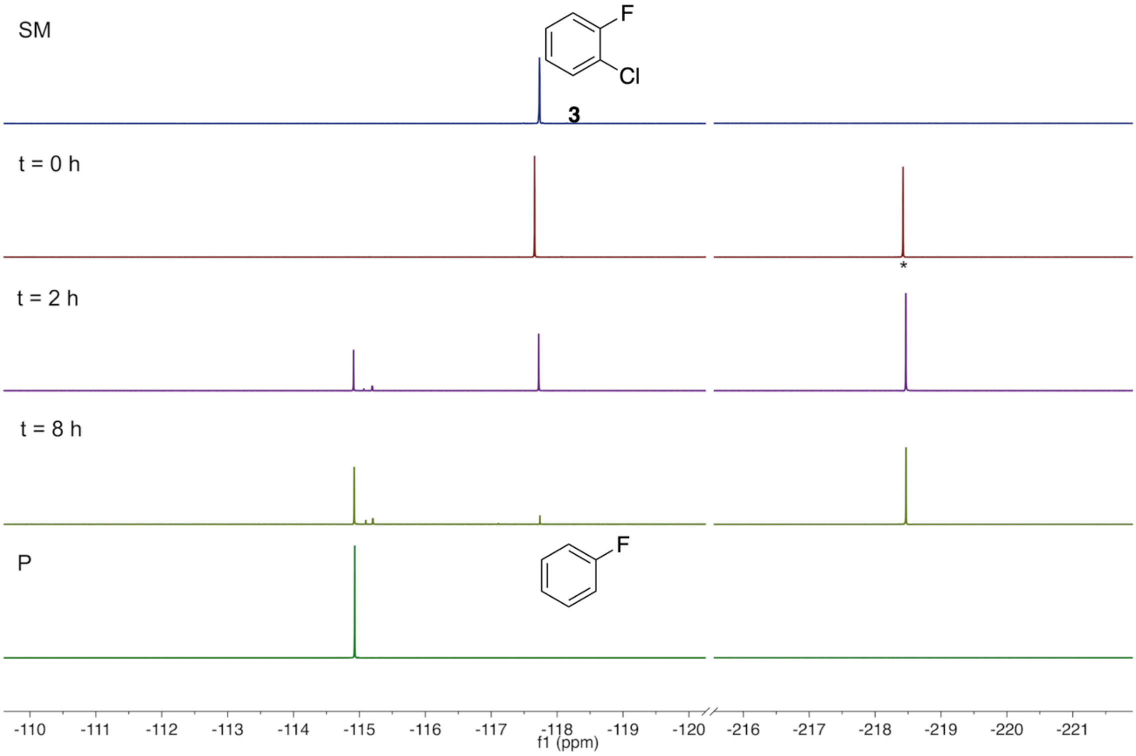

Figure S35 Expansions of the ^{19}F-NMR spectra from **Figure S34**.

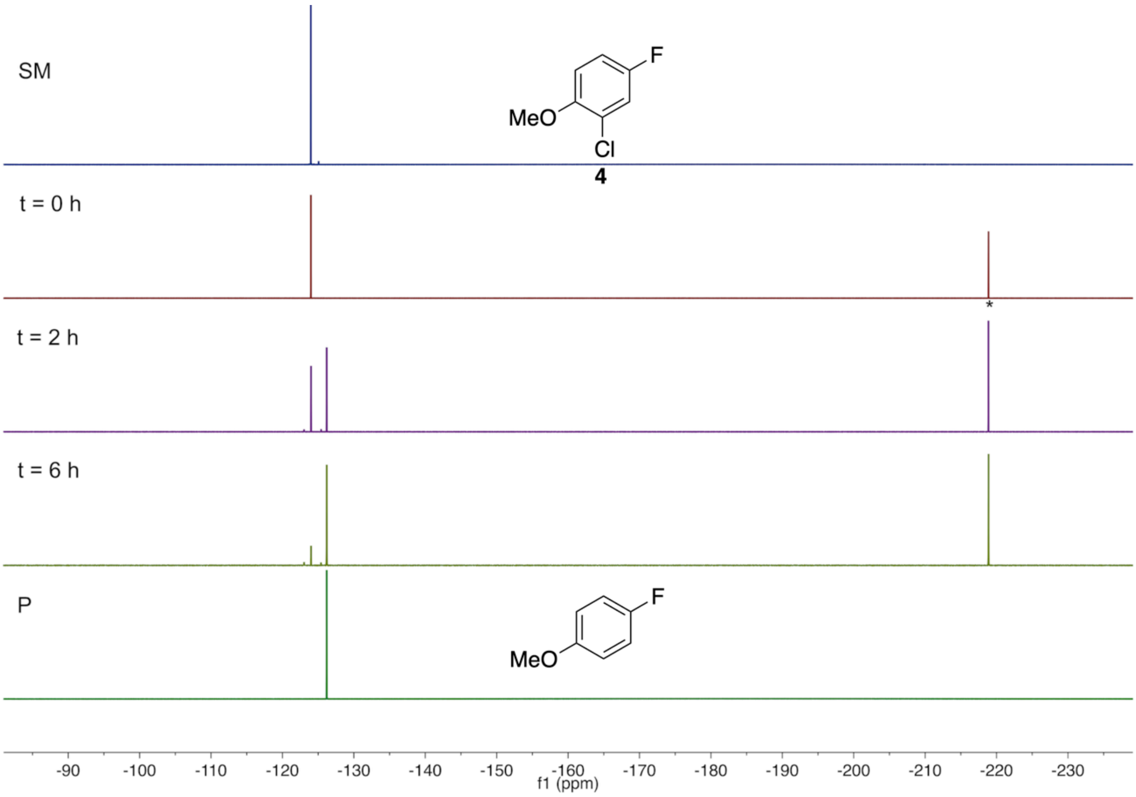

Figure S36 ^{19}F-NMR spectra monitoring dechlorination of substrate **4** over time. Reaction conditions: 100 mM **4**, 1.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

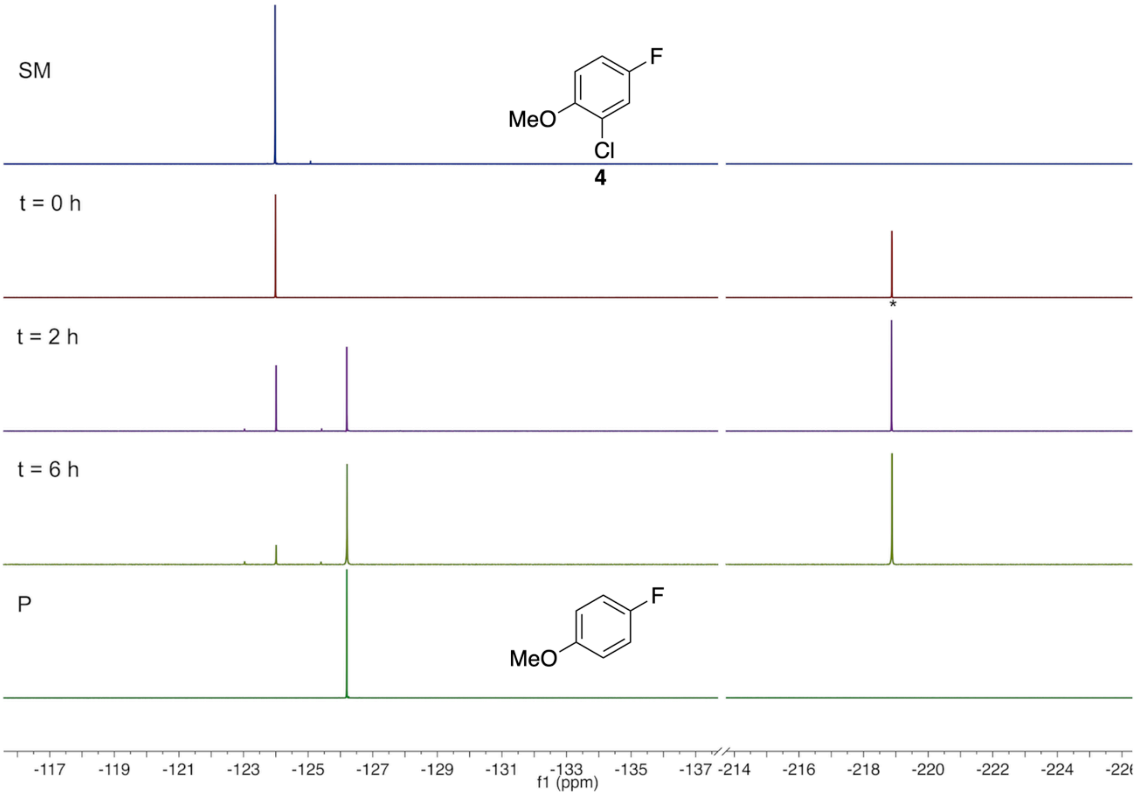

Figure S37 Expansions of the ^{19}F-NMR spectra from **Figure S36**.

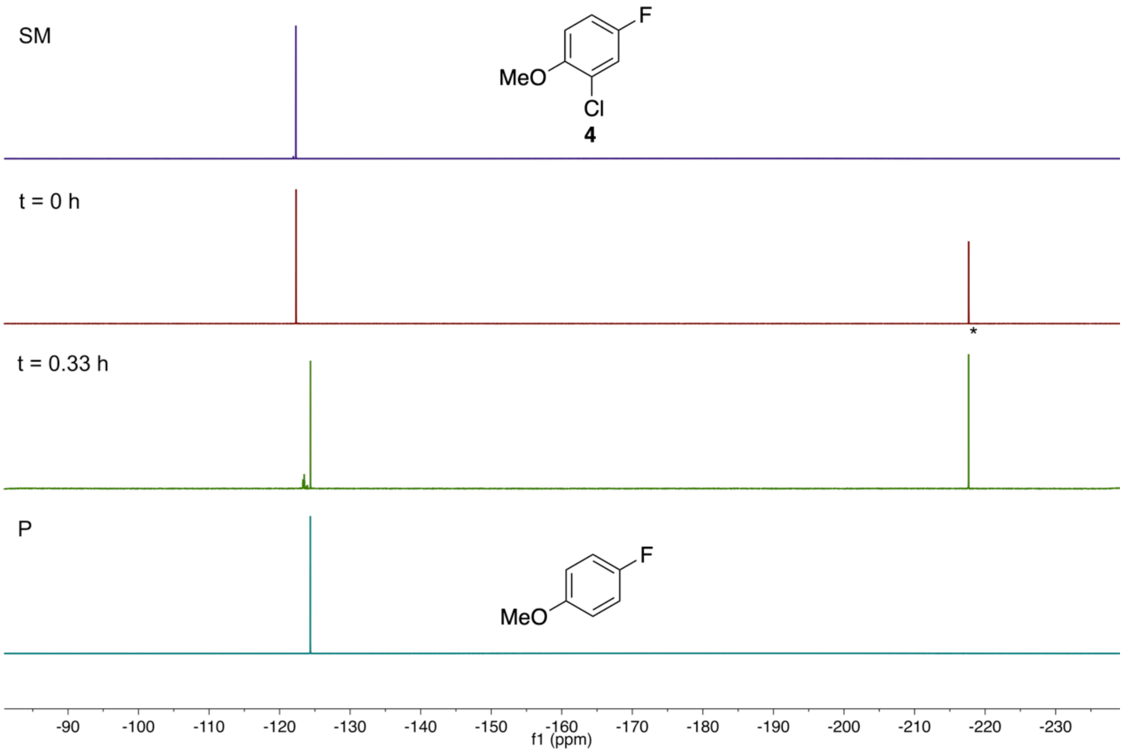

Figure S38 ^{19}F-NMR spectra monitoring dechlorination of substrate **4** over time. Reaction conditions: 50 mM **4**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

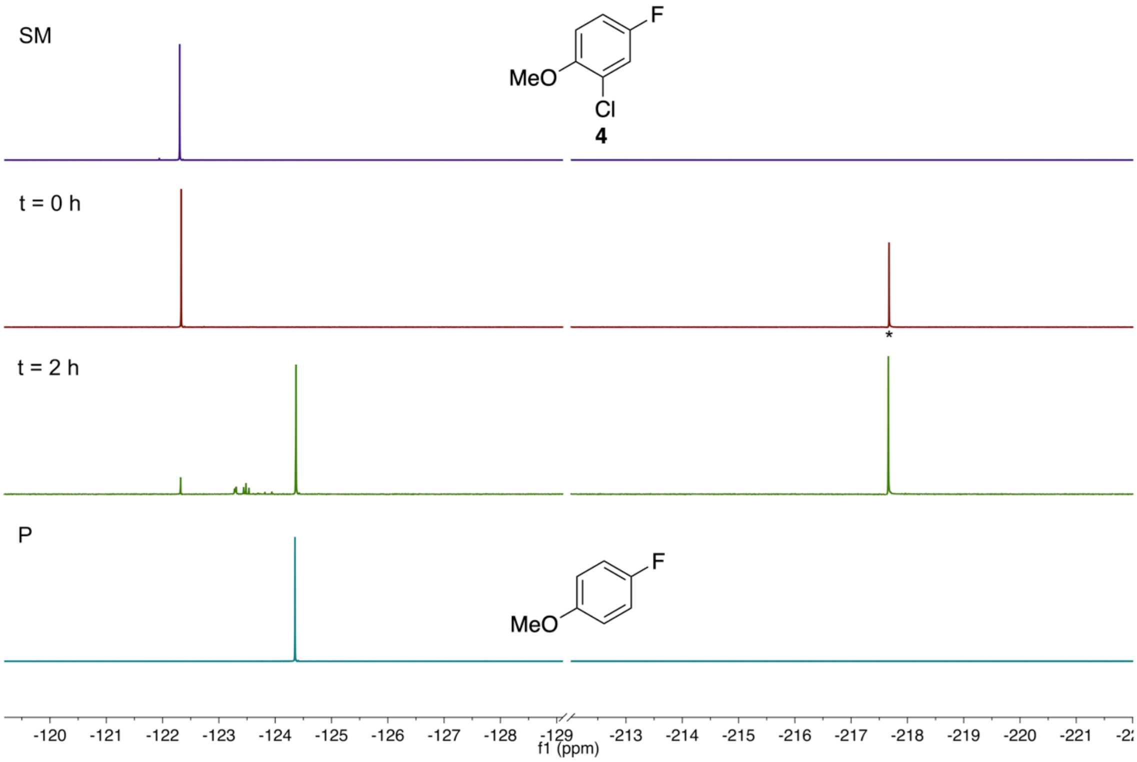

Figure S39 Expansions of the ^{19}F-NMR spectra from **Figure S38**.

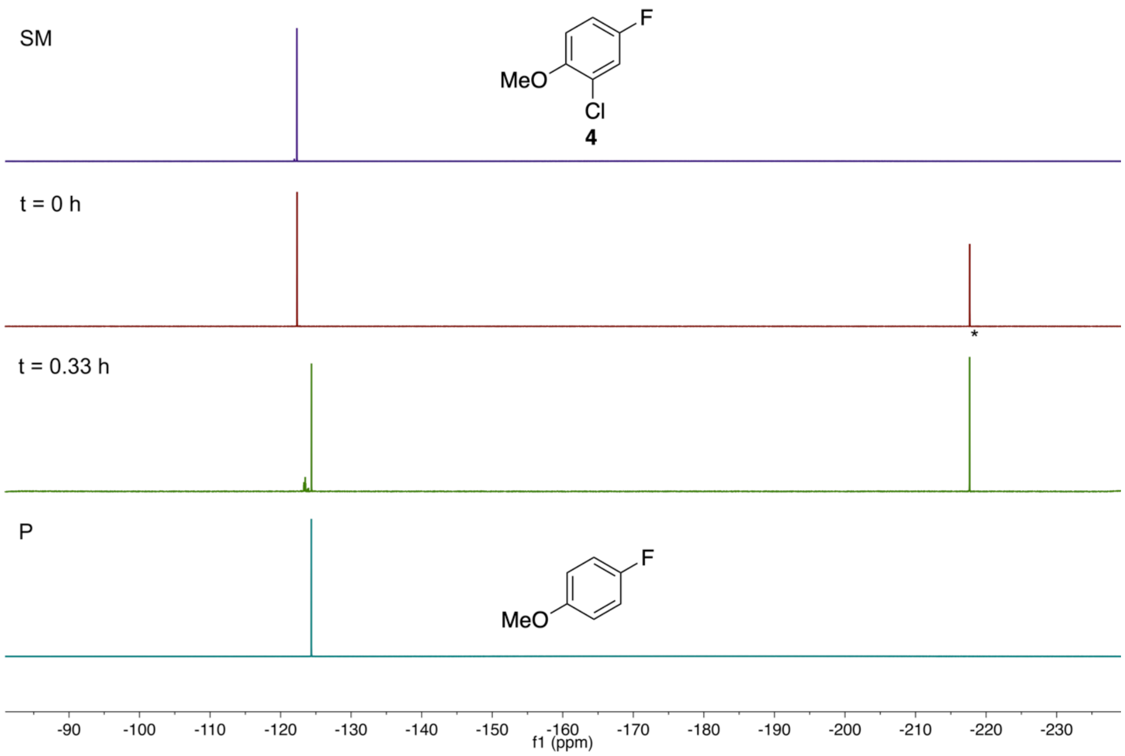

Figure S40 ^{19}F-NMR spectra monitoring dechlorination of substrate **4** over time. Reaction conditions: 50 mM **4**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

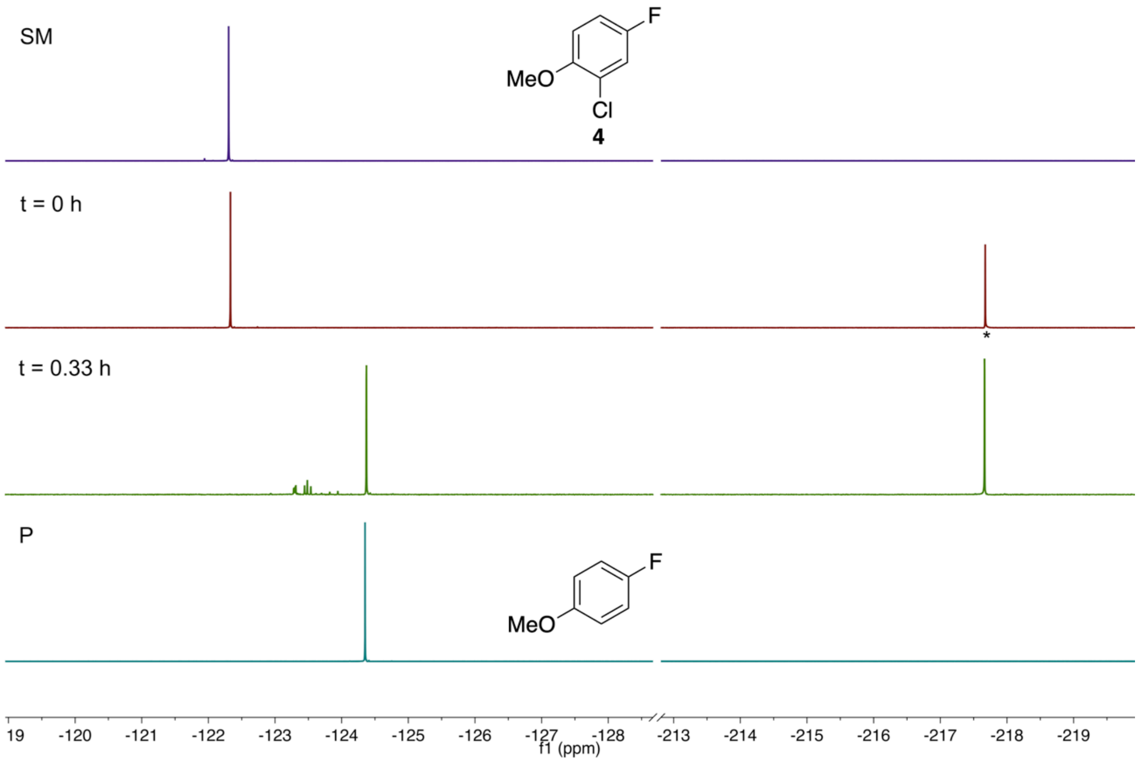

Figure S41 Expansions of the ^{19}F-NMR spectra from **Figure S40**.

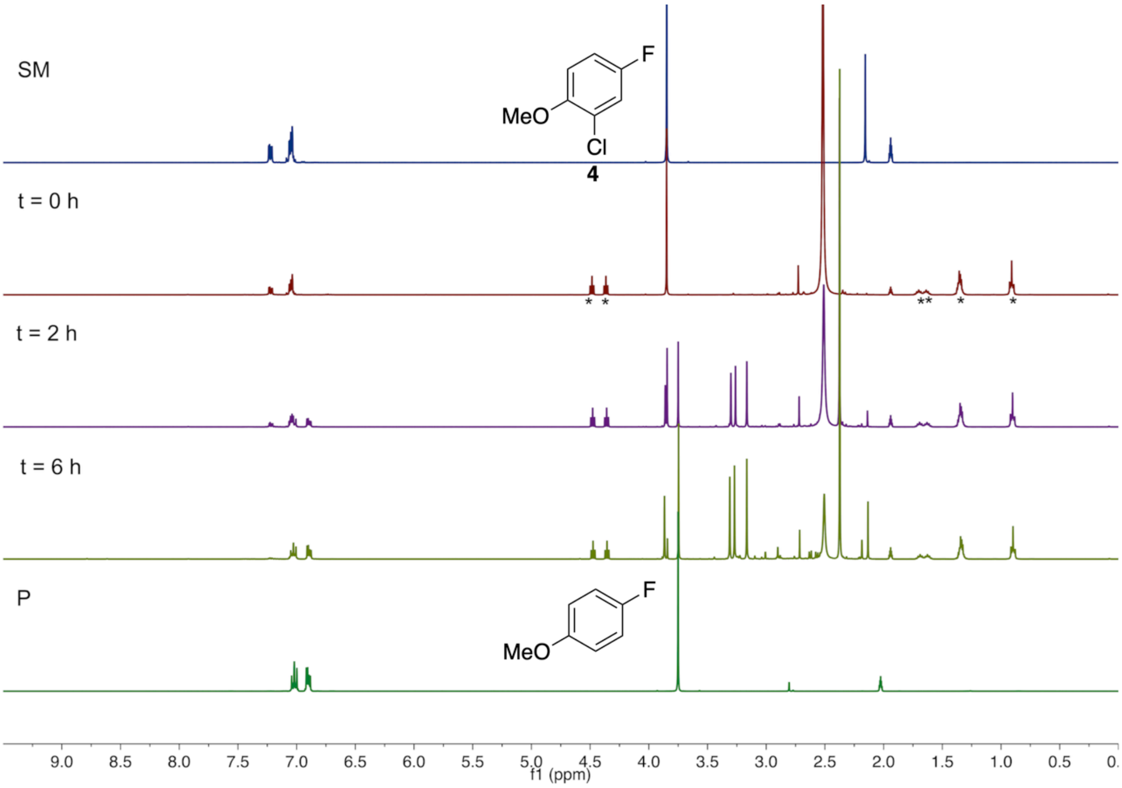

Figure S42 ^{1}H-NMR spectra monitoring dechlorination of substrate **4** over time. Reaction conditions: 100 mM **4**, 1.25 eq. TDAE, MeCN-d$_3$, λ_{ex} = 440 nm. Peaks of internal standard 1-fluoropentane are marked with asterisks. SM = starting material; P = product.

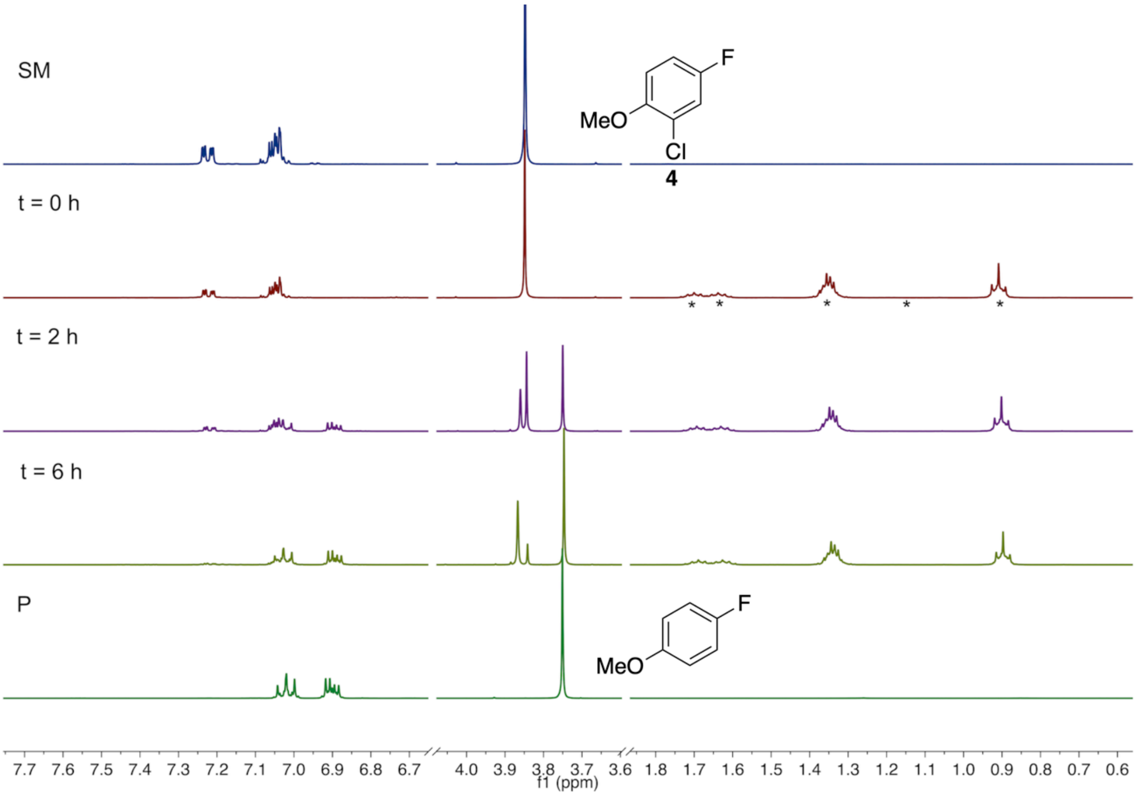

Figure S43 Expansions of the ^{1}H-NMR spectra from **Figure S42**.

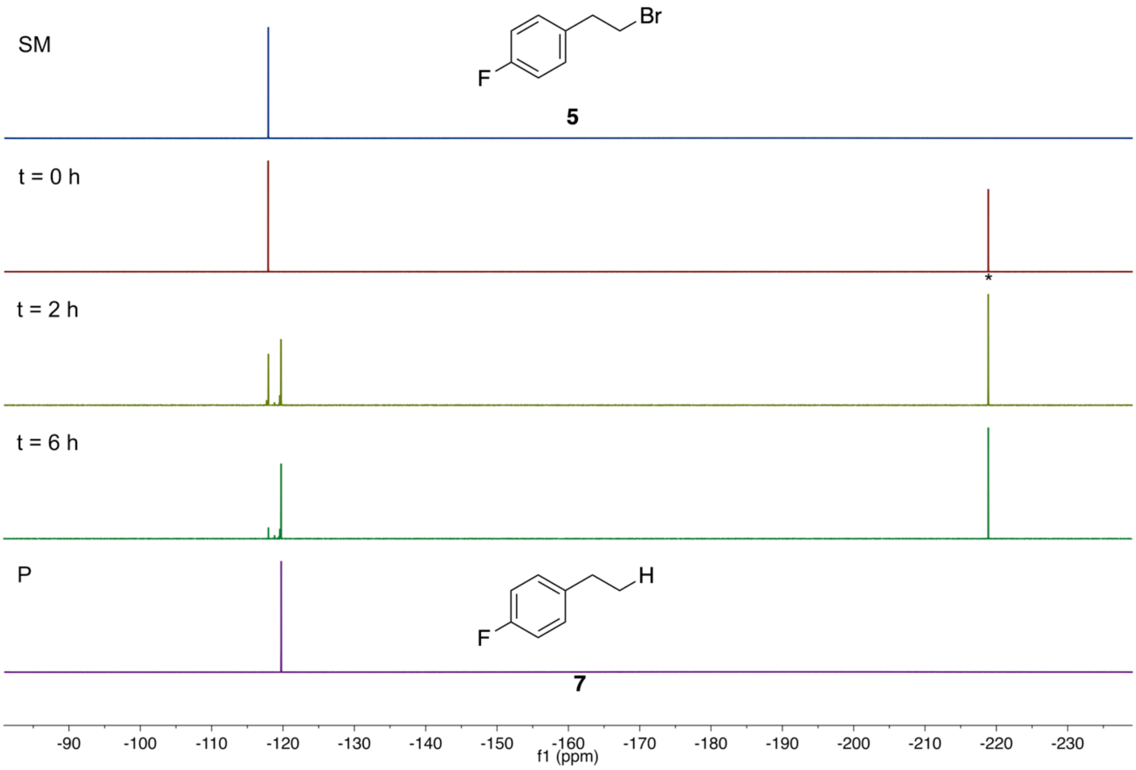

Figure S44 ^{19}F-NMR spectra monitoring debromination of substrate **5** over time. Reaction conditions: 100 mM **5**, 1.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

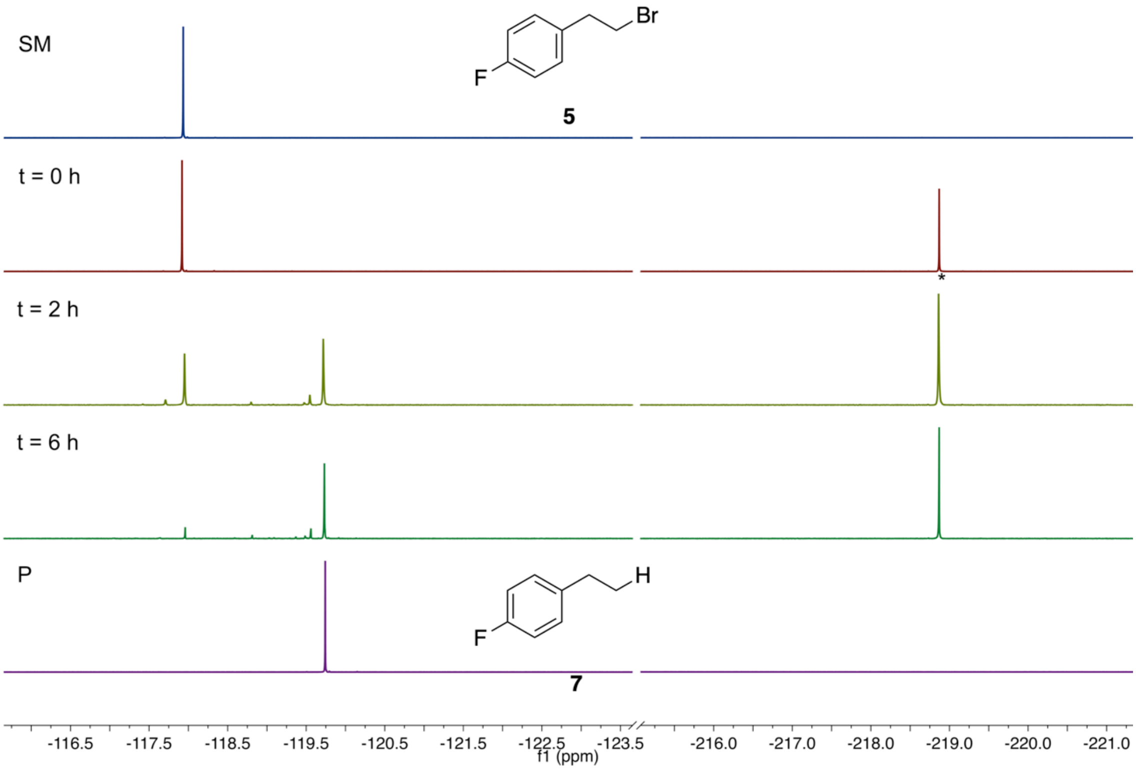

Figure S45 Expansions of the ^{19}F-NMR spectra from **Figure S44**.

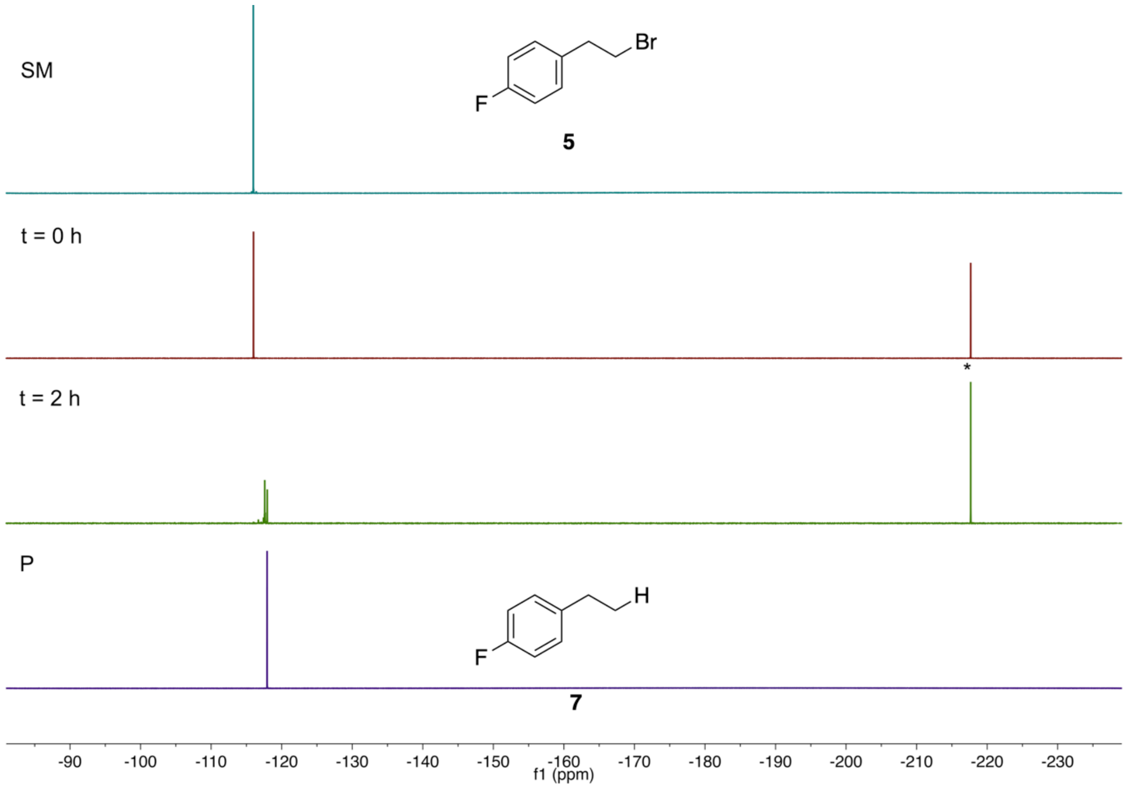

Figure S46 ^{19}F-NMR spectra monitoring debromination of substrate **5** over time. Reaction conditions: 50 mM **5**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

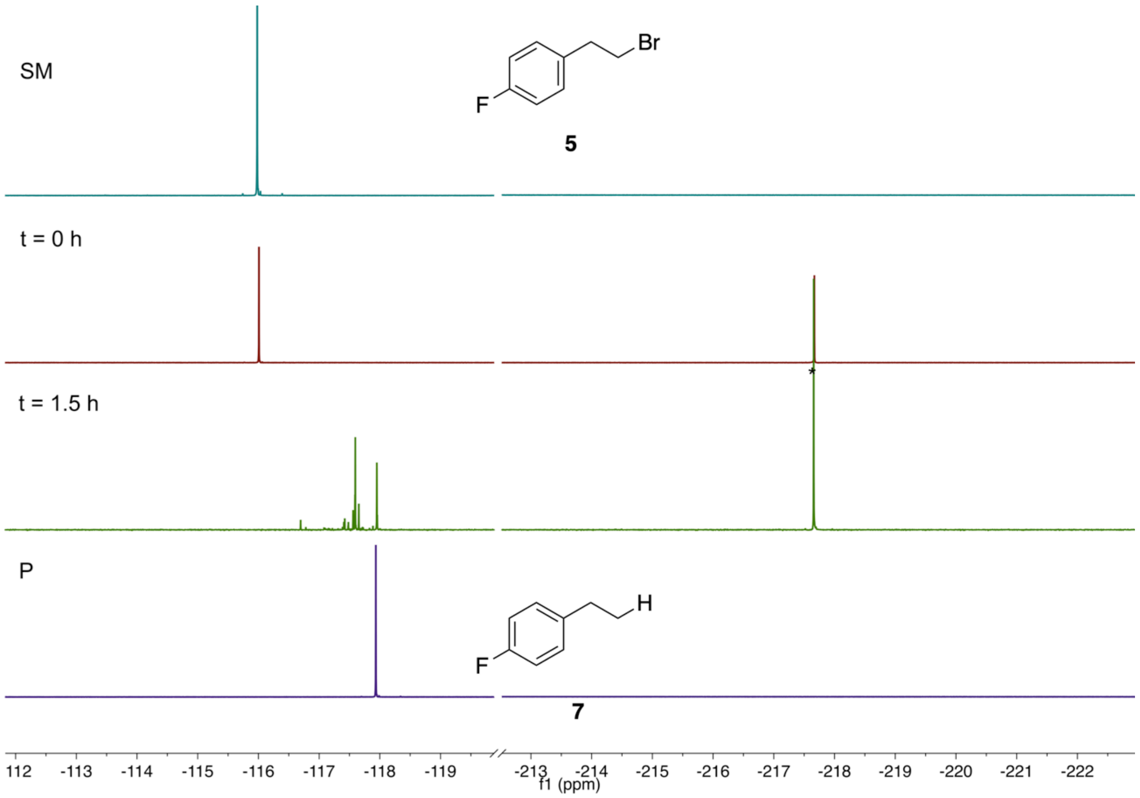

Figure S47 Expansions of the ^{19}F-NMR spectra from **Figure S46**.

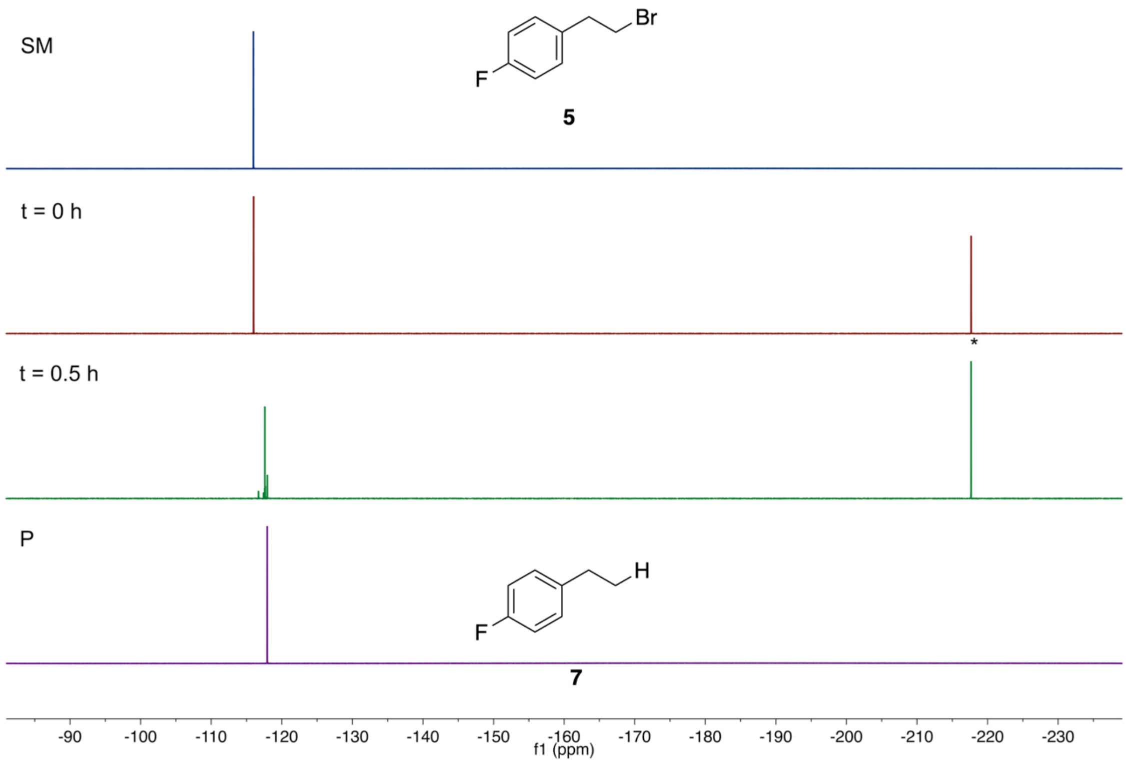

Figure S48 ^{19}F-NMR spectra monitoring debromination of substrate **5** over time. Reaction conditions: 50 mM **5**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

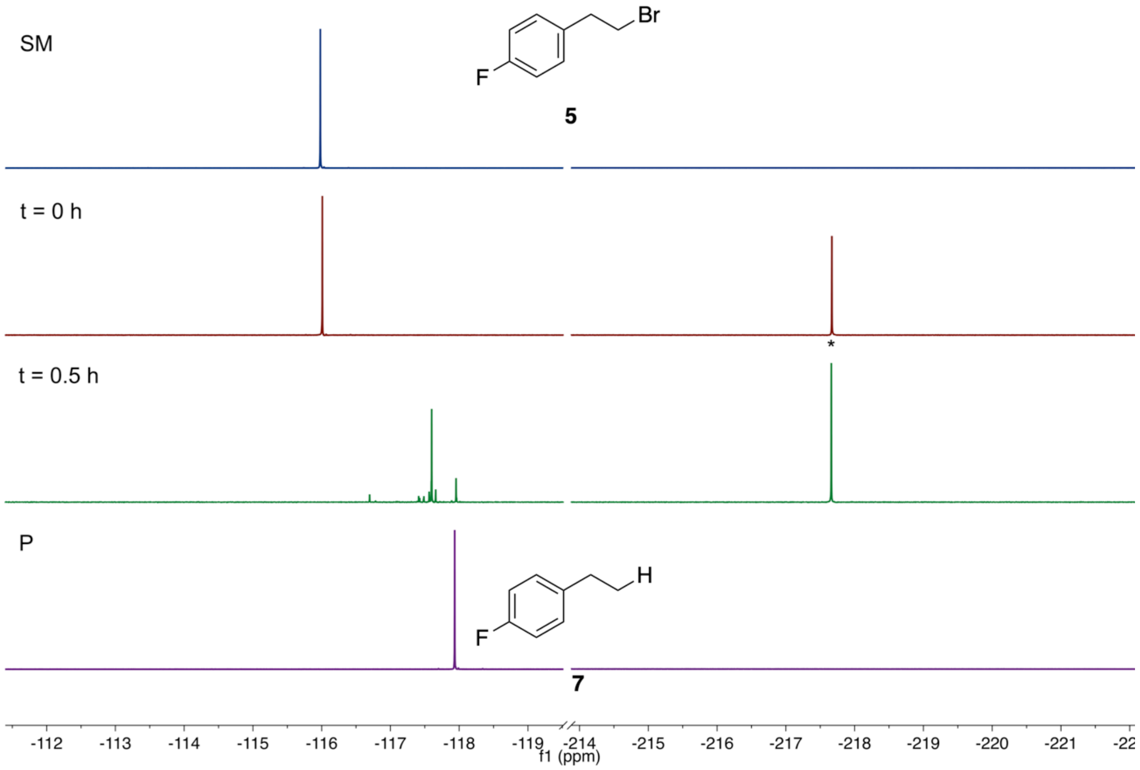

Figure S49 Expansions of the ^{19}F-NMR spectra from **Figure S48**.

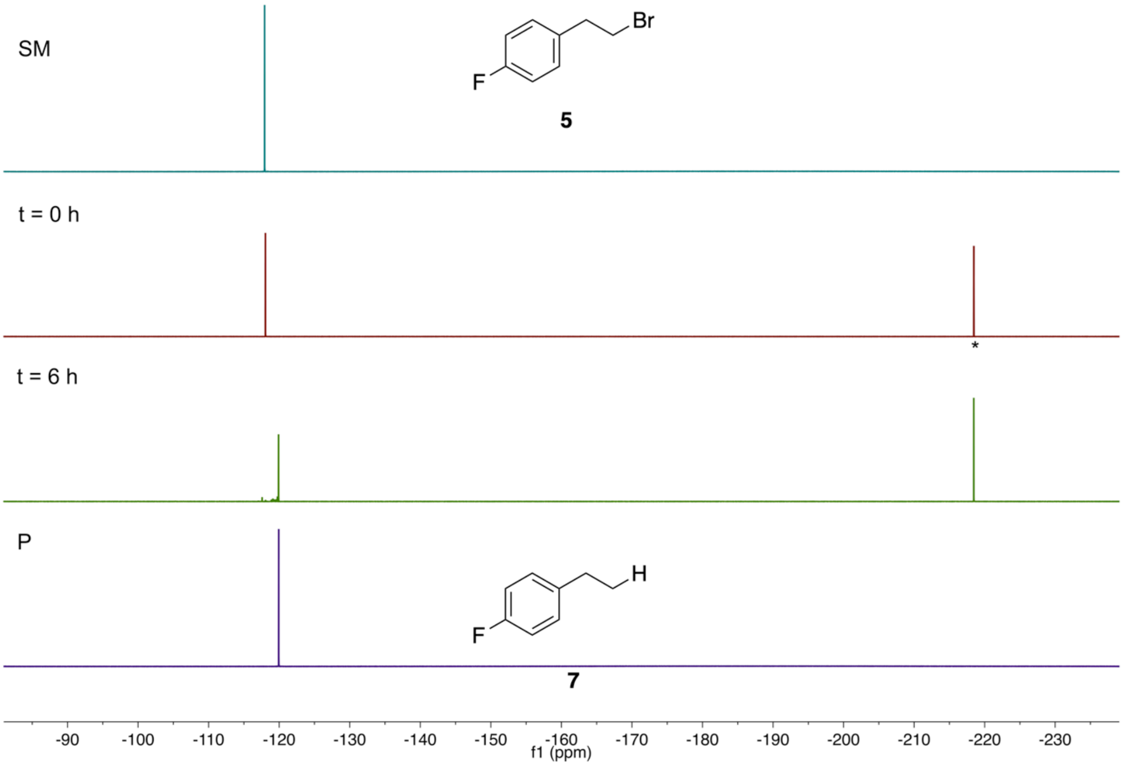

Figure S50 ^{19}F-NMR spectra monitoring debromination of substrate **5** over time. Reaction conditions: 100 mM **5**, 1.25 eq. TDAE, MeCN-d$_3$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

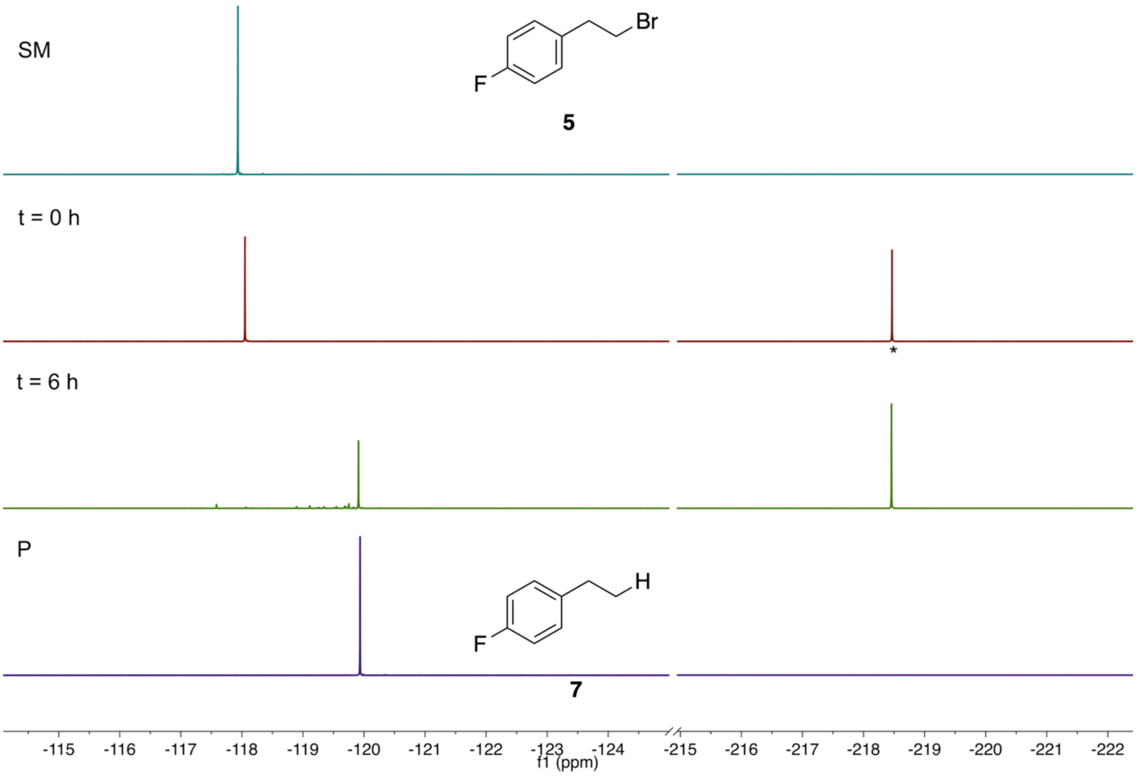

Figure S51 Expansions of the ^{19}F-NMR spectra from **Figure S50**.

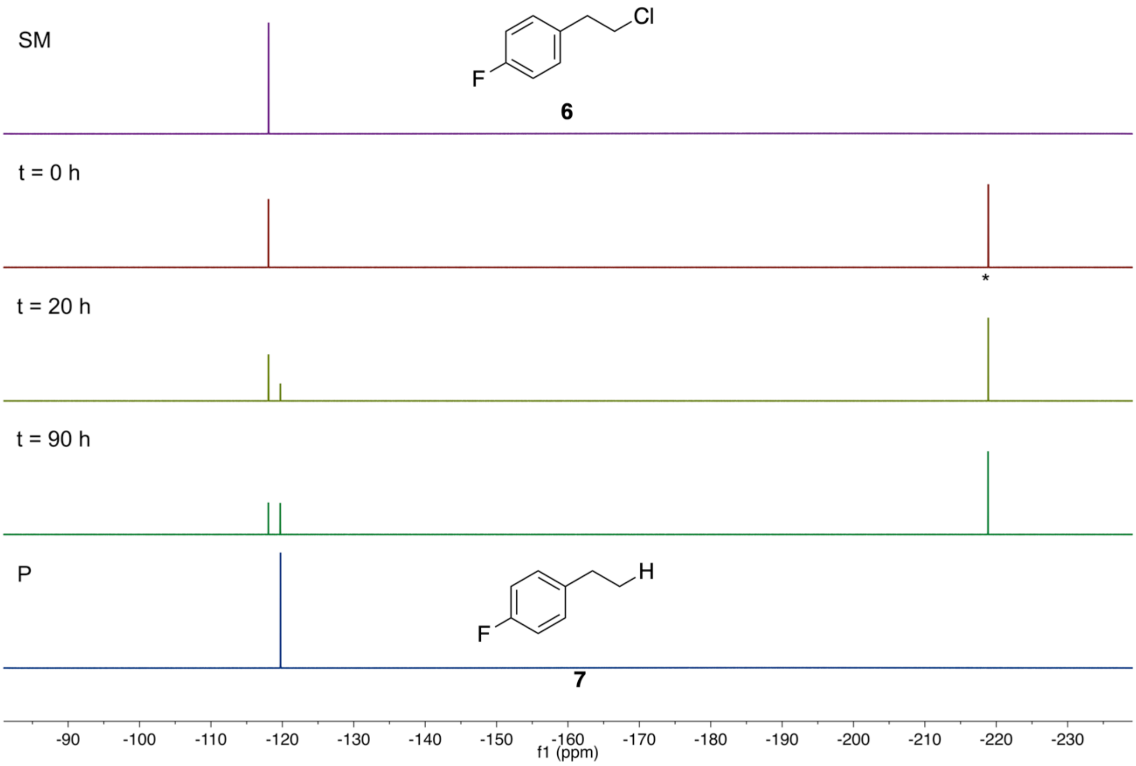

Figure S52 ^{19}F-NMR spectra monitoring dechlorination of substrate **6** over time. Reaction conditions: 100 mM **6**, 1.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

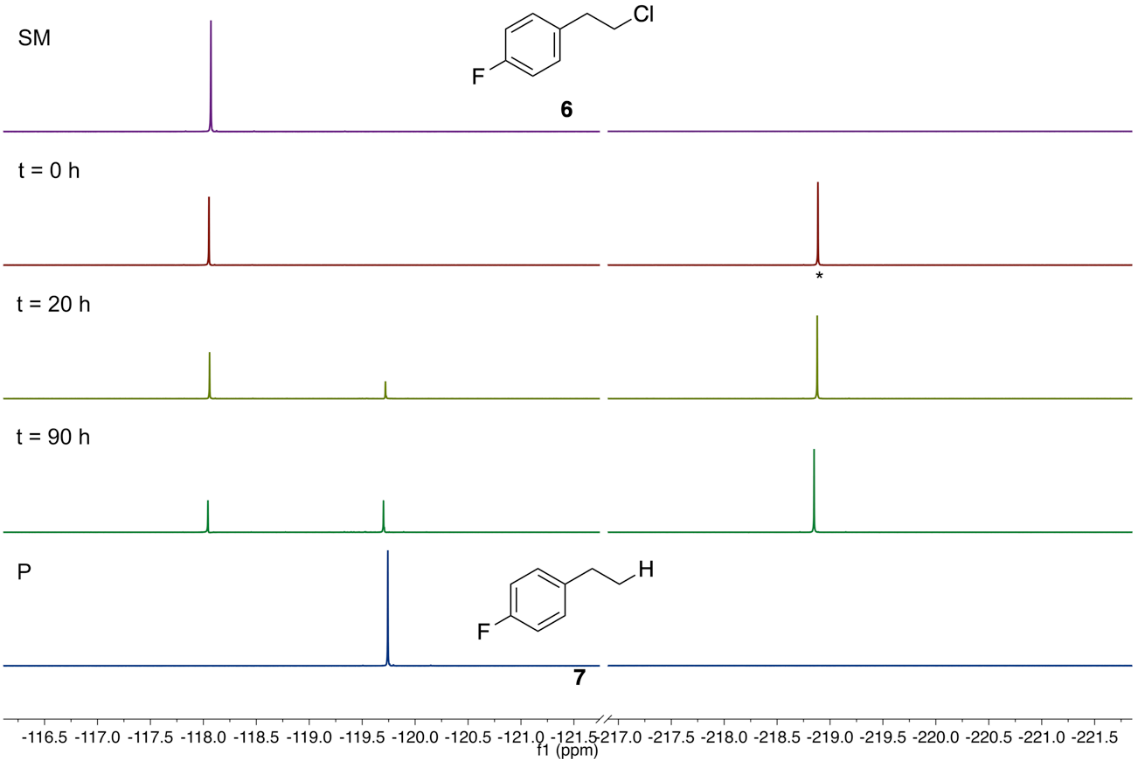

Figure S53 Expansions of the ^{19}F-NMR spectra fro **Figure S52**.

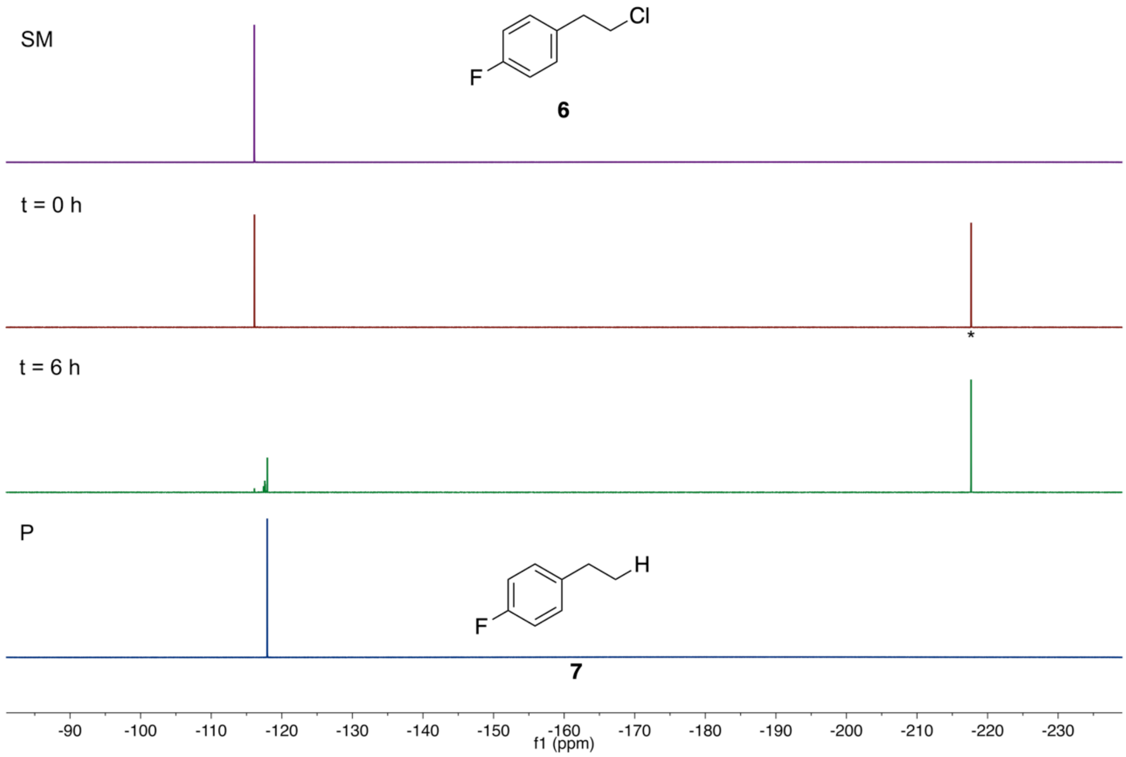

Figure S54 ^{19}F-NMR spectra monitoring dechlorination of substrate **6** over time. Reaction conditions: 50 mM **6**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

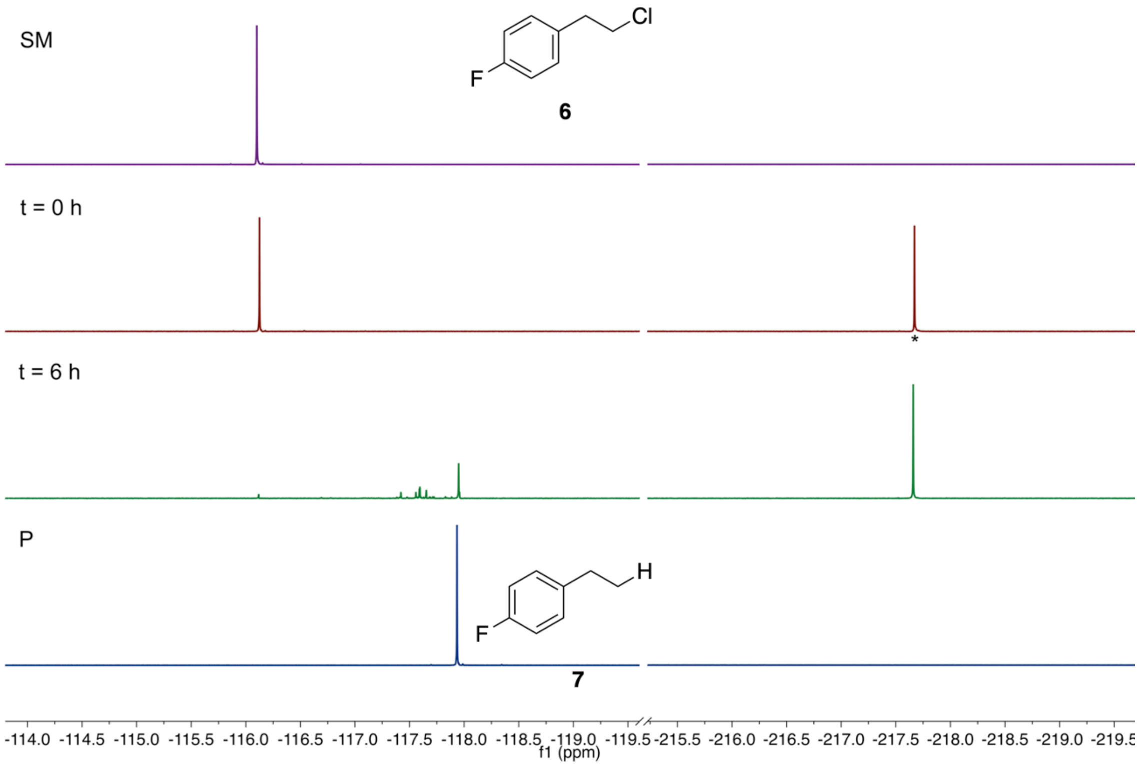

Figure S55 Expansions of the ^{19}F-NMR spectra from **Figure S54**.

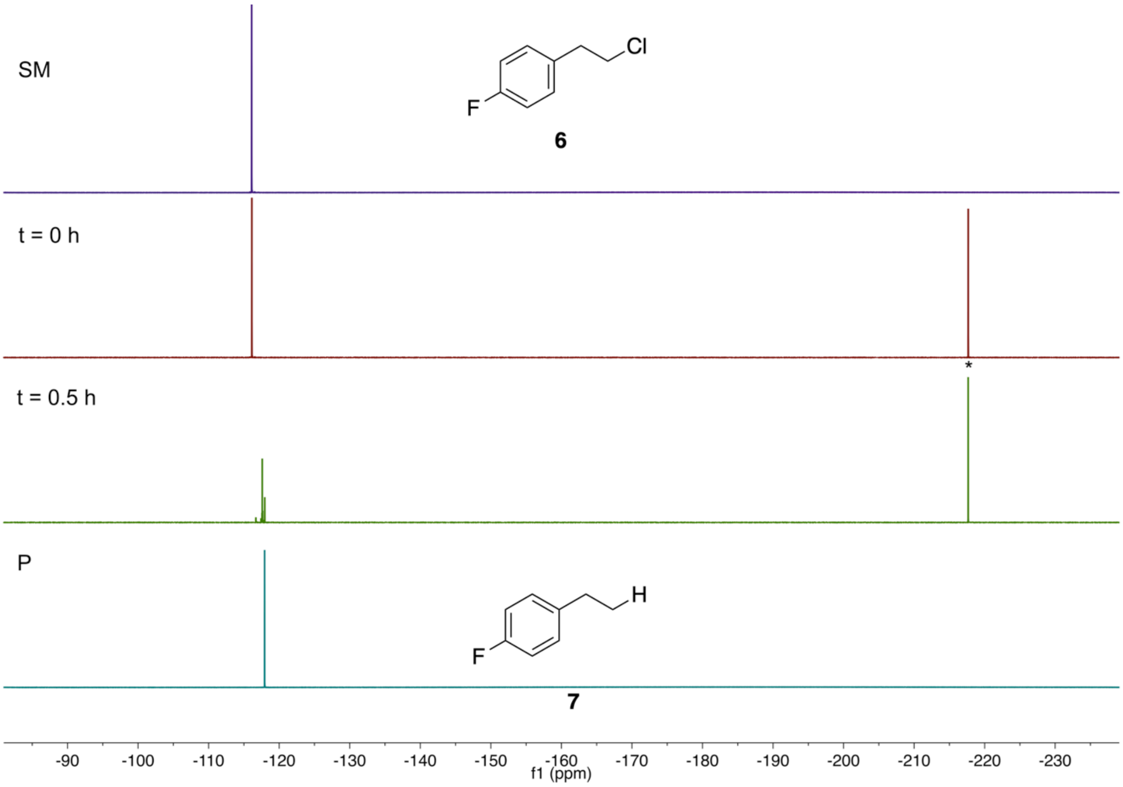

Figure S56 ^{19}F-NMR spectra monitoring dechlorination of substrate **6** over time. Reaction conditions: 50 mM **6**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

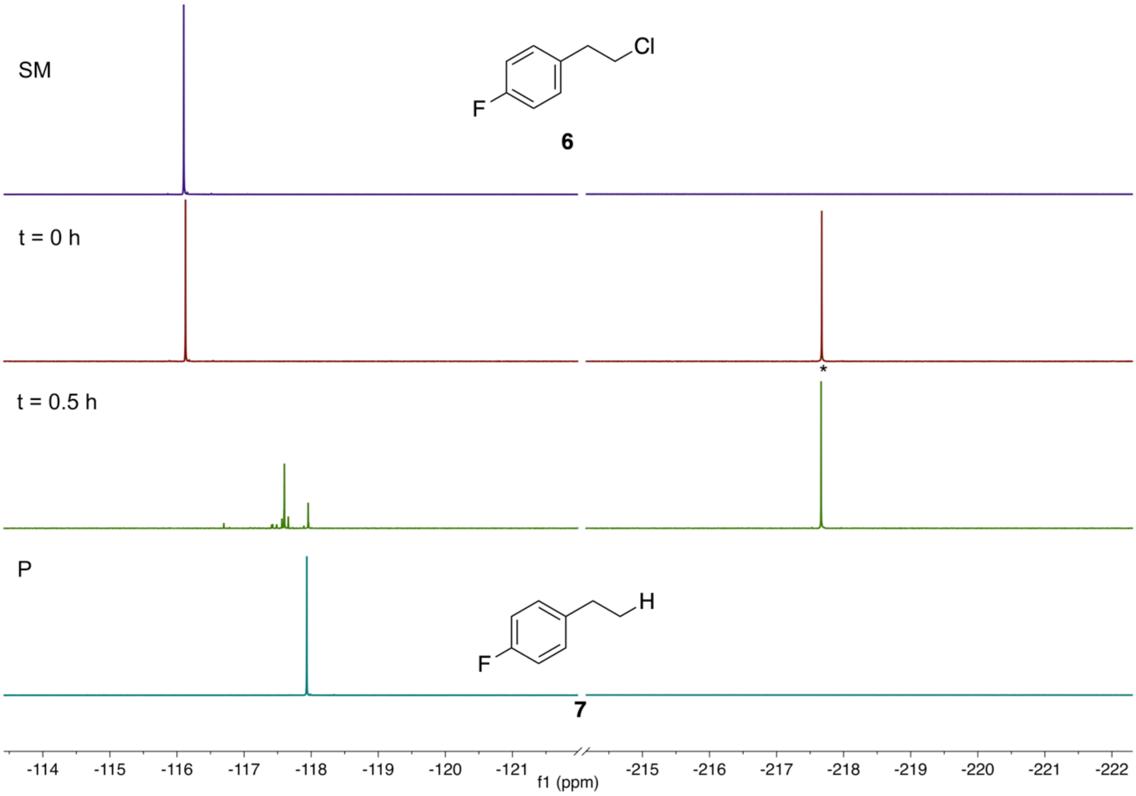

Figure S57 Expansions of the ^{19}F-NMR spectra from **Figure S56**.

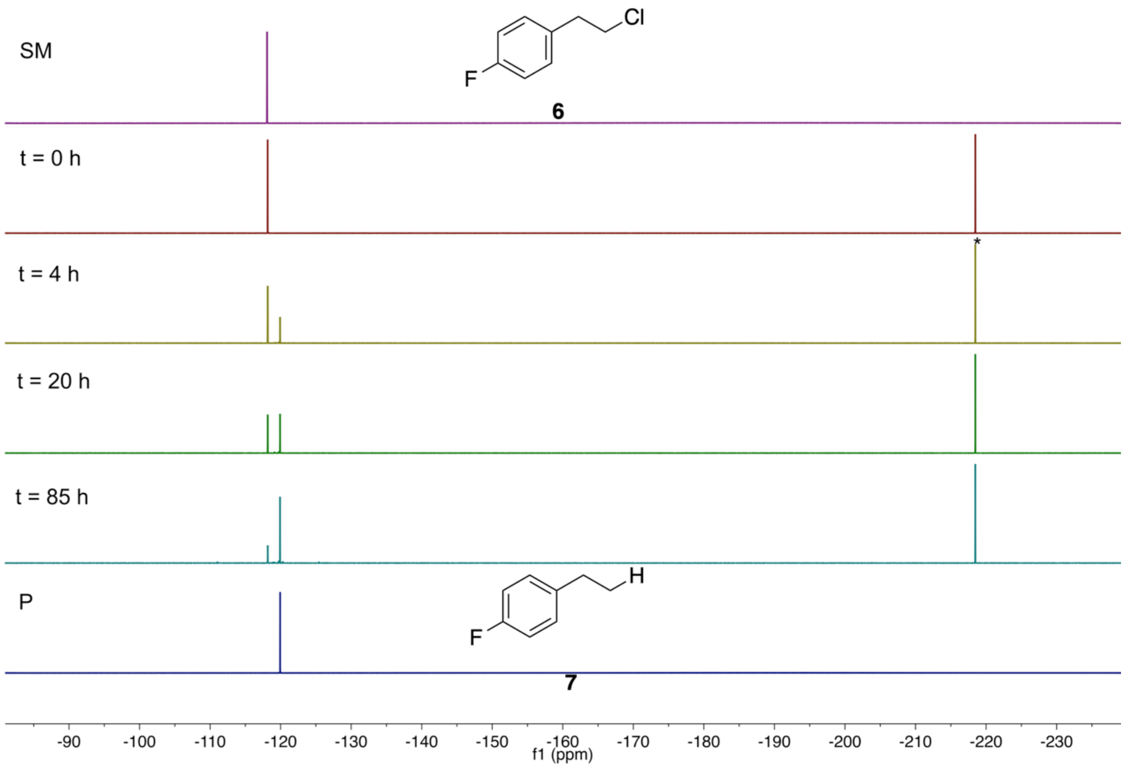

Figure S58 ^{19}F-NMR spectra monitoring dechlorination of substrate **6** over time. Reaction conditions: 100 mM **6**, 1.25 eq. TDAE, MeCN-d$_3$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

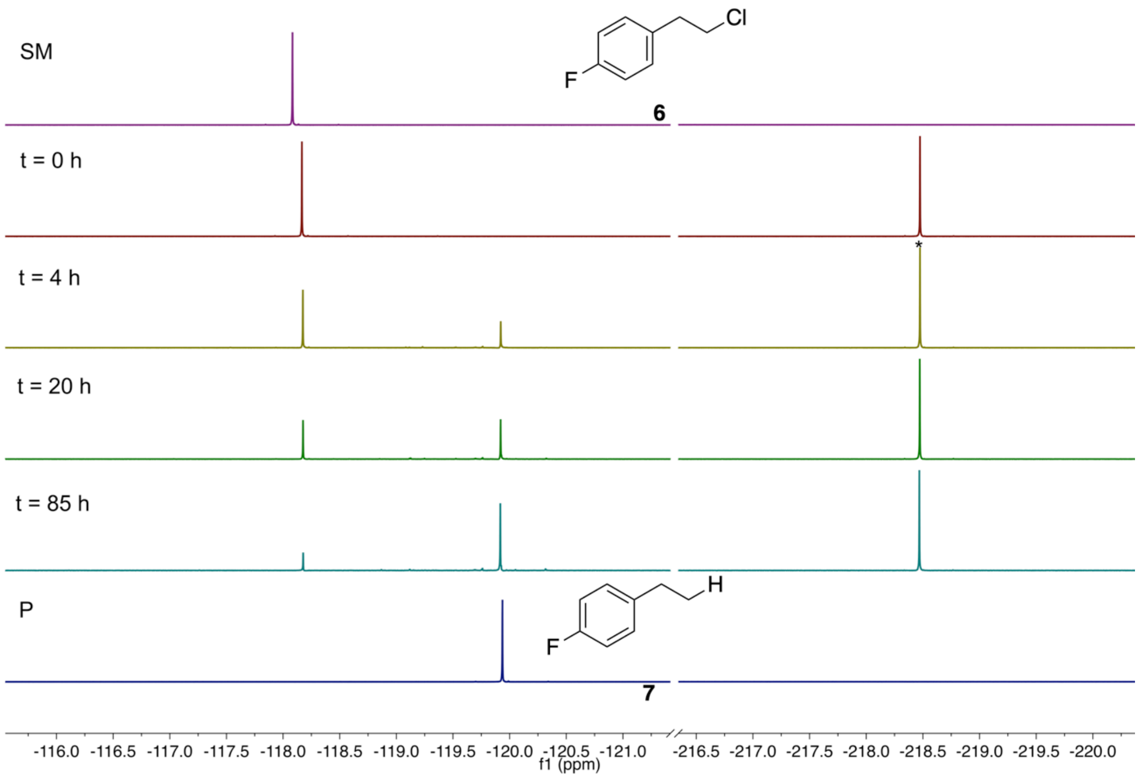

Figure S59 Expansions of the ^{19}F-NMR spectra from **Figure S58**.

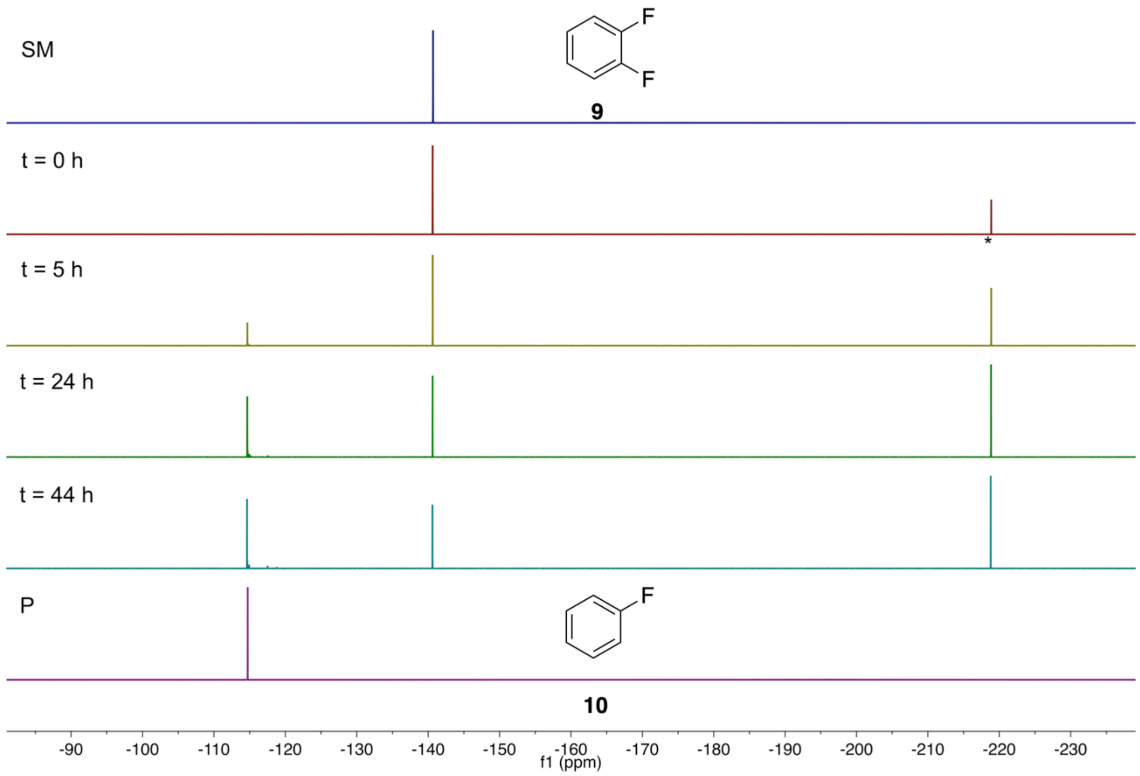

Figure S60 ^{19}F-NMR spectra monitoring defluorination of substrate **9** over time. Reaction conditions: 100 mM **9**, 3.0 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

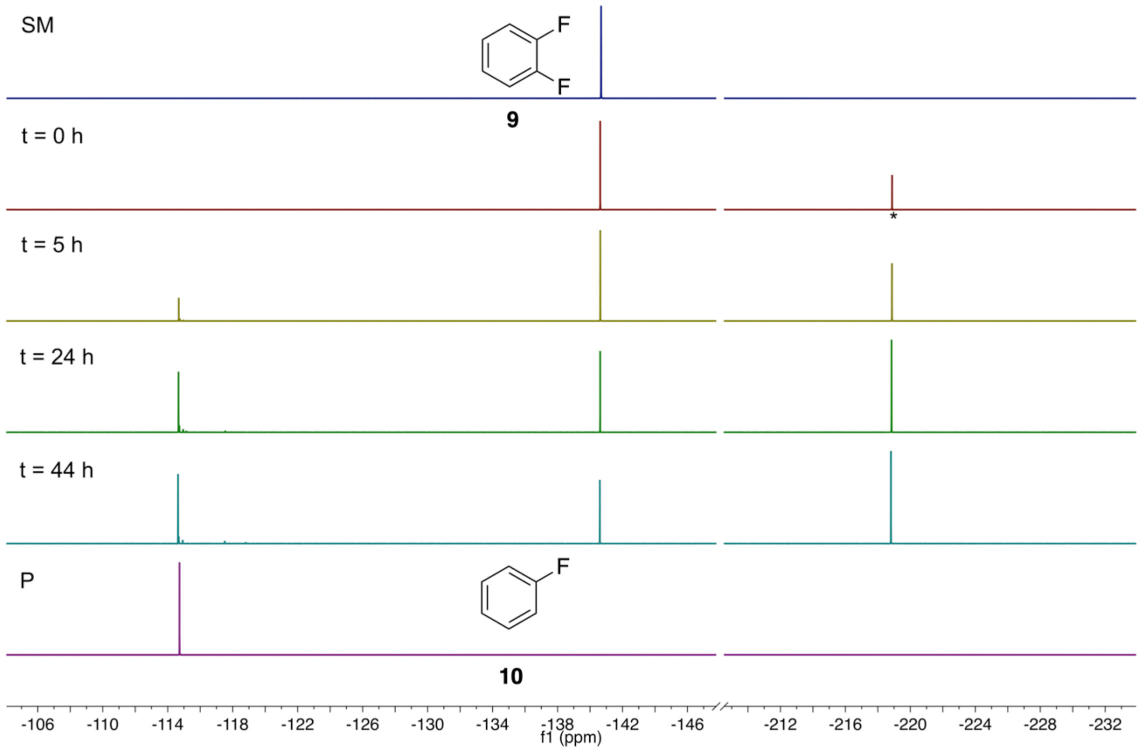

Figure S61 Expansions of the ^{19}F-NMR spectra from **Figure S60**.

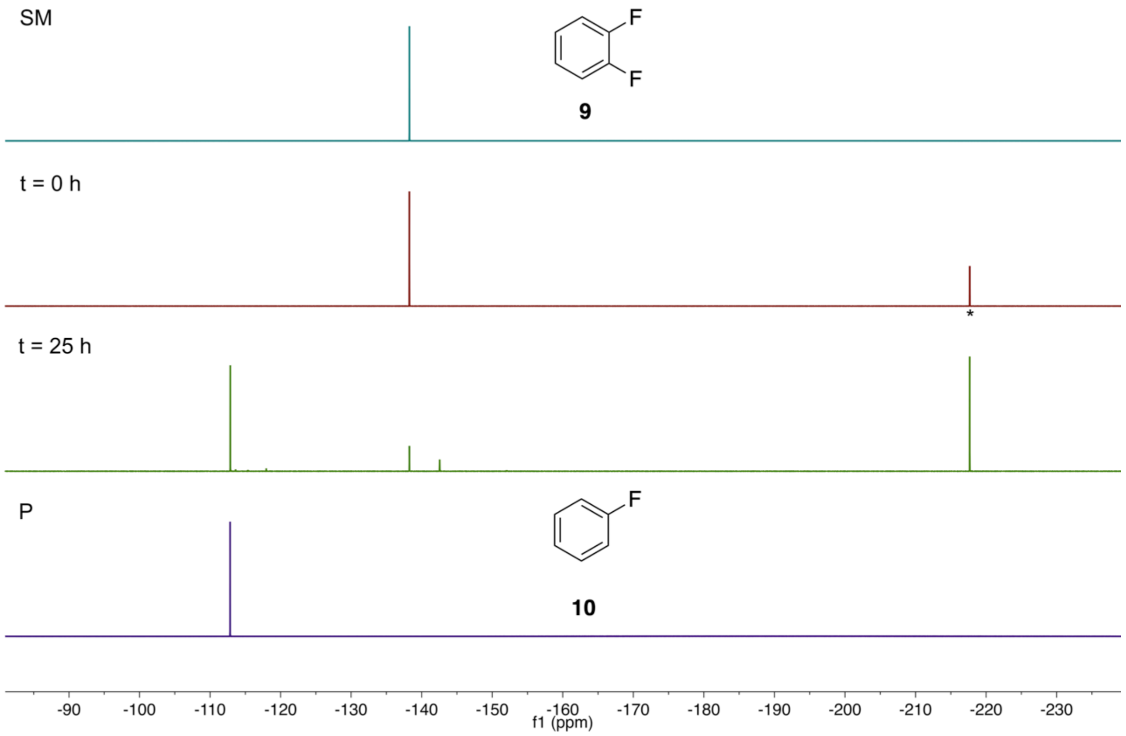

Figure S62 ^{19}F-NMR spectra monitoring defluorination of substrate **9** over time. Reaction conditions: 50 mM **9**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

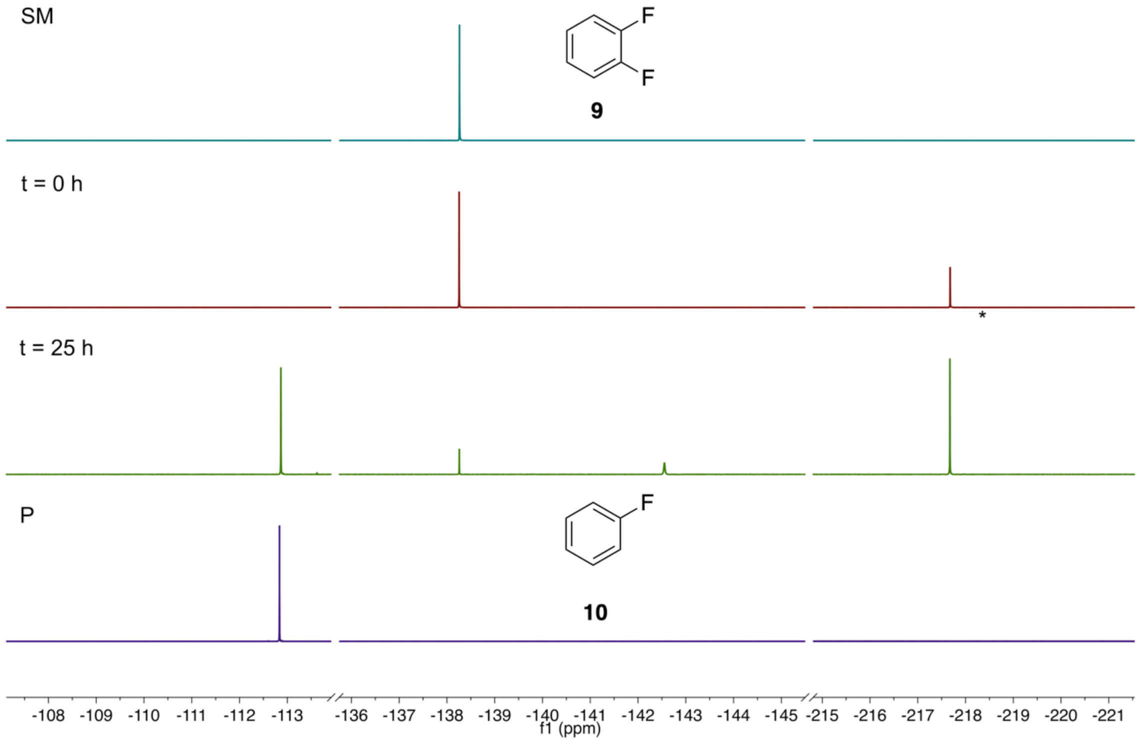

Figure S63 Expansions of the ^{19}F-NMR spectra from **Figure S62**.

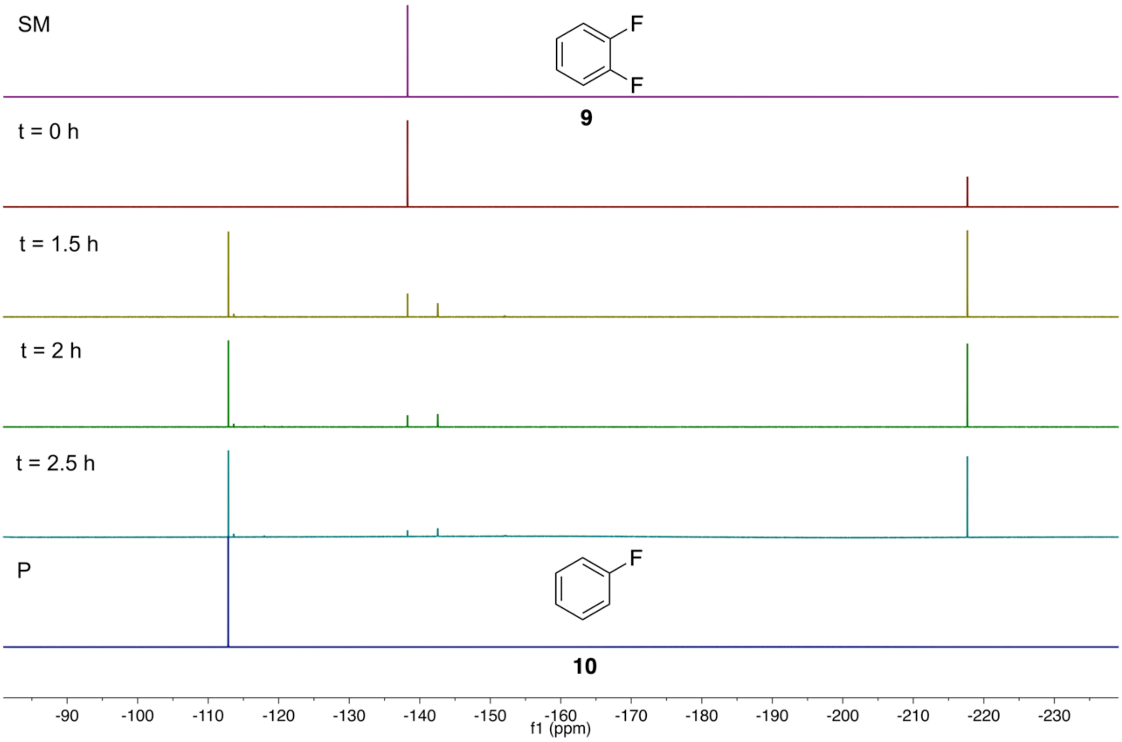

Figure S64 ^{19}F-NMR spectra monitoring defluorination of substrate **9** over time. Reaction conditions: 50 mM **9**, 1.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P = product.

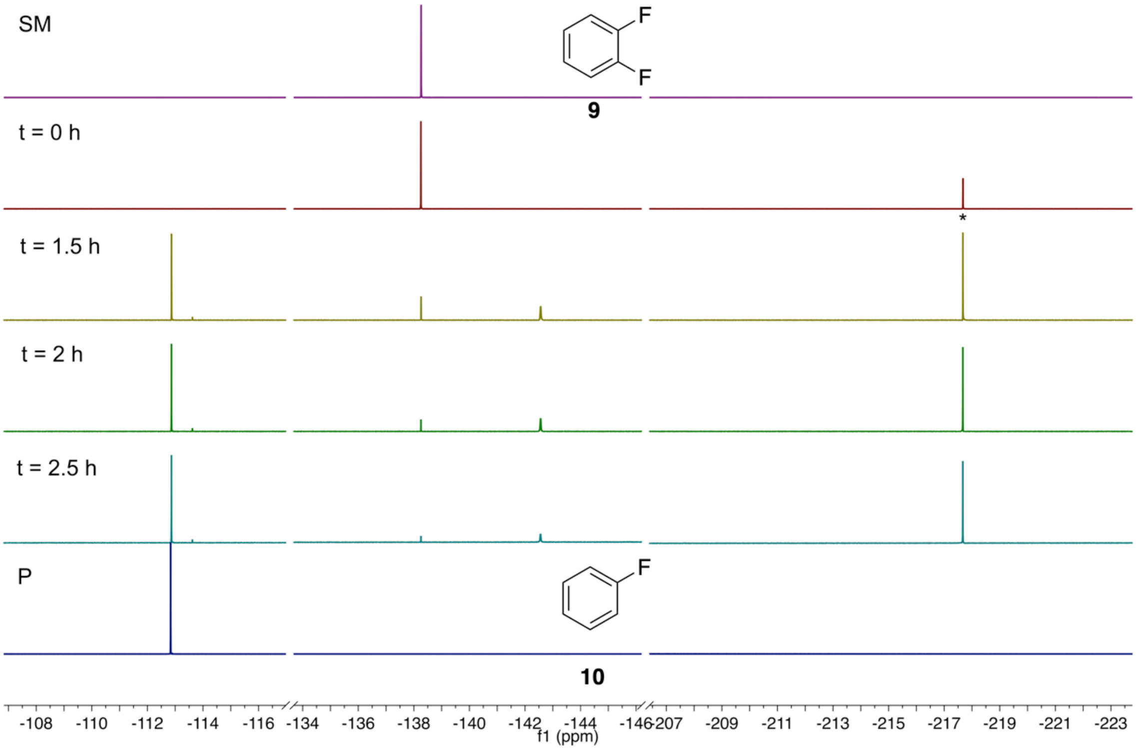

Figure S65 Expansions of the ^{19}F-NMR spectra from **Figure S63**.

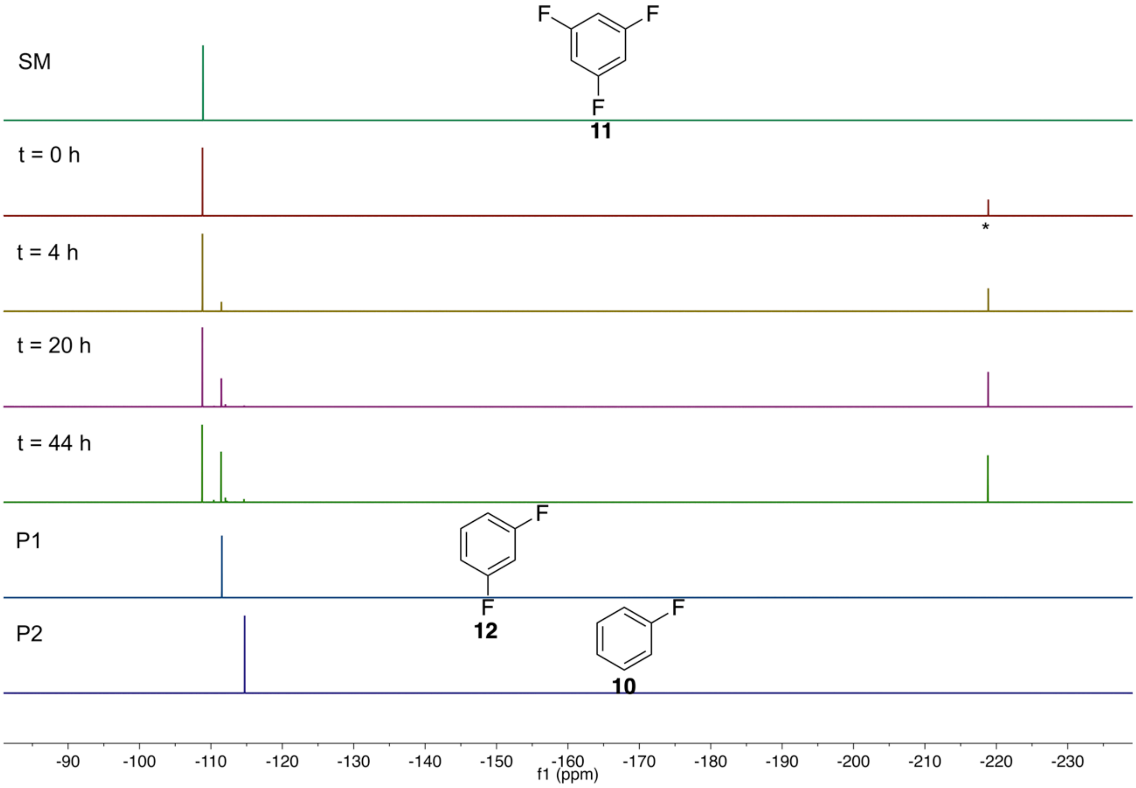

Figure S66 ^{19}F-NMR spectra monitoring defluorination of substrate **11** over time. Reaction conditions: 100 mM **11**, 3.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P1, P2 = products.

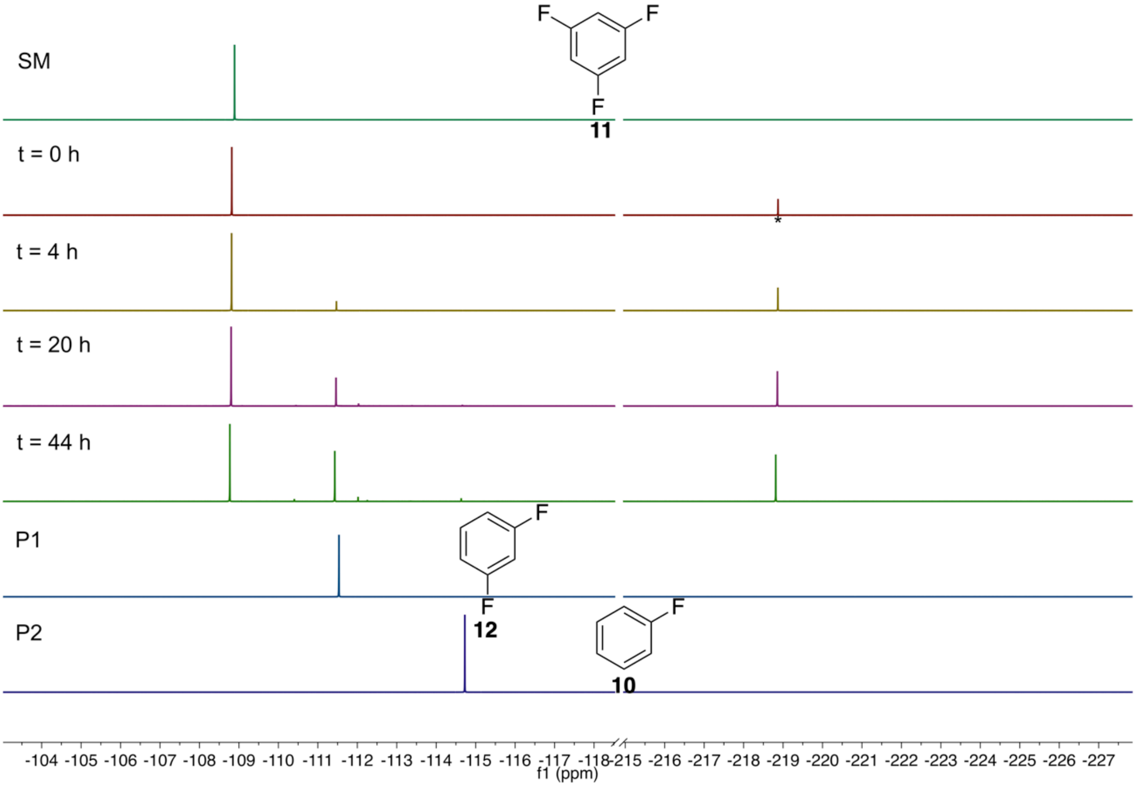

Figure S67 Expansions of the ^{19}F-NMR spectra from **Figure S66**.

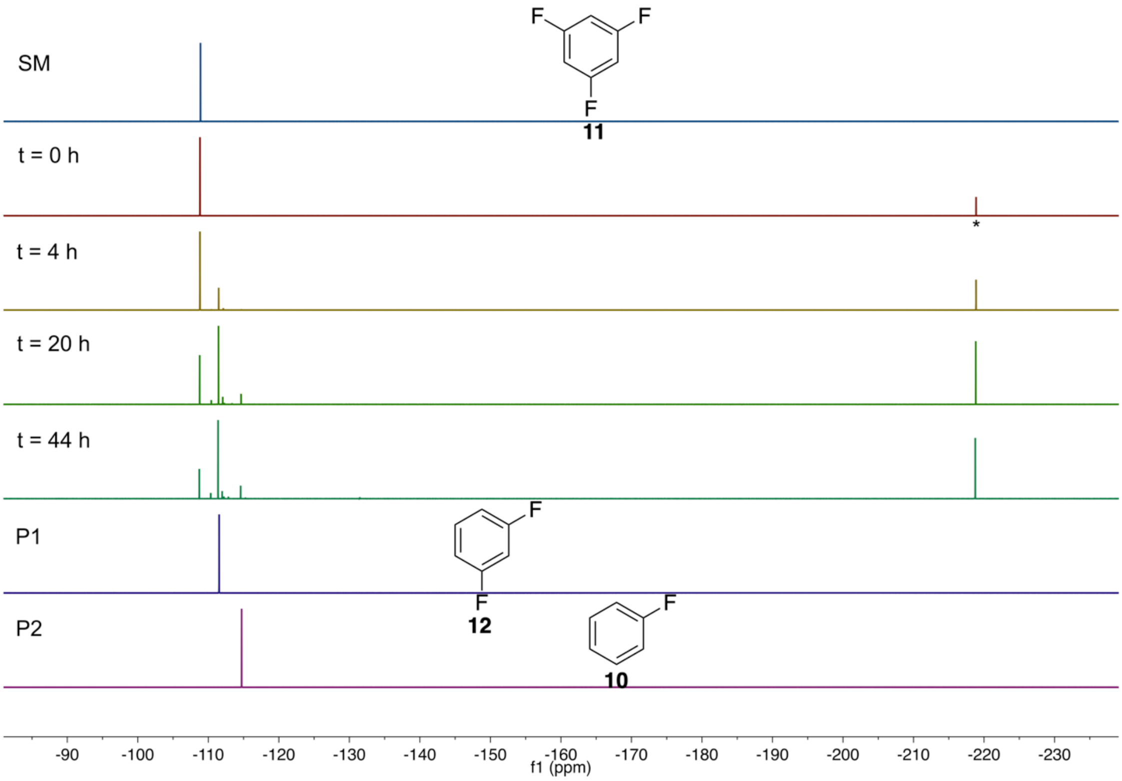

Figure S68 ^{19}F-NMR spectra monitoring defluorination of substrate **11** over time. Reaction conditions: 100 mM **11**, 3.25 eq. TDAE, acetone-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P1, P2 = products.

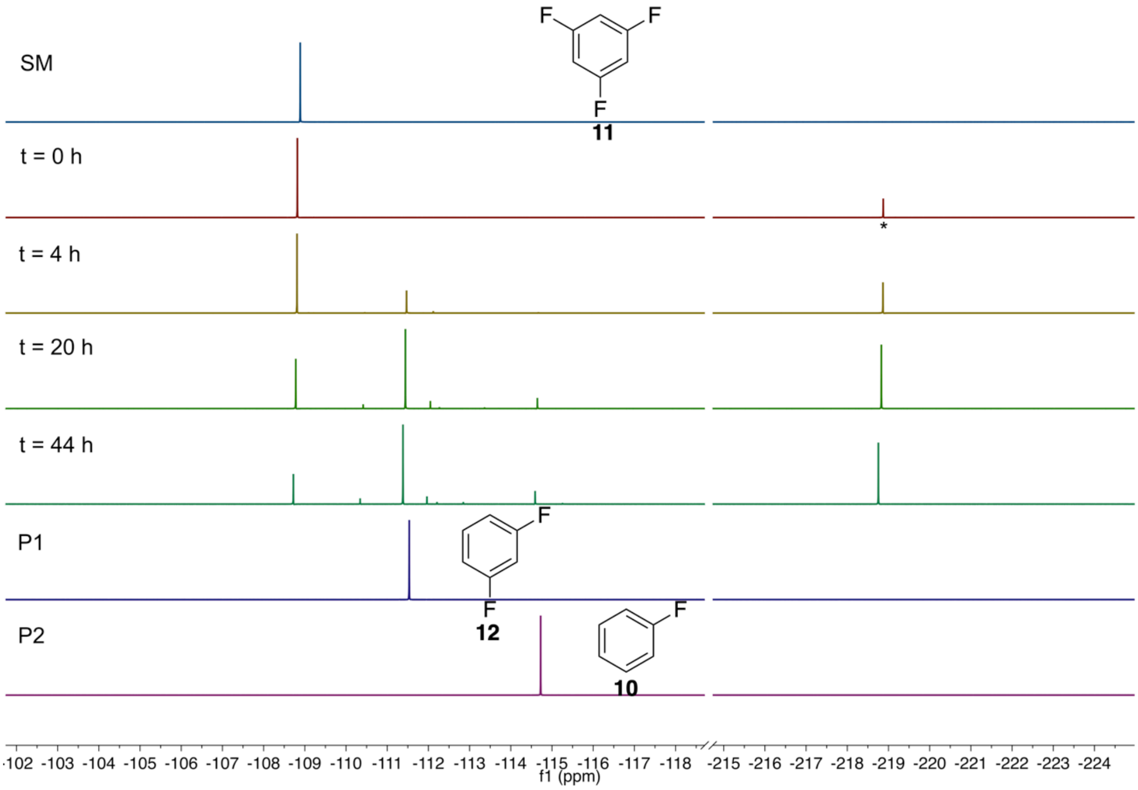

Figure S69 Expansions of the ^{19}F-NMR spectra from **Figure S68**.

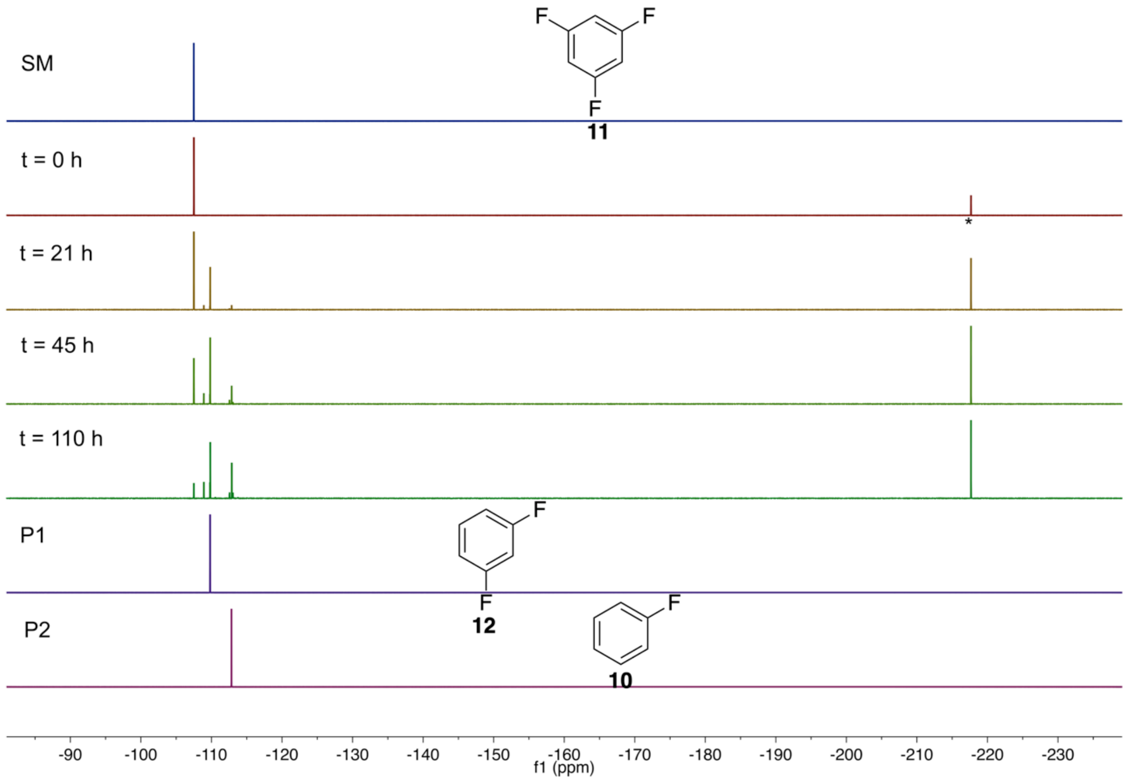

Figure S70 ^{19}F-NMR spectra monitoring defluorination of substrate **11** over time. Reaction conditions: 50 mM **11**, 2.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 440 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P1, P2 = products.

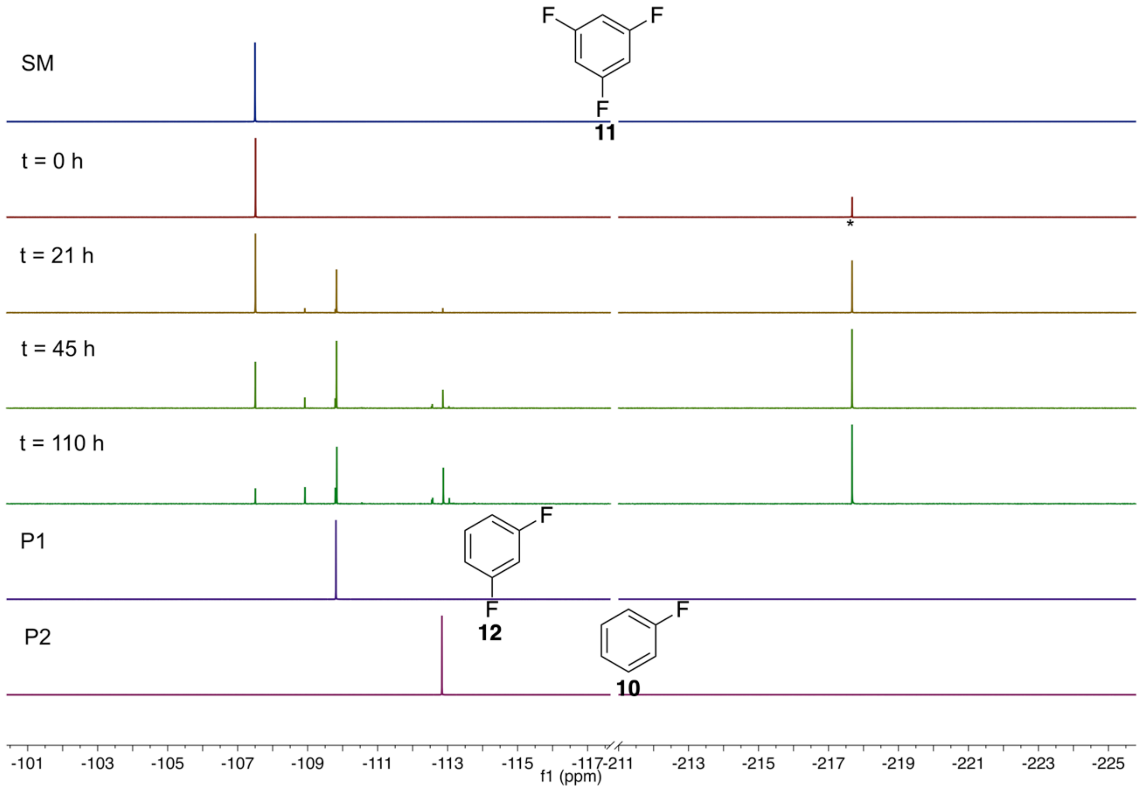

Figure S71 Expansions of the ^{19}F-NMR spectra from **Figure S70**.

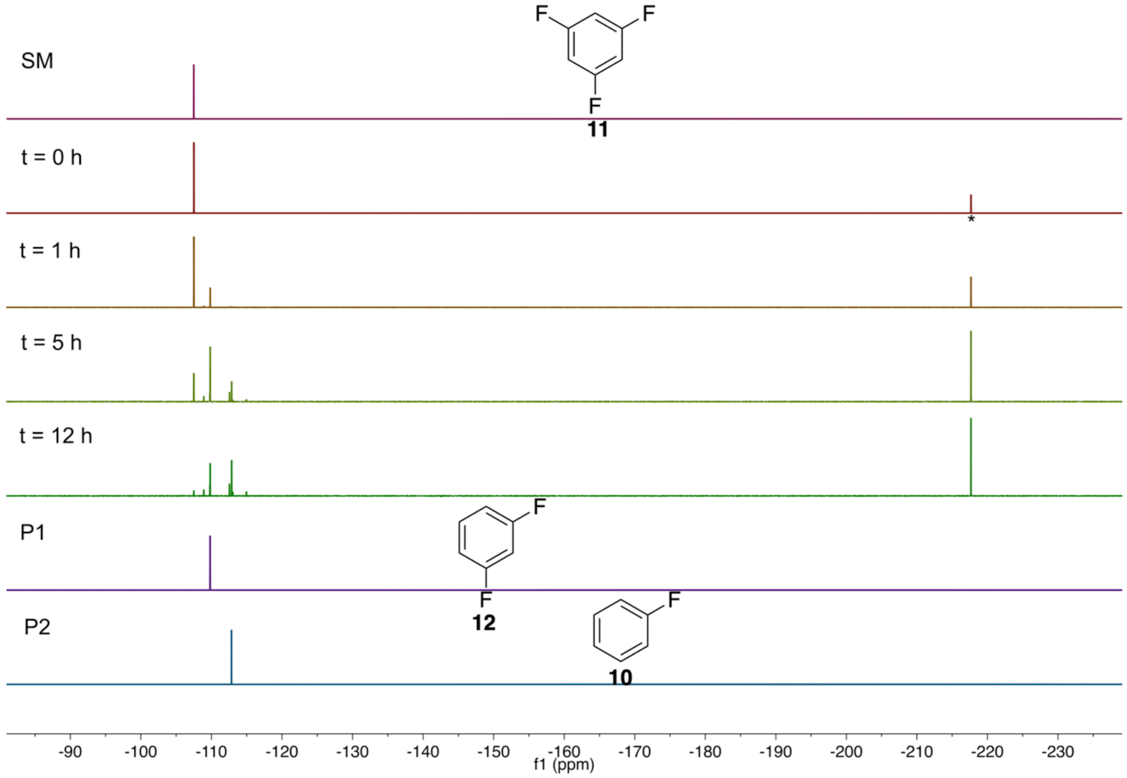

Figure S72 ^{19}F-NMR spectra monitoring defluorination of substrate **11** over time. Reaction conditions: 50 mM **11**, 2.25 eq. TDAE, benzene-d$_6$, λ_{ex} = 390 nm. Peak of internal standard 1-fluoropentane is marked with an asterisk. SM = starting material; P1, P2 = products.

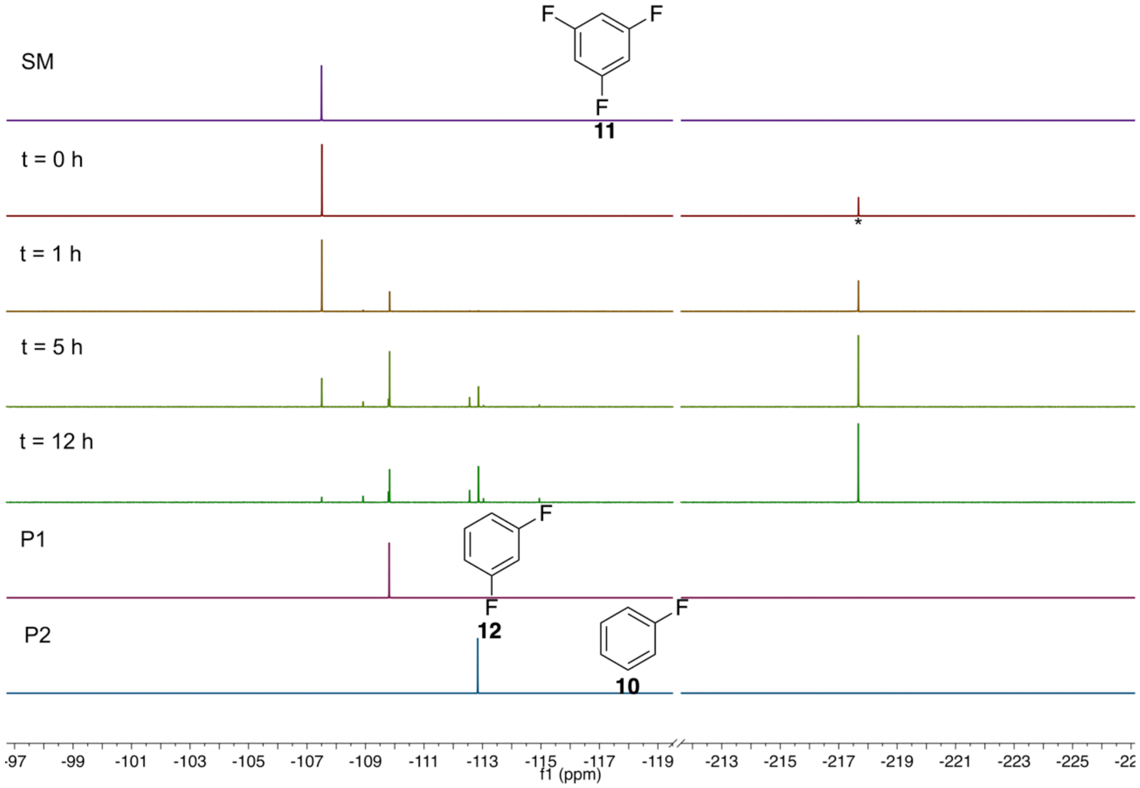

Figure S73 Expansions of the ^{19}F-NMR spectra from **Figure S72**.

6) References

[1] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.