

## Supporting Information

### **Isotope Effect in the Activation of a Mechanophore**

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## 2 General Experimental Details

Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers. All other chemicals were used without further purification. Compounds **S1** – **S2** along with polymers **1<sub>Ha</sub>**, **1<sub>Da</sub>**, **2<sub>Hb</sub>**, **2<sub>Hc</sub>**, **5<sub>Ha</sub>**, **5<sub>Hb</sub>**, **5<sub>Hc</sub>** and **S10** were synthesised according to previously reported procedures.<sup>1</sup>

Gel permeation chromatography (GPC) analyses were performed in THF solution (1 mg mL<sup>-1</sup>) at 35 °C using a Malvern Viscotek GPCmax VE2001 solvent/sample module with 2 × PL gel 10 µm mixed-B and a PL gel 500 Å column, and equipped with a Viscotek VE 3240 UV/vis multichannel detector and Viscotek VE3580 refractive index detector employing narrow polydispersity polystyrene standards (Agilent Technologies) as a calibration reference. Samples were filtered through a Whatman Puradisc 4 mm syringe filter with 0.45 µm PTFE membrane before injection to equipment, and experiments were carried out with injection volume of 100 µL, flow rate of 1 mL min<sup>-1</sup>. Results were analysed using *n*-dodecane as an internal marker using Malvern OmniSEC 5.10 software.

Ultrasound experiments were performed using a Sonics VCX 500 ultrasonic processor equipped with a 13 mm diameter solid probe or replaceable-tip probe. The distance between the titanium tip and the bottom of the Suslick cell was 3 cm. The ultrasonic intensity was calibrated using the method outlined by Hickenboth *et al.*<sup>2</sup> The Suslick cells were fabricated by the Department of Chemistry glass workshop at the University of Manchester.

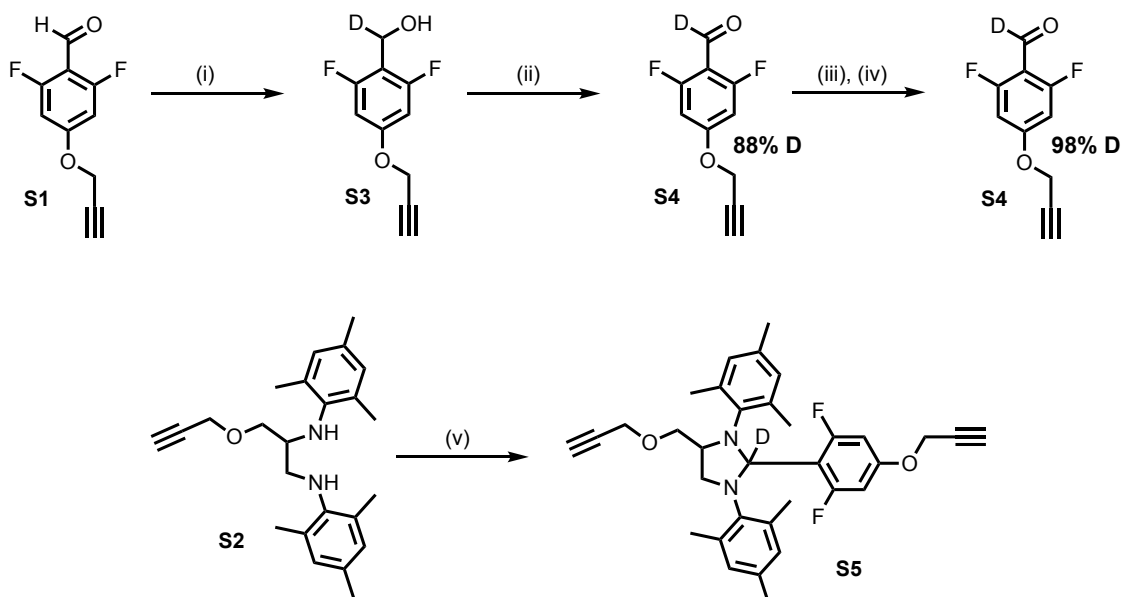
Analytical TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light or stained with either potassium permanganate or phosphomolybdic acid solution. Preparative TLC was performed on precoated silica gel plates: 2 mm, UNIPLATE GF, Analtech Inc., DE, USA. Flash column chromatography was performed with silica gel 60 (230-400 mesh) from Sigma-Aldrich. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using either a Bruker Avance III 500 MHz Prodigy instrument or a Bruker Avance III 400 MHz Prodigy instrument at the University of Manchester. Chemical shifts are reported in parts per million (ppm) from high to low frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in Hertz (Hz) and splitting patterns are designated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet and m = multiplet. Mass spectra were obtained through the Mass Spectrometry services in the Department of Chemistry at the University of Manchester.

Isotopic purity of **S3-5** and **S7-9** was determined from the integration of the residual protic signal in <sup>1</sup>H NMR spectra.

**Abbreviations:** APCI: atmospheric pressure chemical ionization; DCM: dichloromethane; ESI: electrospray ionization; PE: petroleum ether; HRMS: high resolution mass spectrometry; MS: mass spectrometry; PMDETA: *N,N,N',N'',N''*-pentamethyldiethylenetriamine; THF: tetrahydrofuran; TLC: thin layer chromatography.

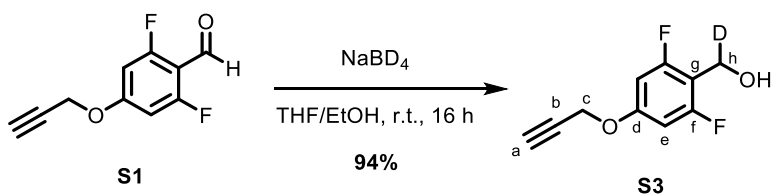
### 3 Synthesis of mechanophores and reference compounds

#### 3.1 Synthetic Route to S5



**Scheme S1.** Synthetic route to **S5**. Conditions: (i) NaBD<sub>4</sub>, THF/EtOH, r.t., 16 h, 94% yield; (ii) PCC, DCM, 0 °C, 1 h; (iii) NaBD<sub>4</sub>, THF/EtOH, r.t., 16 h; (iv) PCC, DCM, 0 °C, 1 h; (v) **S4** (98% D), acetic acid, r.t., 30 min, 38% yield.

##### 3.1.1 Synthesis of S3



**S1** (100 mg, 0.510 mmol, 1 eq.) was dissolved in a mixture of THF (0.6 mL) and ethanol (0.6 mL). NaBD<sub>4</sub> (11 mg, 0.255 mmol, 0.5 eq.) was added and the mixture stirred under N<sub>2</sub> for 16 h. The mixture was carefully washed with water and the aqueous mixture thoroughly extracted with DCM. The organic phase was dried over magnesium sulfate before being filtered and condensed to give the pure product as a white powder (95 mg, 0.477 mmol, 94% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.62 – 6.50 (m, 2H, H<sub>e</sub>), 4.77 – 4.63 (m, 3H, H<sub>c</sub> + H<sub>h</sub>), 2.56 (td,  $J$  = 2.4, 0.7 Hz, 1H, H<sub>a</sub>), 1.77 (d,  $J$  = 6.3 Hz, 1H, H<sub>i</sub>).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 162.19 (dd,  $J$  = 247.5, 11.7 Hz, C<sub>f</sub>), 158.81 (t,  $J$  = 14.4 Hz, C<sub>d</sub>), 109.65 (t,  $J$  = 20.4 Hz, C<sub>g</sub>), 99.65 – 98.60 (m, C<sub>e</sub>), 77.36 (C<sub>b</sub>), 76.63 (C<sub>a</sub>), 56.42 (C<sub>c</sub>), 53.16 – 52.11 (m, C<sub>h</sub>).

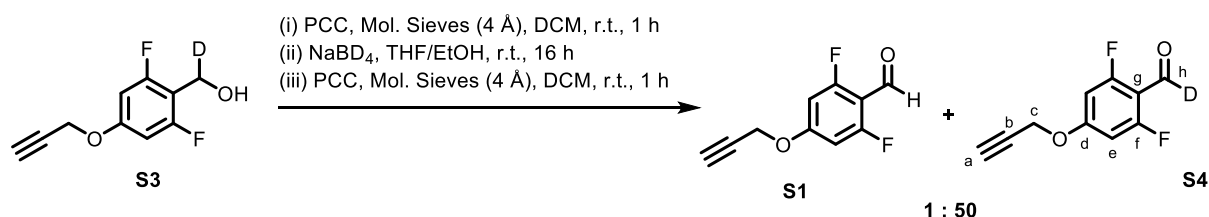
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -115.20 (F<sub>f</sub>).

**<sup>2</sup>H NMR** (61 MHz, CHCl<sub>3</sub>)  $\delta$  = 4.73 (s, 1D, D<sub>h</sub>).

**HRMS-API(+)**: 182.0519 [M-OH]<sup>+</sup>, calculated for C<sub>10</sub>H<sub>6</sub>DF<sub>2</sub>O: 182.0522.



### 3.1.2 Synthesis of S4



PCC (541 mg, 2.51 mmol, 5 eq.) and molecular sieves (4 Å, 0.5 g) were added to DCM (2.5 mL) and the mixture was cooled in an ice bath. **S3** (100 mg, 0.510 mmol, 1 eq.) was dissolved in DCM (2.5 mL) and the solution added dropwise to the reaction mixture. The mixture was stirred for 30 min. After warming to room temperature the mixture was stirred for a further 30 min. The mixture was passed through a silica plug using DCM. The collected solution was condensed to give the product mixture as an off-white powder (88% D).

The product mixture, containing both **S1** and **S4**, was taken and used again in the reduction process detailed in Section 3.1.1, *Synthesis of S3*. After, the resulting product mixture was subjected once more to the oxidation procedure described here to yield the product as an off-white powder (98% D).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 6.69 – 6.50 (m, 2H, H<sub>e</sub>), 4.75 (d, *J* = 2.4 Hz, 2H, H<sub>c</sub>), 2.62 (t, *J* = 2.4 Hz, 1H, H<sub>a</sub>).

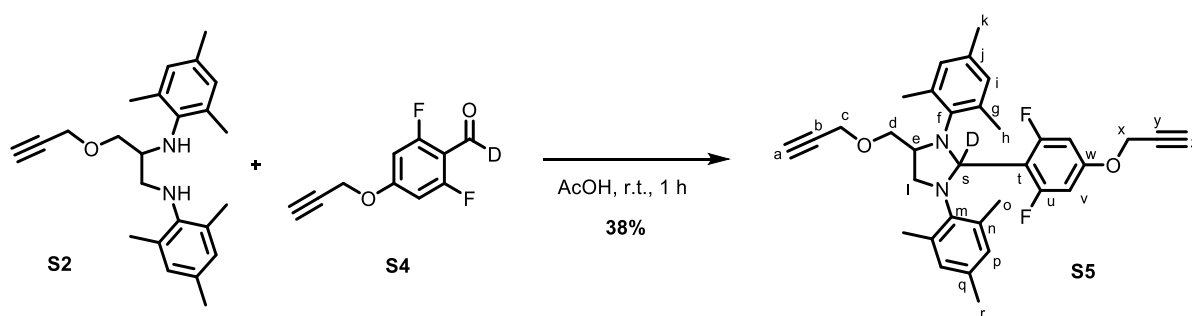
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ = 183.87 – 182.63 (m, C<sub>h</sub>), 165.82 – 163.40 (m, C<sub>i</sub>), 163.86 – 163.46 (m, C<sub>d</sub>), 109.12 – 108.61 (m, C<sub>g</sub>), 100.01 – 99.56 (m, C<sub>e</sub>), 77.53 (d, *J* = 8.4 Hz, C<sub>b</sub>), 76.56 (d, *J* = 1.9 Hz, C<sub>a</sub>), 56.81 (C<sub>c</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -112.56 (F<sub>f</sub>).

**<sup>2</sup>H NMR** (61 MHz, CHCl<sub>3</sub>) δ = 10.25 (s, 1D, D<sub>h</sub>).

**HRMS-ESI(+)**: 198.0469 [M+H]<sup>+</sup>, calculated for C<sub>10</sub>H<sub>6</sub>DF<sub>2</sub>O<sub>2</sub>: 198.0471.

### 3.1.3 Synthesis of S5



**S2** (100 mg, 0.274 mmol, 1 eq.) was dissolved in minimal acetic acid. **S4** (81 mg, 0.411 mmol, 1.5 eq.) was added and the mixture was stirred for 30 min during which a large amount of precipitate formed. The mixture was filtered and the filtered solid thoroughly washed with cold methanol. The filtered white solid was the pure product (57 mg, 0.105 mmol, 38% yield, 99% D).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 6.88 (d, *J* = 2.2 Hz, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.82 – 6.62 (m, 3H, H<sub>i</sub> + H<sub>p</sub>), 6.38 (dt, *J* = 12.6, 2.1 Hz, 1H, H<sub>v</sub>), 6.11 (dt, *J* = 12.0, 2.0 Hz, 1H, H<sub>v</sub>), 4.52 (d, *J* = 2.4 Hz, 2H, H<sub>x</sub>), 4.15 (dd, *J* = 3.5, 2.4 Hz, 2H, H<sub>c</sub>), 4.06 – 4.00 (m, 1H, H<sub>d</sub>), 3.91 – 3.84 (m, 1H, H<sub>i</sub>), 3.82 – 3.74 (m, 1H, H<sub>e</sub>), 3.68 – 3.62 (m, 2H, H<sub>d</sub> + H<sub>i</sub>), 2.52 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.50 (t, *J* = 2.4 Hz, 1H, H<sub>z</sub>), 2.46 (br, 6H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>),

2.41 (t,  $J = 2.4$  Hz, 1H, H<sub>a</sub>), 2.21 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.17 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>), 1.98 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>).

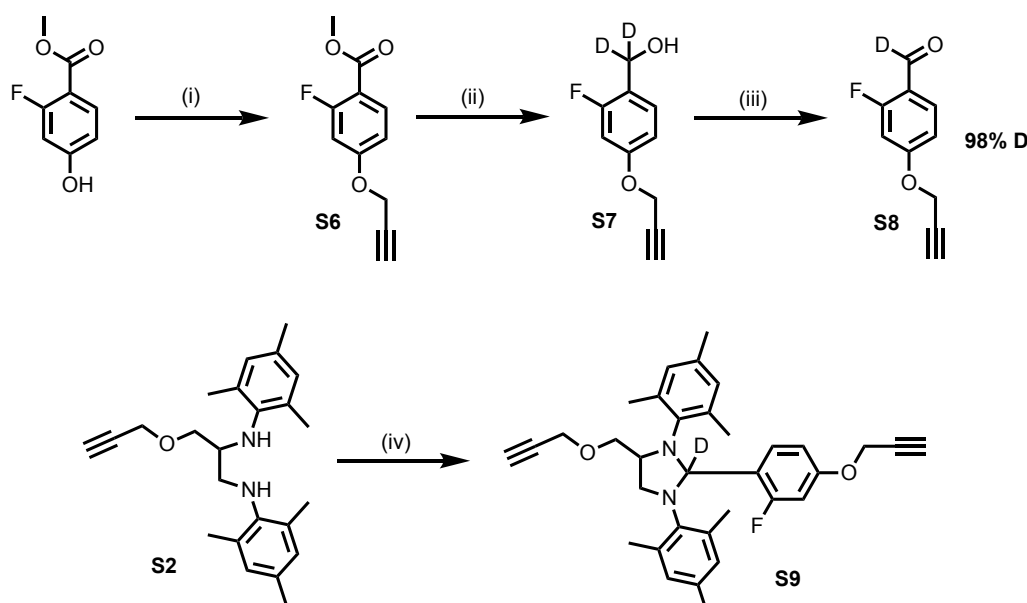
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta = 164.80 - 161.38$  (m, C<sub>u</sub>), 158.15 (t,  $J = 14.7$  Hz, C<sub>w</sub>), 140.86 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 140.71 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 138.32 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 137.10 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 135.91 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 134.91 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 130.87 (C<sub>i</sub> or C<sub>p</sub>), 130.32 (br, C<sub>i</sub> or C<sub>p</sub>), 129.76 (br, C<sub>i</sub> or C<sub>p</sub>), 129.32 (C<sub>i</sub> or C<sub>p</sub>), 110.23 (t,  $J = 12.9$  Hz, C<sub>t</sub>), 98.95 (ddd,  $J = 303.3, 27.4, 3.3$  Hz, C<sub>v</sub>), 80.12 (C<sub>b</sub>), 77.61 (C<sub>y</sub>), 76.35 (C<sub>z</sub>), 74.38 (d,  $J = 2.3$  Hz, C<sub>a</sub>), 73.36 (C<sub>d</sub>), 72.91 – 72.24 (m, C<sub>s</sub>), 62.27 (C<sub>e</sub>), 58.52 (C<sub>c</sub>), 56.21 (C<sub>x</sub>), 53.58 (C<sub>l</sub>), 20.88 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 20.74 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 20.28 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 18.96 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 18.44 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta = -103.90$  (d,  $J = 5.7$  Hz, 1F, F<sub>u</sub>),  $-116.72$  (d,  $J = 5.6$  Hz, 1F, F<sub>u</sub>).

<sup>2</sup>H NMR (77 MHz, CHCl<sub>3</sub>)  $\delta = 6.31$  (br, 1D, D<sub>s</sub>).

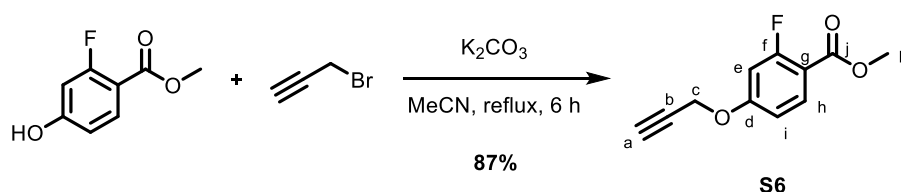
HRMS-APCI(+): 544.2871 [M+H]<sup>+</sup>, calculated for C<sub>34</sub>H<sub>36</sub>DF<sub>2</sub>O<sub>2</sub>N<sub>2</sub>: 544.2880.

### 3.2 Synthetic Route to S9



**Scheme S2.** Synthetic route to **S9**. Conditions: (i) K<sub>2</sub>CO<sub>3</sub>, propargyl bromide, MeCN, reflux, 6 h, 87% yield; (ii) NaBD<sub>4</sub>, THF/EtOH, 40 °C, 48 h, 48% yield; (iii) PCC, DCM, 0 °C, 1 h, 79% yield; (iv) **S8**, acetic acid, r.t., 30 min, 60% yield.

#### 3.2.1 Synthesis of S6



Methyl 2-fluoro-4-hydroxybenzoate (1.00 g, 5.88 mmol, 1 eq.) and potassium carbonate (1.22 g, 8.82 mmol, 1.5 eq.) were added to acetonitrile (29 mL). Propargyl bromide (80% in toluene, 0.79 mL, 8.82 mmol, 1.5 eq.) was added and the mixture was refluxed for 6 h. The mixture was cooled to room temperature before being diluted with water to dissolve any salts. The aqueous mixture was thoroughly extracted with DCM. The organic extracts were dried over magnesium sulfate before being filtered and condensed to give the pure product as a pale yellow solid (1.06 g, 5.09 mmol, 87 % yield).

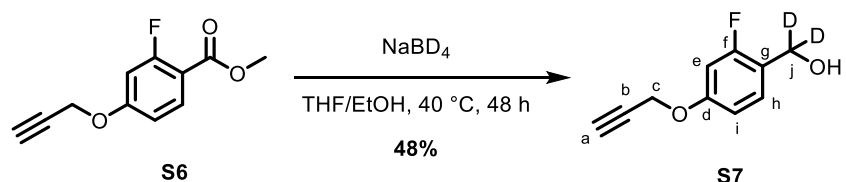
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 7.92 (t, *J* = 8.6 Hz, 1H, H<sub>h</sub>), 6.80 (ddd, *J* = 8.9, 2.5, 0.8 Hz, 1H, H<sub>i</sub>), 6.73 (dd, *J* = 12.4, 2.5 Hz, 1H, H<sub>e</sub>), 4.73 (d, *J* = 2.4 Hz, 2H, H<sub>c</sub>), 3.90 (s, 3H, H<sub>k</sub>), 2.57 (t, *J* = 2.4 Hz, 1H, H<sub>a</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 164.67 (C<sub>j</sub>), 163.40 (d, *J* = 265.9 Hz, C<sub>f</sub>), 162.39 (d, *J* = 11.5 Hz, C<sub>d</sub>), 133.60 (d, *J* = 2.5 Hz, C<sub>h</sub>), 111.87 (d, *J* = 9.8 Hz, C<sub>g</sub>), 110.94 (d, *J* = 3.0 Hz, C<sub>i</sub>), 103.58 (d, *J* = 26.4 Hz, C<sub>e</sub>), 77.38 (C<sub>b</sub>), 76.71 (C<sub>a</sub>), 56.34 (C<sub>c</sub>), 52.24 (C<sub>k</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -105.84 (F<sub>f</sub>).

**HRMS-APCI(+)**: 209.0608 [M+H]<sup>+</sup>, calculated for C<sub>11</sub>H<sub>10</sub>FO<sub>3</sub>: 209.0608.

### 3.2.2 Synthesis of S7



**S6** (0.50 g, 2.40 mmol, 1 eq.) was dissolved in a mixture of THF (2.4 mL) and ethanol (2.4 mL). NaBD<sub>4</sub> (0.20 g, 4.80 mmol, 2 eq.) was added and the mixture stirred at 40 °C under N<sub>2</sub> for 48 h. The mixture was carefully washed with water and the aqueous mixture thoroughly extracted with DCM. The organic phase was dried over magnesium sulfate before being filtered and condensed to give the pure product as a white powder (0.21 g, 1.15 mmol, 48% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 7.32 (t, *J* = 8.5 Hz, 1H, H<sub>h</sub>), 6.76 (ddd, *J* = 8.4, 2.5, 0.8 Hz, 1H, H<sub>i</sub>), 6.71 (dd, *J* = 11.6, 2.5 Hz, 1H, H<sub>e</sub>), 4.68 (d, *J* = 2.4 Hz, 2H, H<sub>c</sub>), 2.54 (t, *J* = 2.4 Hz, 1H, H<sub>a</sub>), 1.75 (d, *J* = 7.0 Hz, 1H, H<sub>k</sub>).

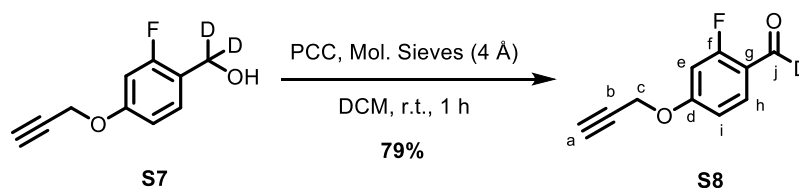
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ = 161.39 (d, *J* = 246.6 Hz, C<sub>f</sub>), 158.56 (d, *J* = 11.1 Hz, C<sub>d</sub>), 130.44 (d, *J* = 6.9 Hz, C<sub>h</sub>), 120.88 (dd, *J* = 15.5, 5.7 Hz, C<sub>g</sub>), 110.78 (d, *J* = 3.3 Hz, C<sub>i</sub>), 102.98 (d, *J* = 25.4 Hz, C<sub>e</sub>), 78.08 (C<sub>b</sub>), 76.12 (C<sub>a</sub>), 59.37 – 58.35 (m, C<sub>j</sub>), 56.23 (C<sub>c</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -117.25 (F<sub>f</sub>).

**<sup>2</sup>H NMR** (77 MHz, CDCl<sub>3</sub>) δ = 4.67 (s, 2H, D<sub>j</sub>).

**MS-ESI(+)**: *m/z* = 165.0 (100, [M-OH]<sup>+</sup>).

### 3.2.3 Synthesis of S8



PCC (549 mg, 2.74 mmol, 5 eq.) and molecular sieves (4 Å, 0.5 g) were added to DCM (2.5 mL) and the mixture cooled in an ice bath. **S7** (100 mg, 0.549 mmol, 1 eq.) was dissolved in DCM (2.5 mL) and the solution was added dropwise to the reaction mixture. The mixture was stirred for 30 min. After warming to room temperature the mixture was stirred for a further 30 min. The mixture was passed through a silica plug using DCM. The collected solution was condensed to give the pure product as an off-white powder (78 mg, 0.435 mmol, 79% yield, 98% D).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 7.83 (t, *J* = 8.5 Hz, 1H, H<sub>h</sub>), 6.85 (d, *J* = 8.8 Hz, 1H, H<sub>i</sub>), 6.74 (d, *J* = 12.1 Hz, 1H, H<sub>e</sub>), 4.76 (s, 2H, H<sub>c</sub>), 2.59 (s, 1H, H<sub>a</sub>).

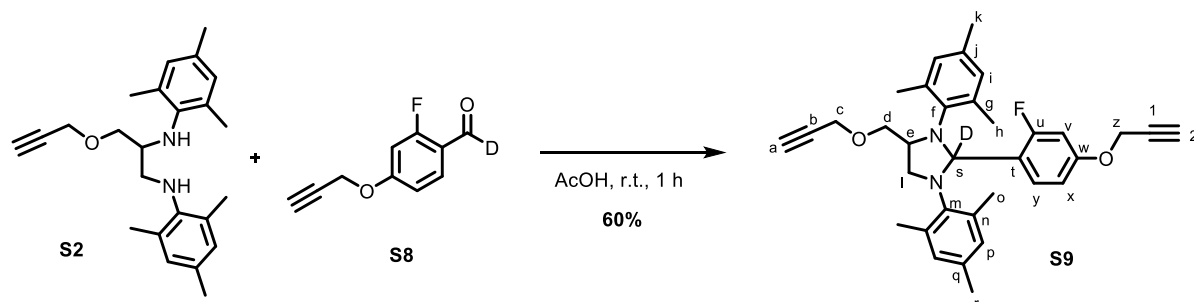
**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 186.13 – 185.31 (m, C<sub>i</sub>), 166.15 (d, *J* = 258.8 Hz, C<sub>f</sub>), 163.95 (d, *J* = 11.8 Hz, C<sub>d</sub>), 130.26 (d, *J* = 3.8 Hz, C<sub>h</sub>), 118.51 (d, *J* = 9.4 Hz, C<sub>g</sub>), 111.97 (C<sub>i</sub>), 102.70 (dd, *J* = 24.5, 4.2 Hz, C<sub>e</sub>), 77.09 (C<sub>b</sub>), 77.03 (C<sub>a</sub>), 56.46 (C<sub>c</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -118.91 (F<sub>f</sub>).

**<sup>2</sup>H NMR** (61 MHz, CDCl<sub>3</sub>) δ = 10.27 (s, 1D, D<sub>j</sub>).

**HRMS-ESI(+)**: 180.0562 [M+H]<sup>+</sup>, calculated for C<sub>10</sub>H<sub>7</sub>DFO<sub>2</sub>: 180.0566.

### 3.2.4 Synthesis of S9



**S2** (100 mg, 0.274 mmol, 1 eq.) was dissolved in minimal acetic acid. **S9** (84 mg, 0.466 mmol, 1.7 eq.) was added and the mixture stirred for 30 min during which a large amount of precipitate formed. The mixture was filtered and the filtered solid thoroughly washed with cold methanol. The filtered white solid was the pure product (87 mg, 0.165 mmol, 60% yield). The extent of protonation at C<sub>s</sub> could not be determined by <sup>1</sup>H NMR but can be assumed to be ≤2% considering the isotopic purity of **S8**.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 7.75 (s, 1H, H<sub>v</sub> or H<sub>x</sub> or H<sub>y</sub>), 6.89 (d, *J* = 2.2 Hz, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.70 (d, *J* = 13.8 Hz, 4H, H<sub>i</sub> + H<sub>p</sub> + H<sub>v</sub> or H<sub>x</sub> or H<sub>y</sub>), 6.27 (d, *J* = 12.0 Hz, 1H, H<sub>v</sub> or H<sub>x</sub> or H<sub>y</sub>), 4.53 (d, *J* = 2.4 Hz, 2H, H<sub>z</sub>), 4.25 – 4.10 (m, 2H, H<sub>c</sub>), 3.90 (dt, *J* = 16.2, 8.8 Hz, 2H, H<sub>d</sub> + H<sub>i</sub>), 3.78 – 3.69 (m, 1H, H<sub>e</sub>), 3.61 (dd, *J* = 8.5, 5.0 Hz, 2H, H<sub>d</sub> + H<sub>i</sub>), 2.54 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.48 (t, *J* = 2.4 Hz, 1H, H<sub>2</sub>), 2.41 (s, 7H, H<sub>a</sub> + H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.21 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.16 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>), 1.79 (s, 3H, H<sub>h</sub> or H<sub>k</sub> or H<sub>o</sub> or H<sub>r</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 162.60 (d, *J* = 247.2 Hz, C<sub>u</sub>), 158.09 (d, *J* = 11.2 Hz, C<sub>w</sub>), 140.34 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 138.42 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 137.15 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 135.83 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 134.89 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 131.82 (d, *J* = 5.8 Hz, C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 130.78 (C<sub>i</sub> or C<sub>p</sub>), 130.53 (br, C<sub>i</sub> or C<sub>p</sub>), 129.40 (br, C<sub>i</sub> or C<sub>p</sub>), 129.19 (C<sub>i</sub> or C<sub>p</sub>), 120.23 (C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 110.78 (C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 101.13 (C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 101.02 (C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 80.06 (C<sub>b</sub>), 78.18 (C<sub>1</sub>), 75.82 (C<sub>2</sub>), 74.49 (C<sub>a</sub>), 73.77 (C<sub>d</sub>), 72.44 (br, C<sub>s</sub>), 61.64 (C<sub>e</sub>), 58.49 (C<sub>c</sub>), 55.99 (C<sub>z</sub>), 52.94 (C<sub>i</sub>), 20.88 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 20.71 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 20.28 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 19.29 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 18.92 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>), 18.43 (C<sub>h</sub> or C<sub>k</sub> or C<sub>o</sub> or C<sub>r</sub>).

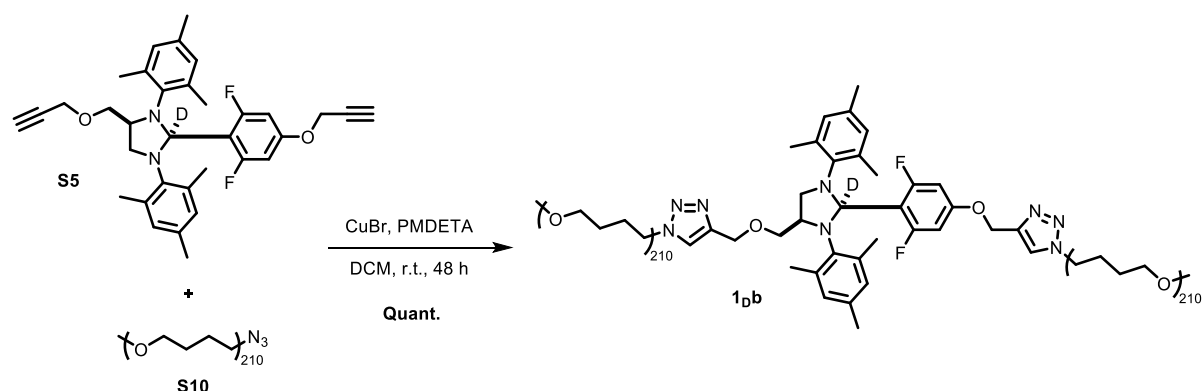
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -121.22 (F<sub>u</sub>).

**<sup>2</sup>H NMR** (61 MHz, CHCl<sub>3</sub>) δ = 6.23 (br, 1D, D<sub>s</sub>).

**HRMS-APCI(+)**: 526.2963 [M+H]<sup>+</sup>, calculated for C<sub>34</sub>H<sub>37</sub>DFO<sub>2</sub>N<sub>2</sub>: 526.2975.

## 4 Synthesis of Polymers:

### 4.1 Representative procedure: synthesis of 1<sub>Db</sub>



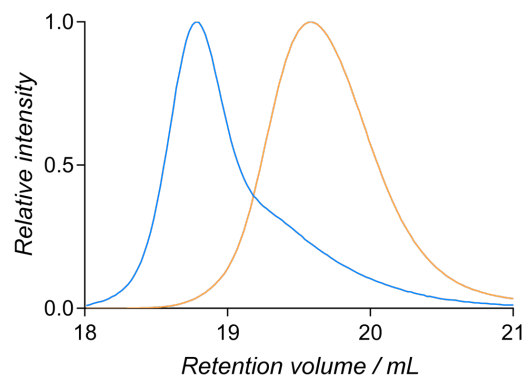
**S10** (240 mg, 16  $\mu$ mol, 2.5 eq.) and **S5** (3.5 mg, 6  $\mu$ mol, 1.0 eq.) were dissolved in DCM (20 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (1 mL) and PMDETA (23  $\mu$ L, 110  $\mu$ mol, 18.0 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (10 mg, 72  $\mu$ mol, 12.0 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer was carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

### 4.2 List of polymers

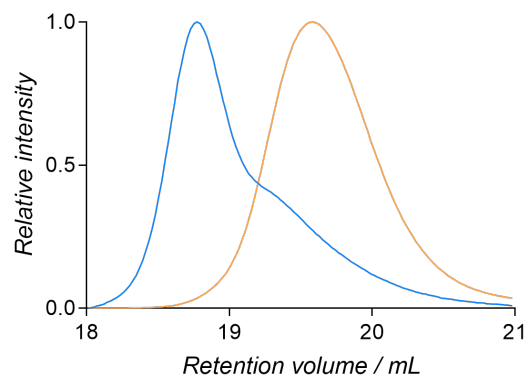
All polymers were analysed using GPC with the obtained results visible in *Table S1* and *Figures S1 – S6*. It should be noted that in the time between when GPC analysis was carried out for polymers **1<sub>Ha</sub>**/**1<sub>Da</sub>** and polymers **1<sub>Hb</sub>**/**1<sub>Db</sub>**/**1<sub>Hc</sub>**/**1<sub>Dc</sub>** the instrument's columns and calibrations were changed while polymer **1** was analysed using both configurations; this accounts for the visual discrepancy between GPC traces observed in *Figures S1 – S6*.

**Table S1.**  $M_n$  and  $\bar{D}$  values for polymers **1<sub>xa-c</sub>** and **S10** as measured by GPC.

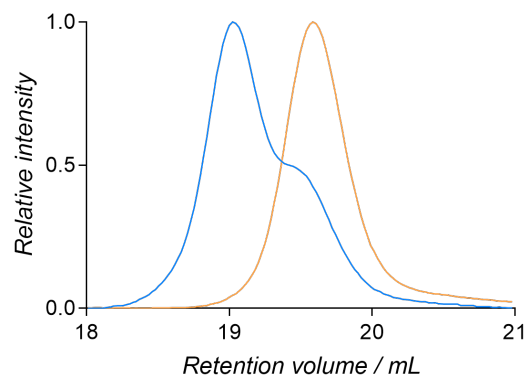
Polymer	$M_n$ (GPC) / kDa	$\bar{D}$
<b>S10</b>	47.0	1.12
<b>1<sub>Ha</sub></b>	78.4	1.12
<b>1<sub>Da</sub></b>	72.9	1.20
<b>1<sub>Hb</sub></b>	72.4	1.14
<b>1<sub>Db</sub></b>	74.2	1.13
<b>1<sub>Hc</sub></b>	72.7	1.14
<b>1<sub>Dc</sub></b>	71.6	1.15



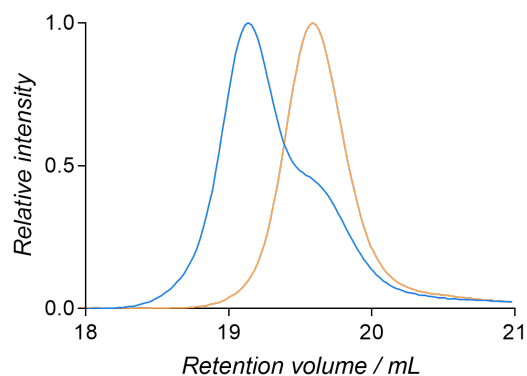
**Figure S1.** GPC traces showing polymers **1<sub>Ha</sub>** (left) and **S10** (right).



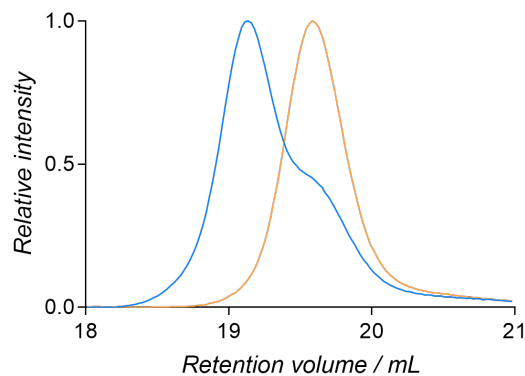
**Figure S2.** GPC traces showing polymers **1<sub>Pa</sub>** (left) and **S10** (right).



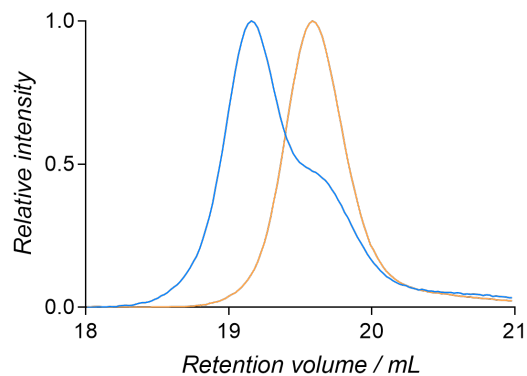
**Figure S3.** GPC traces showing polymers **1<sub>Hb</sub>** (left) and **S10** (right).



**Figure S4.** GPC traces showing polymers **1<sub>Pb</sub>** (left) and **S10** (right).



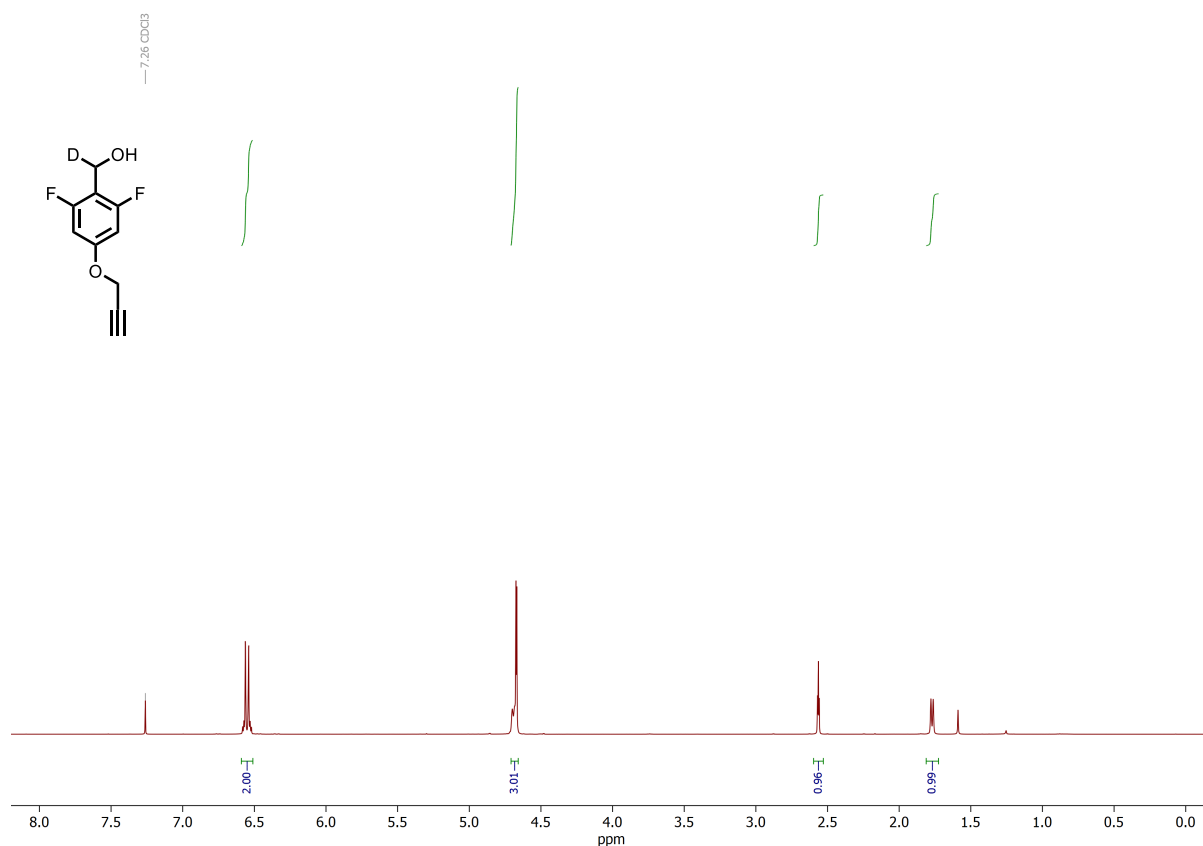
**Figure S5.** GPC traces showing polymers **1<sub>Hc</sub>** (left) and **S10** (right).



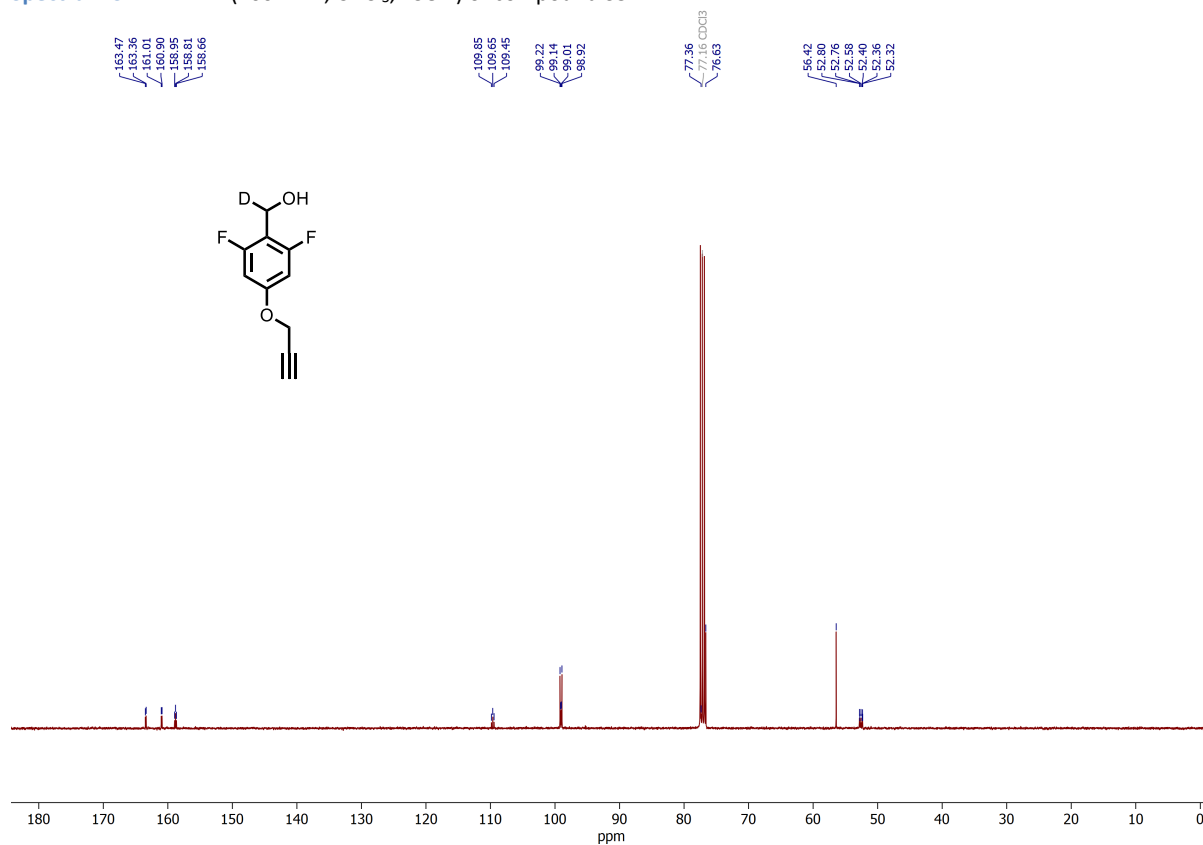
**Figure S6.** GPC traces showing polymers **1<sub>Pc</sub>** (left) and **S10** (right).

## 5 NMR Spectra

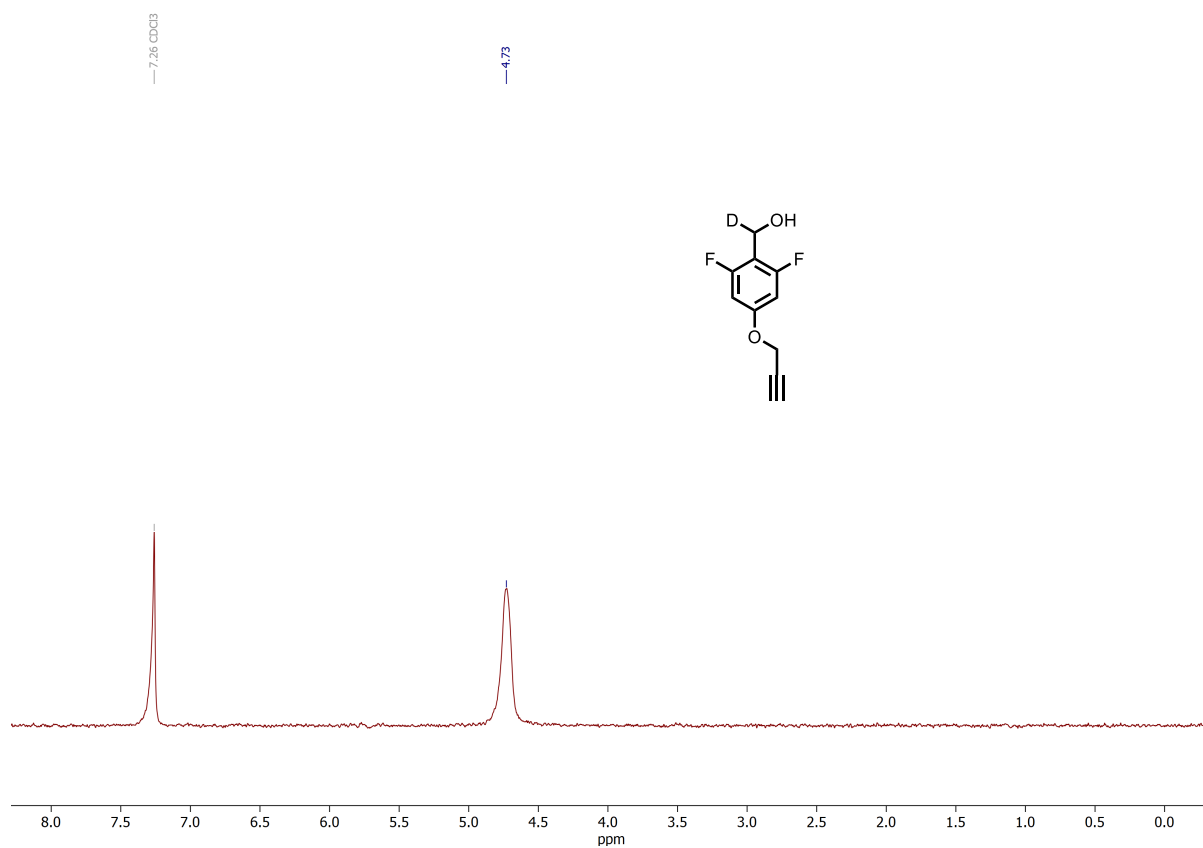
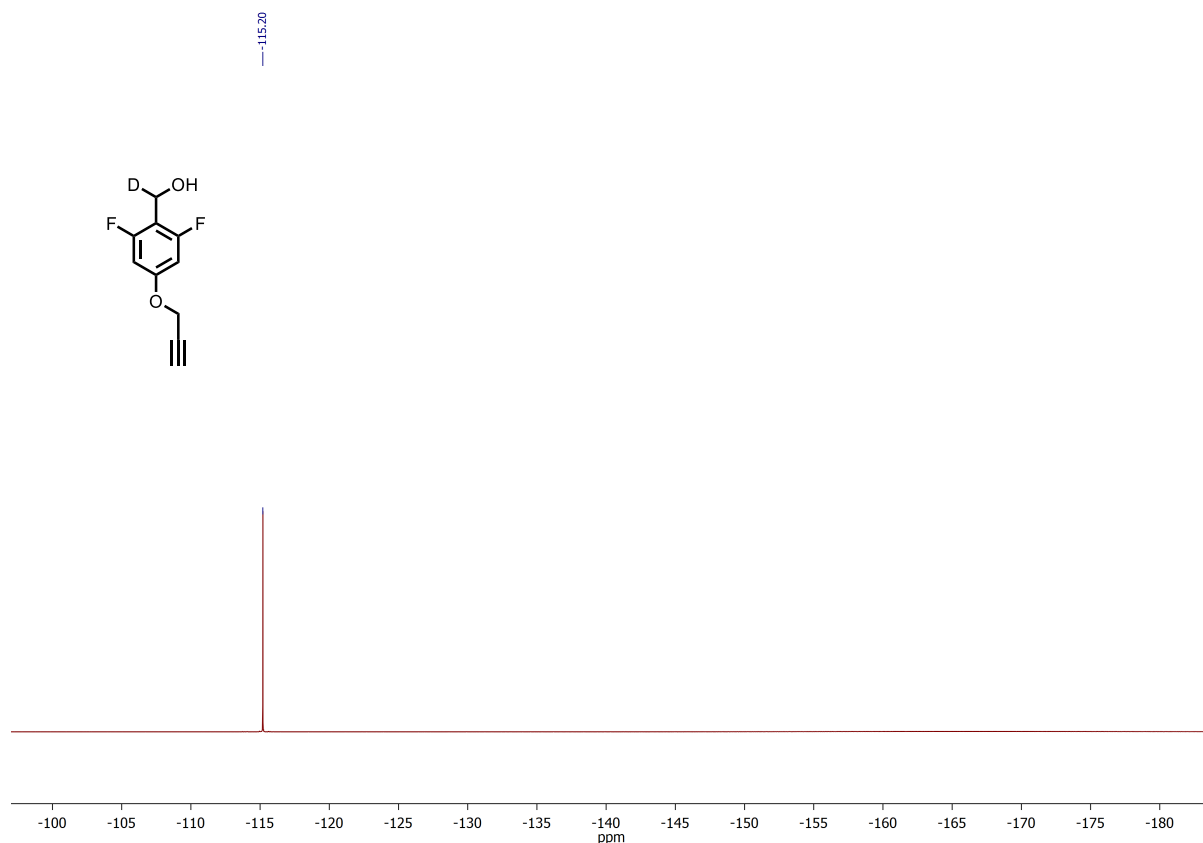
### 5.1 Spectra of S3



**Spectrum S1.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound **S3**.

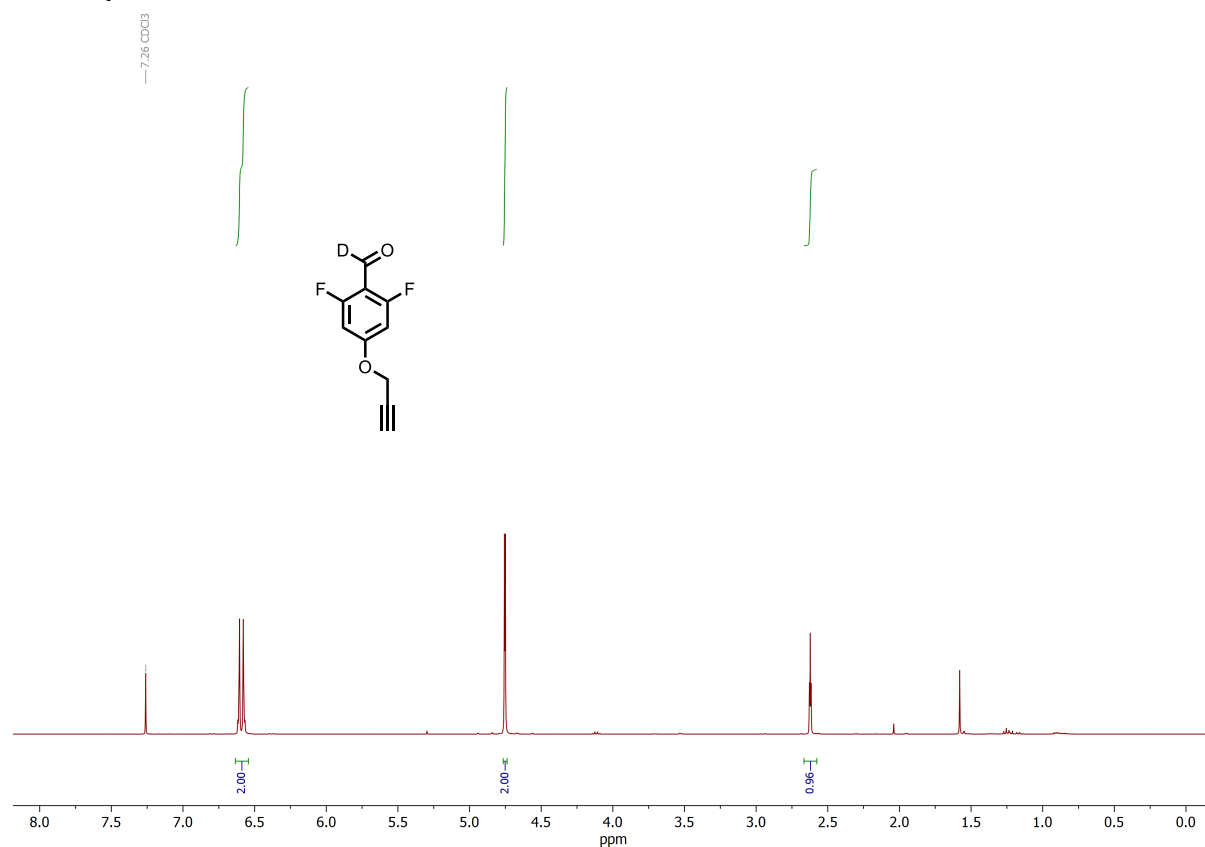


**Spectrum S2.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K) of compound **S3**.

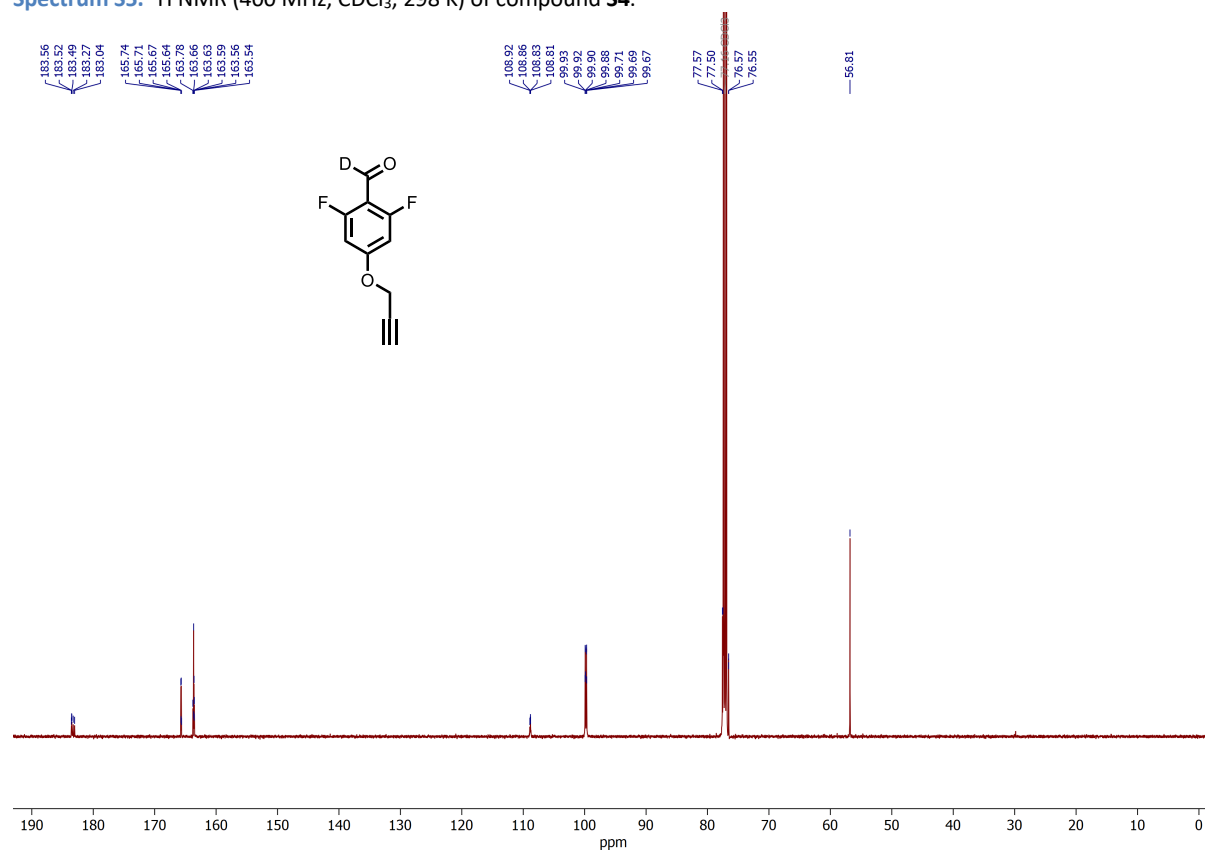




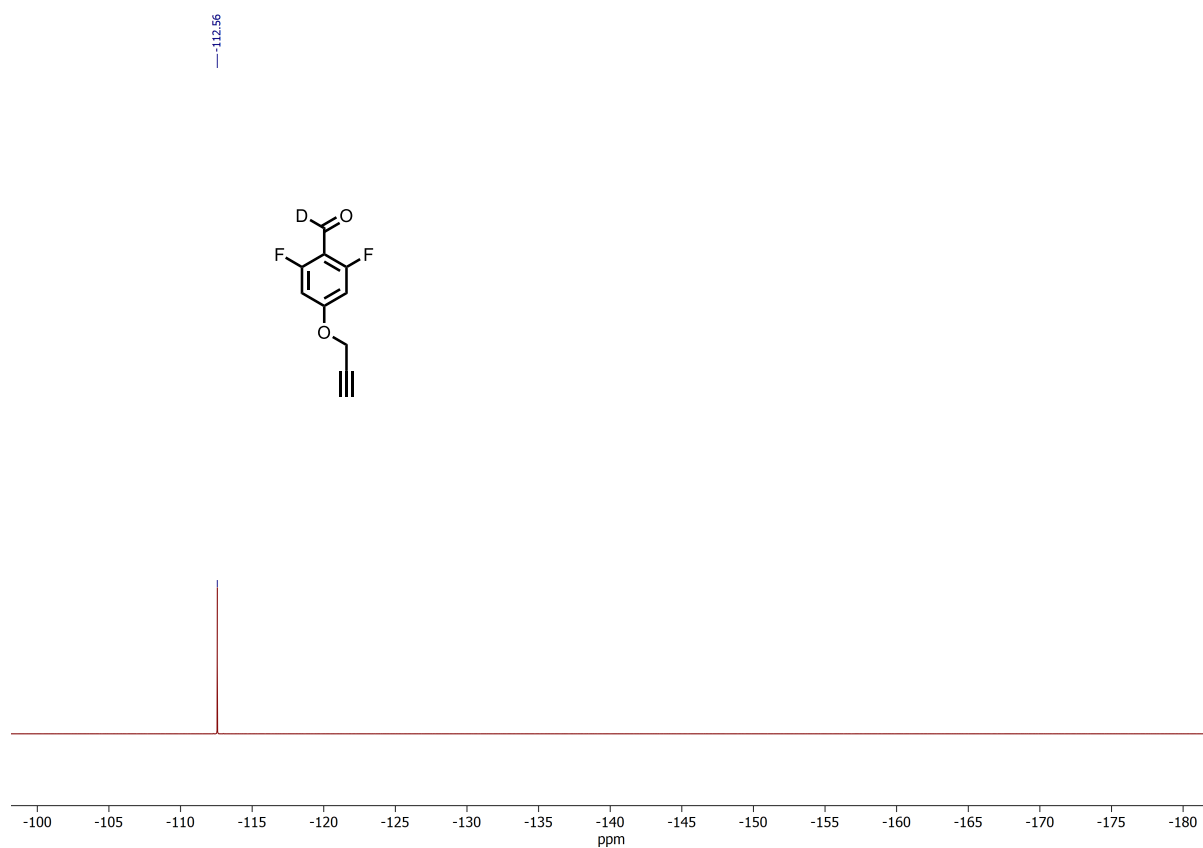
## 5.2 Spectra of S4



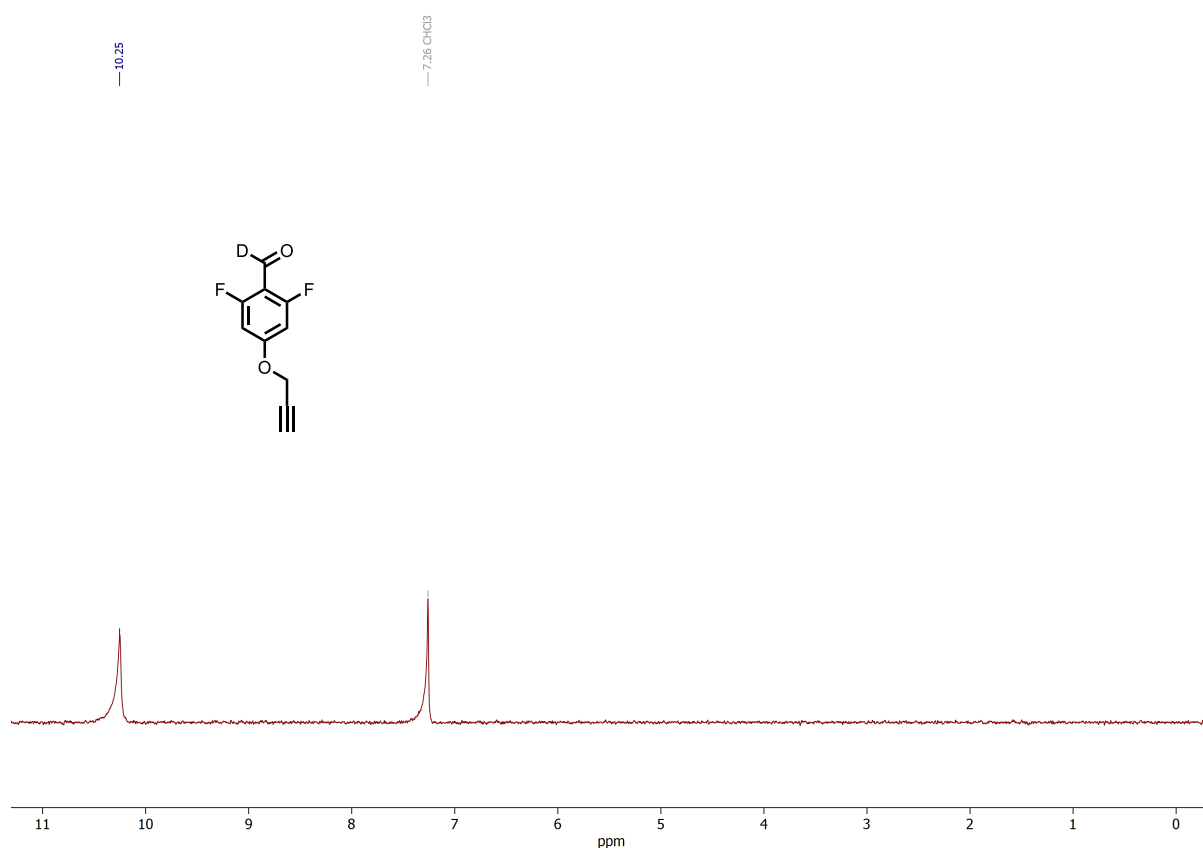
**Spectrum S5.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound **S4**.



**Spectrum S6.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K) of compound **S4**.

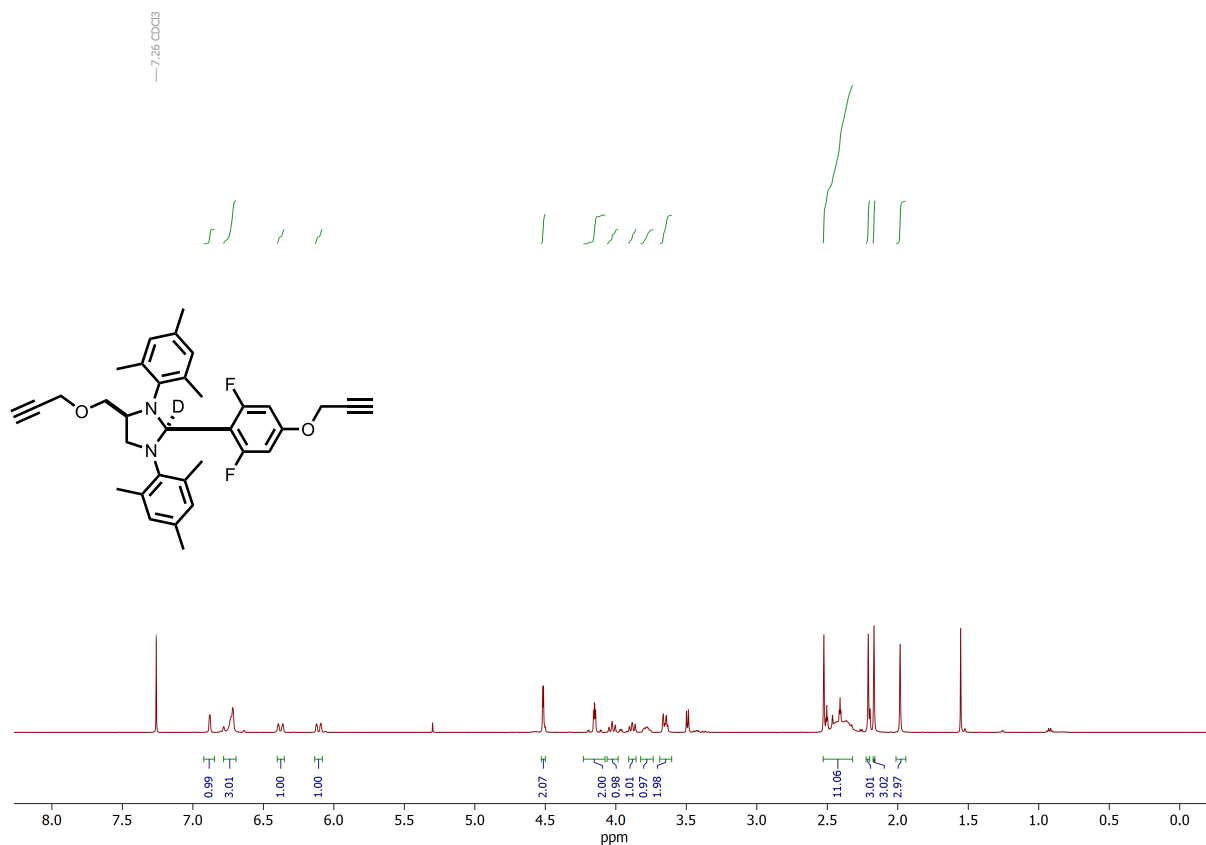


**Spectrum S7.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S4**.

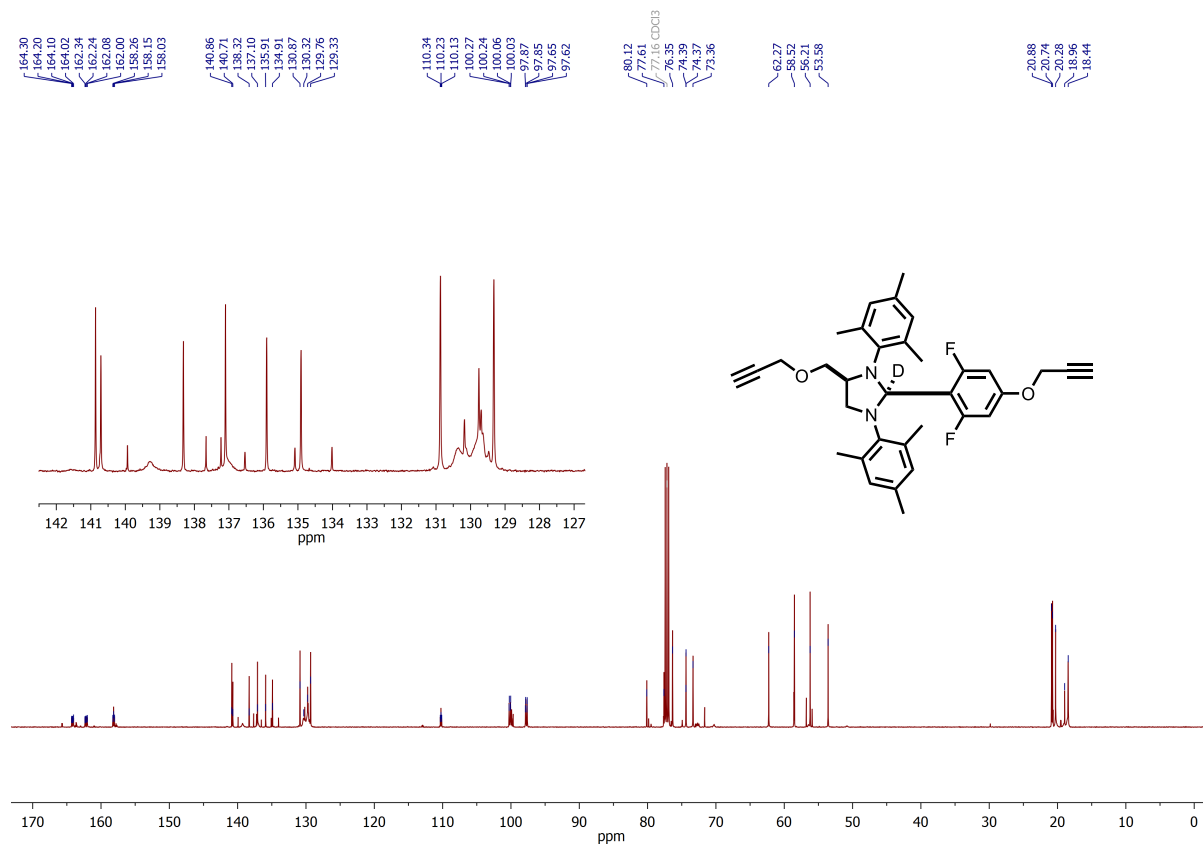


**Spectrum S8.**  $^2\text{H}$  NMR (61 MHz,  $\text{CHCl}_3$ , 298 K) of compound **S4**.

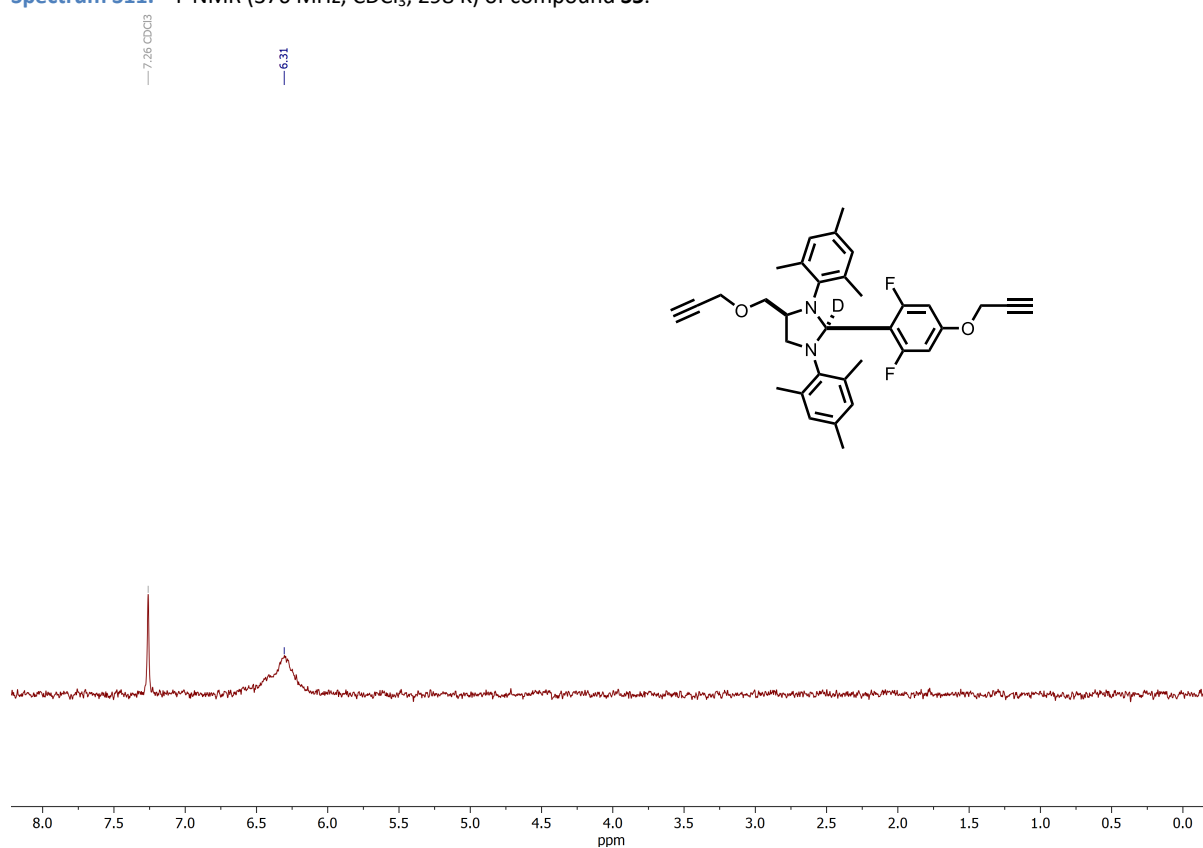
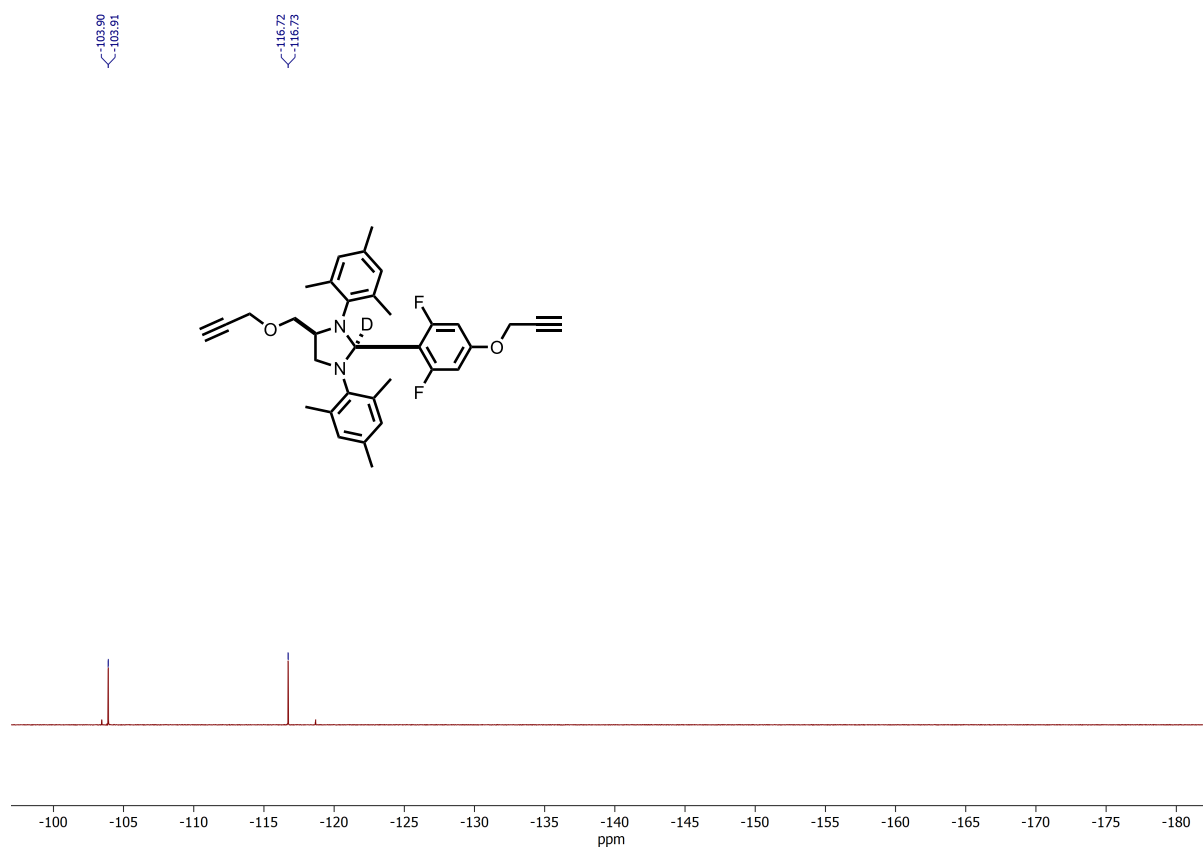
### 5.3 Spectra of S5



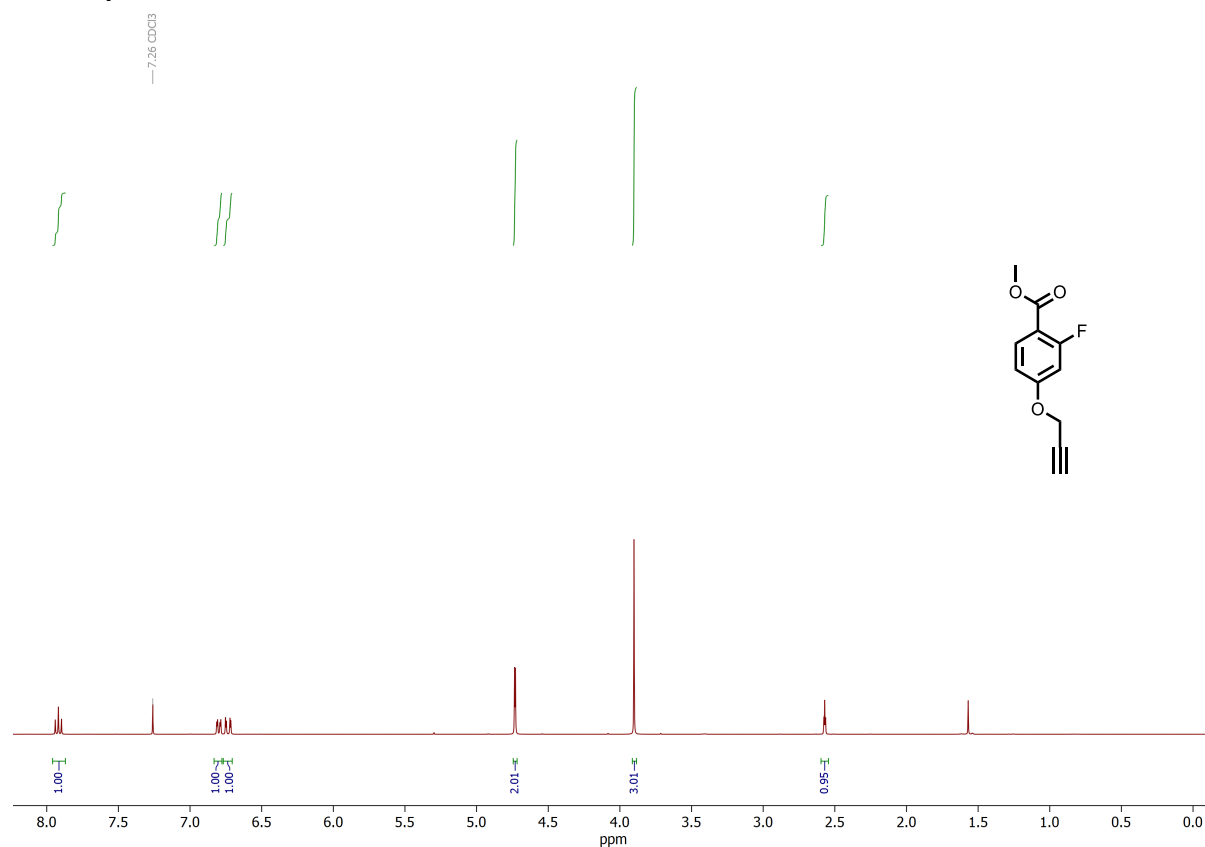
**Spectrum S9.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **S5**.



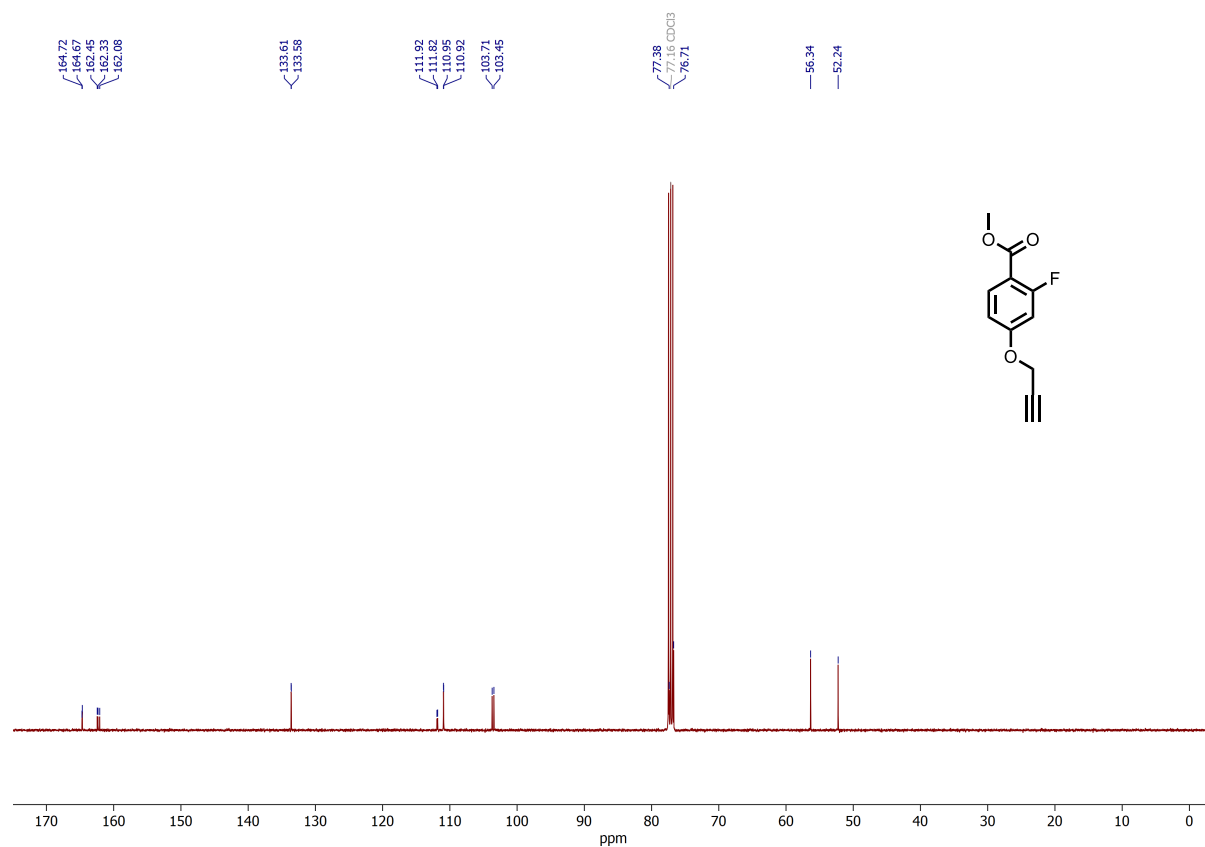
**Spectrum S10.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S5**.



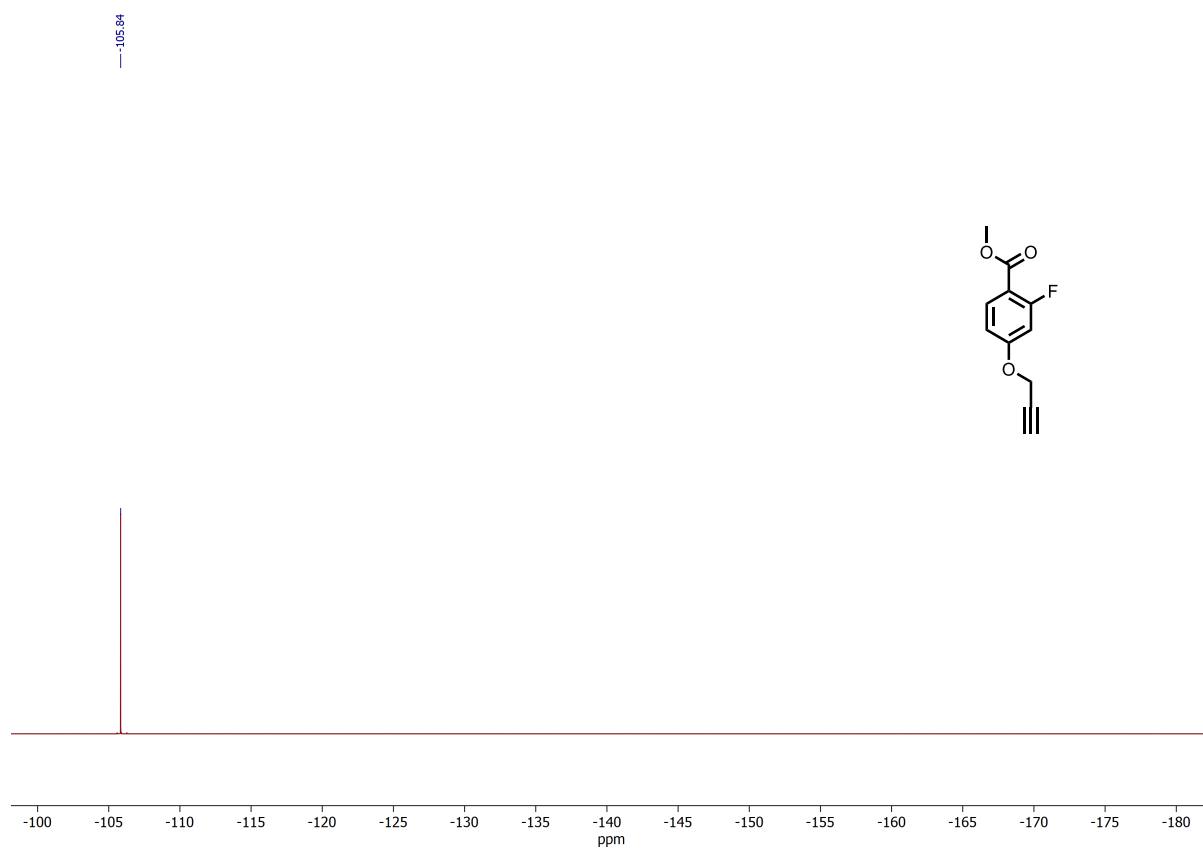
## 5.4 Spectra of S6



**Spectrum S13.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound S6.

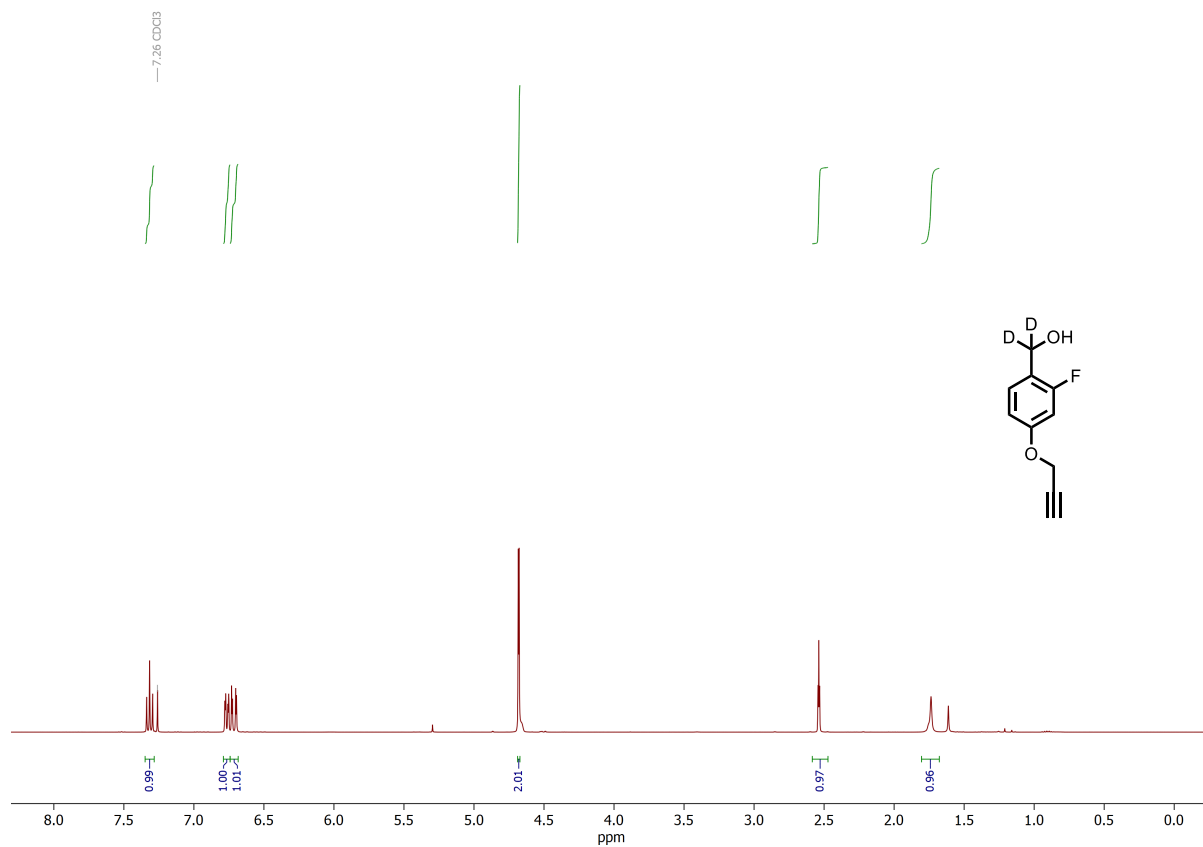


**Spectrum S14.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound S6.

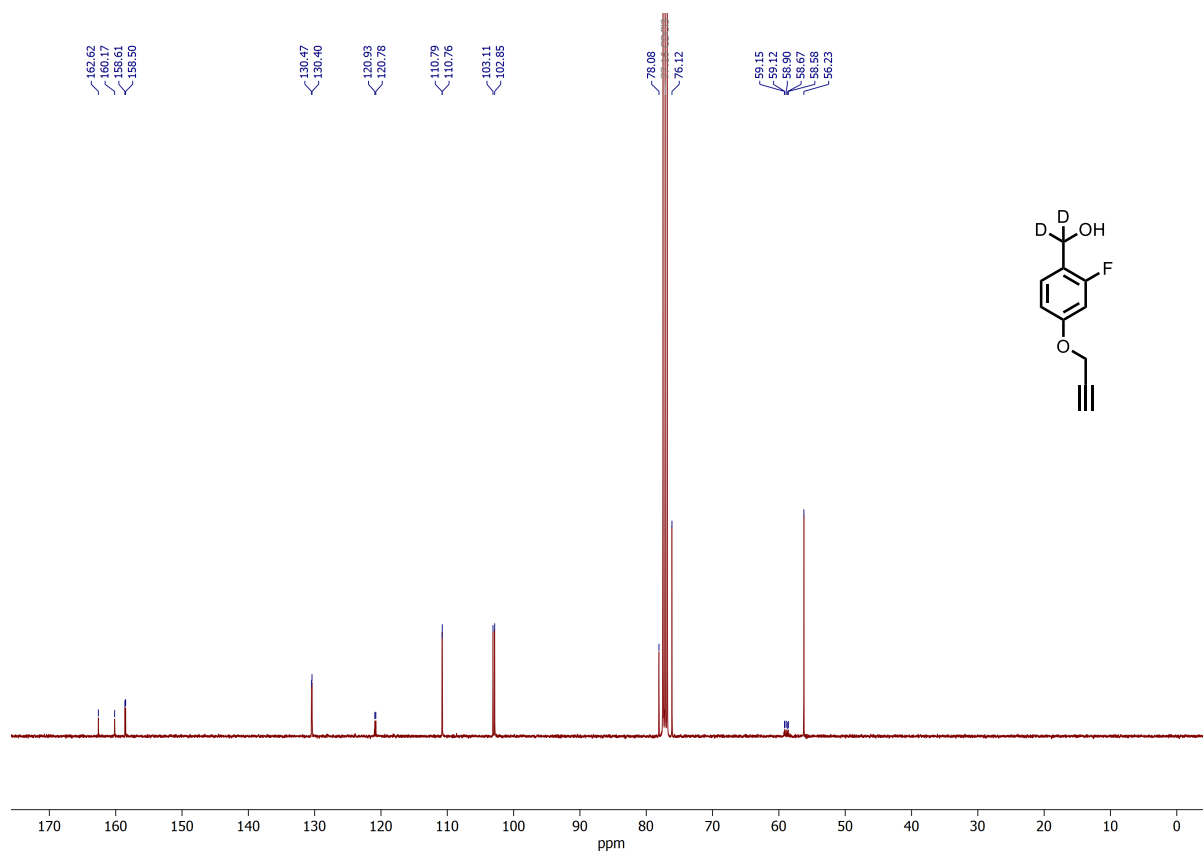


**Spectrum S15.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **S6**.

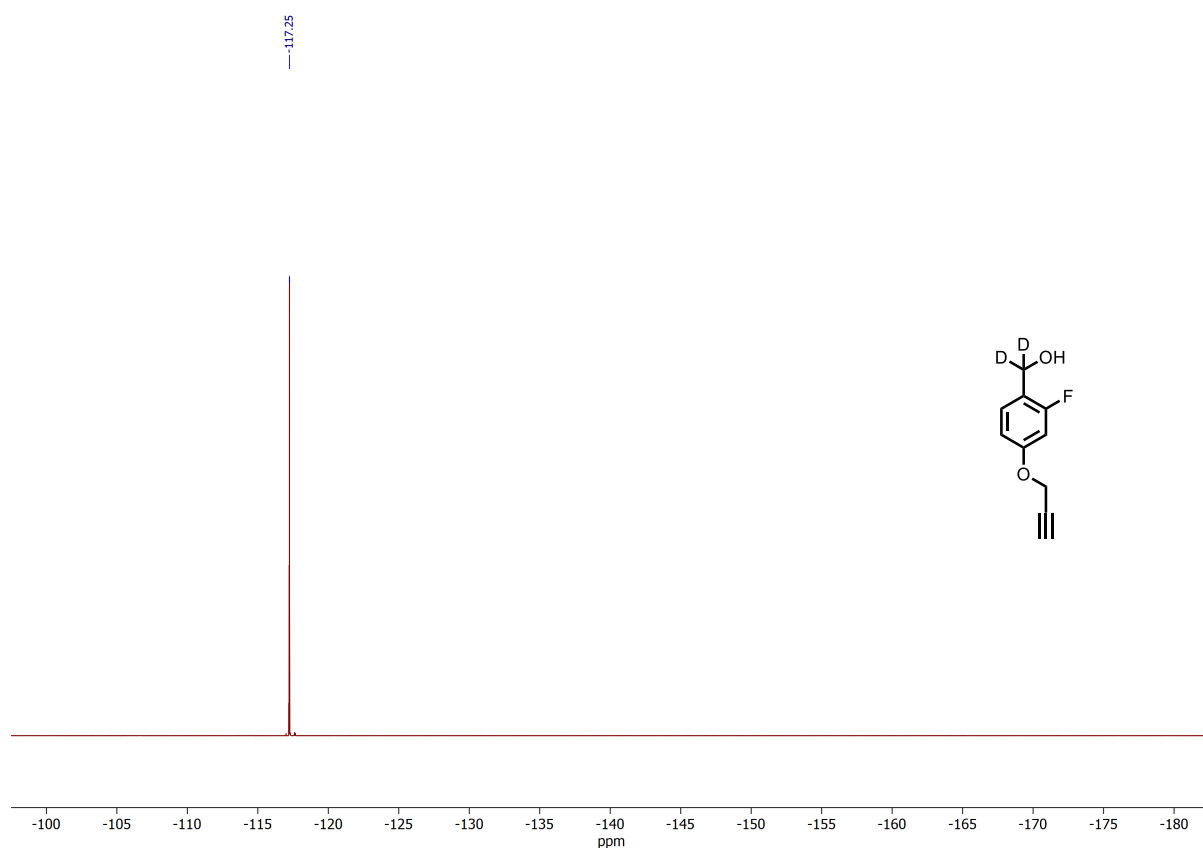
## 5.5 Spectra of S7



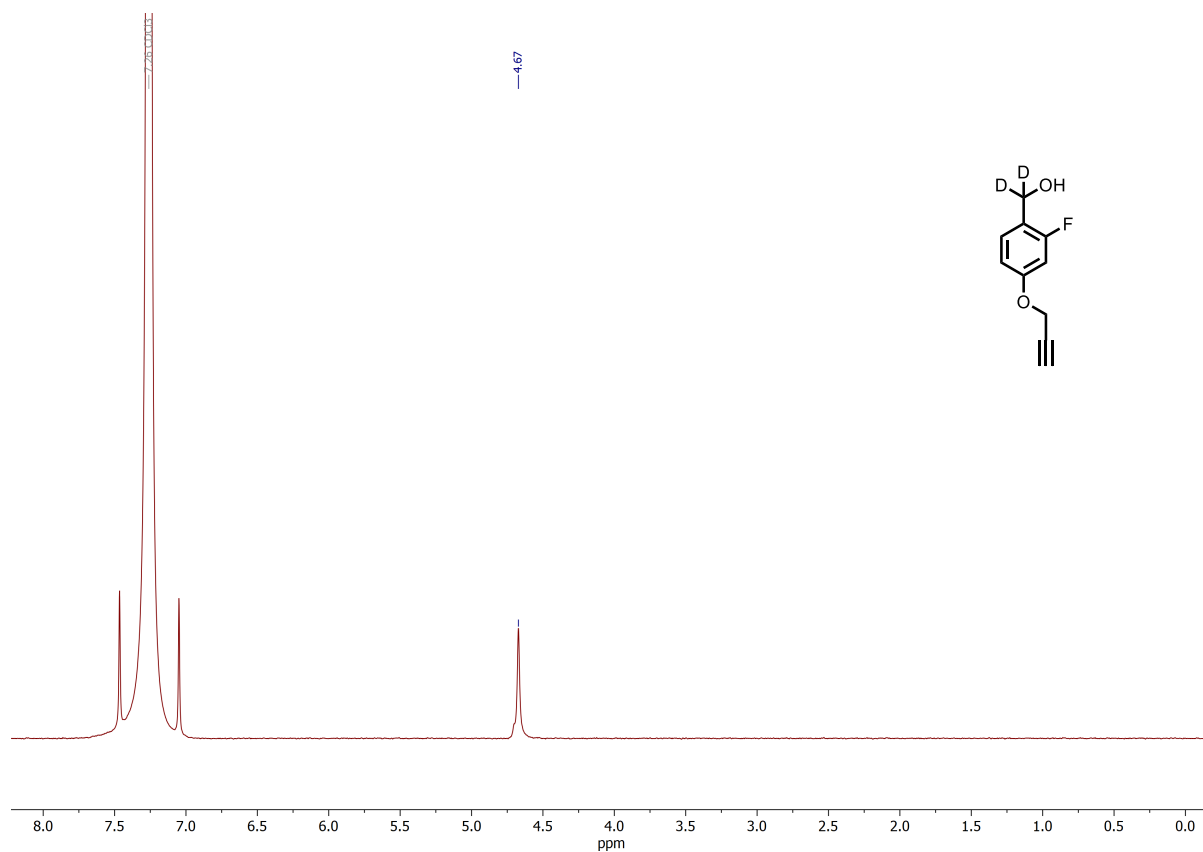
**Spectrum S16.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound **S7**.



**Spectrum S17.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S7**.

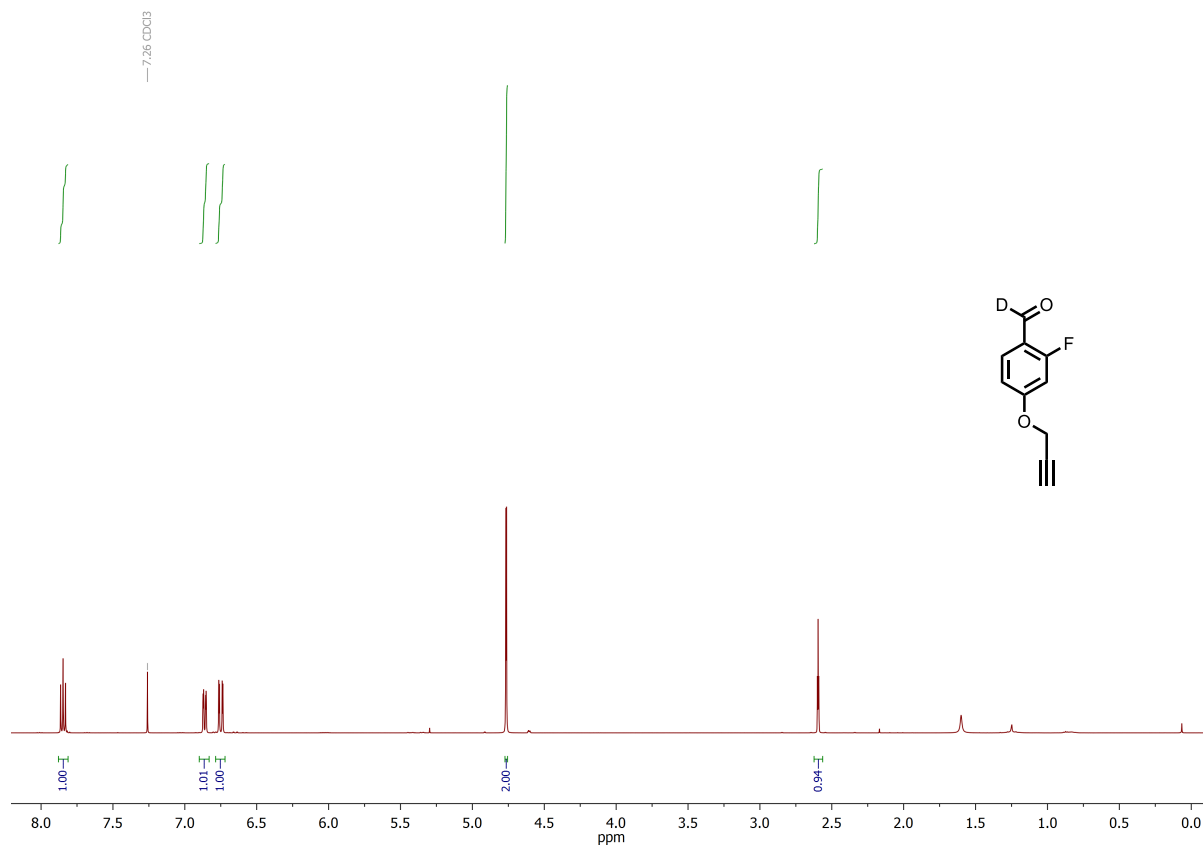


**Spectrum S18.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S7**.



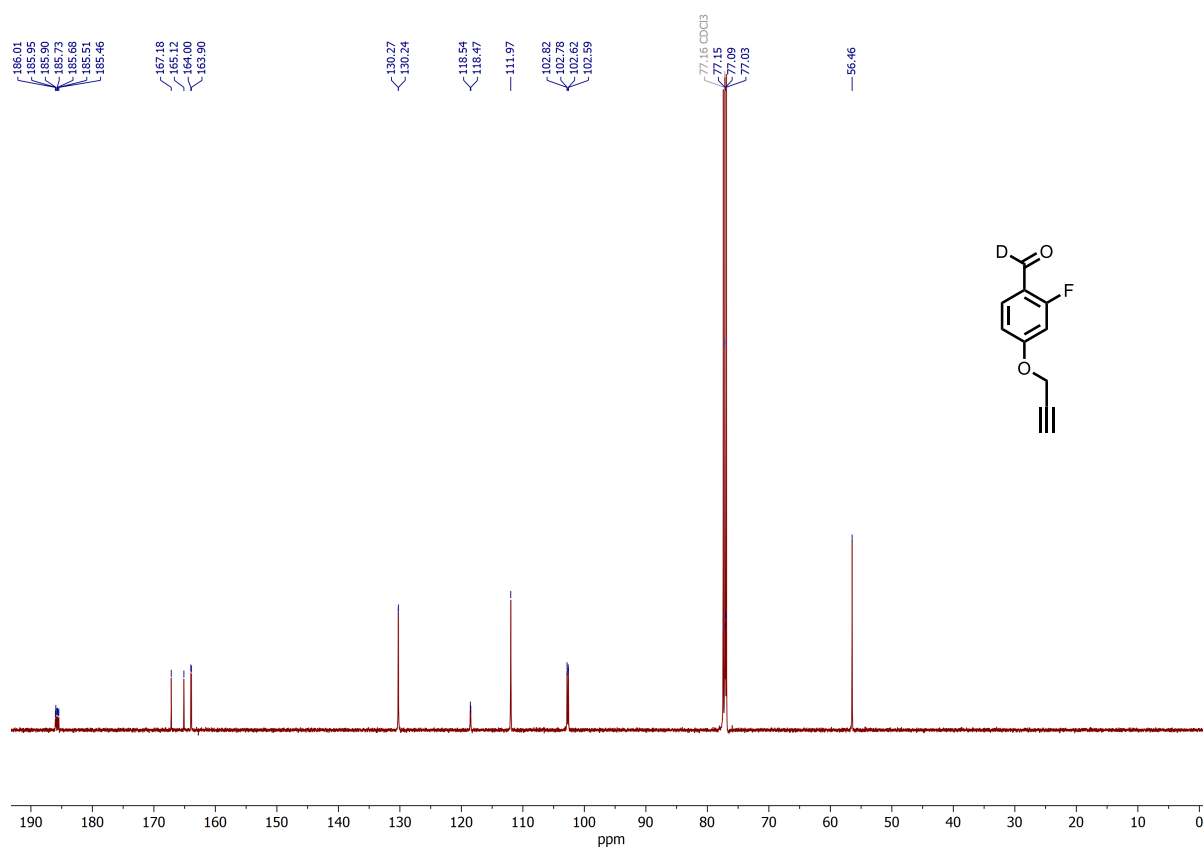
**Spectrum S19.**  $^2\text{H}$  NMR (77 MHz,  $\text{CHCl}_3$ , 298 K) of compound **57**.

## 5.6 Spectra of S8

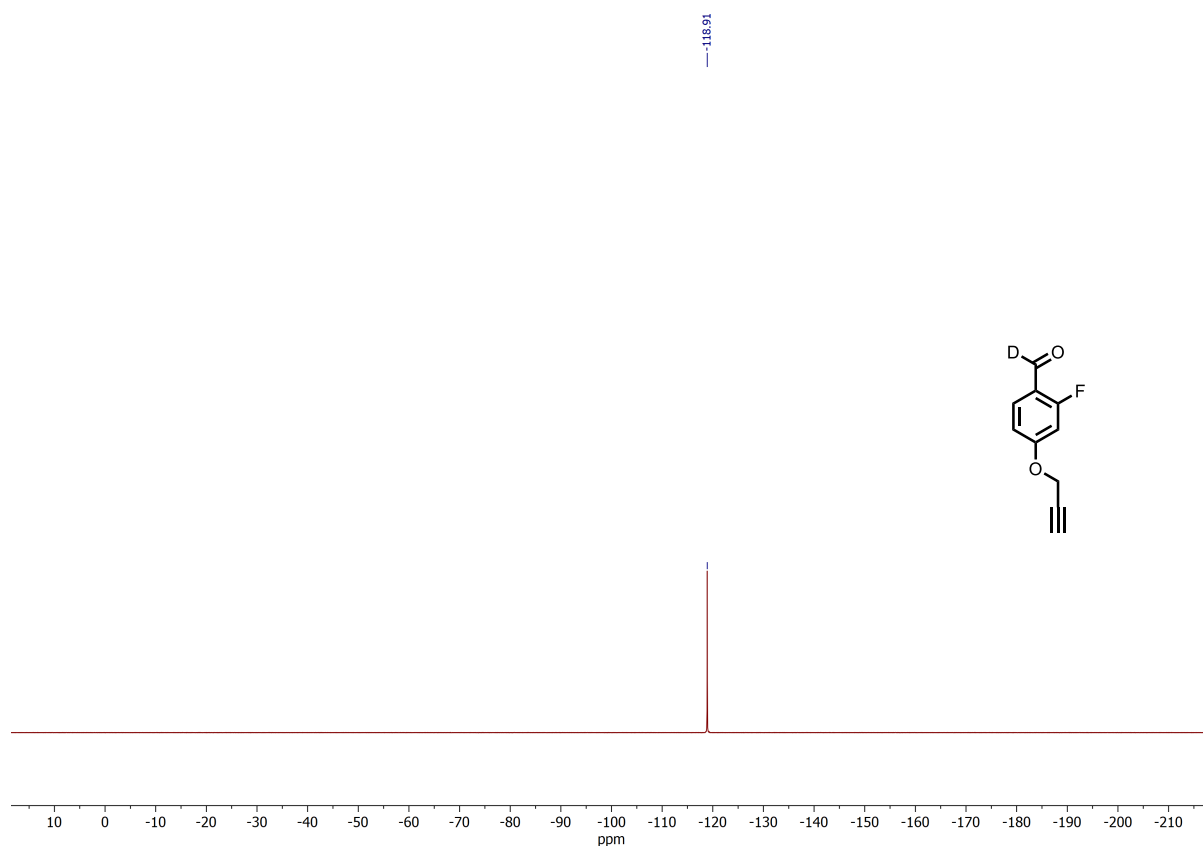


**Spectrum S20.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of compound **58**.

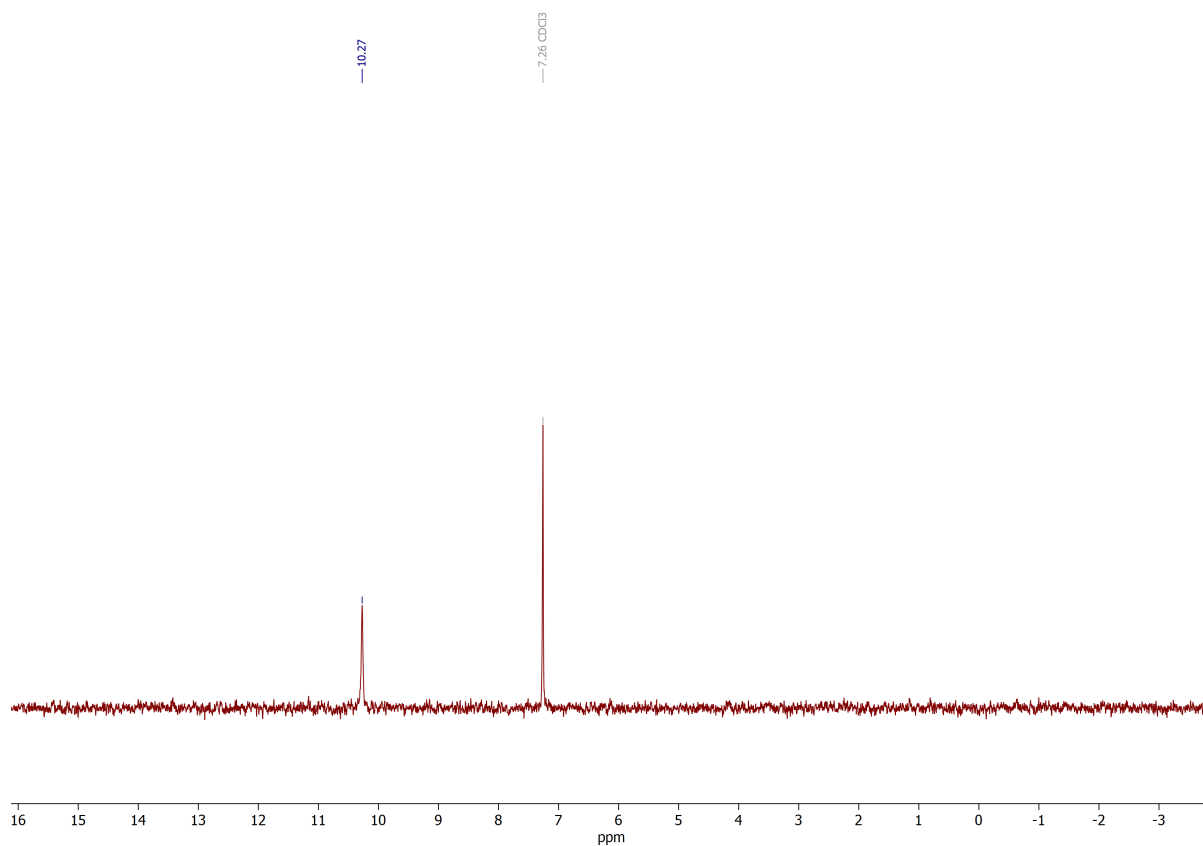




**Spectrum S21.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S8**.

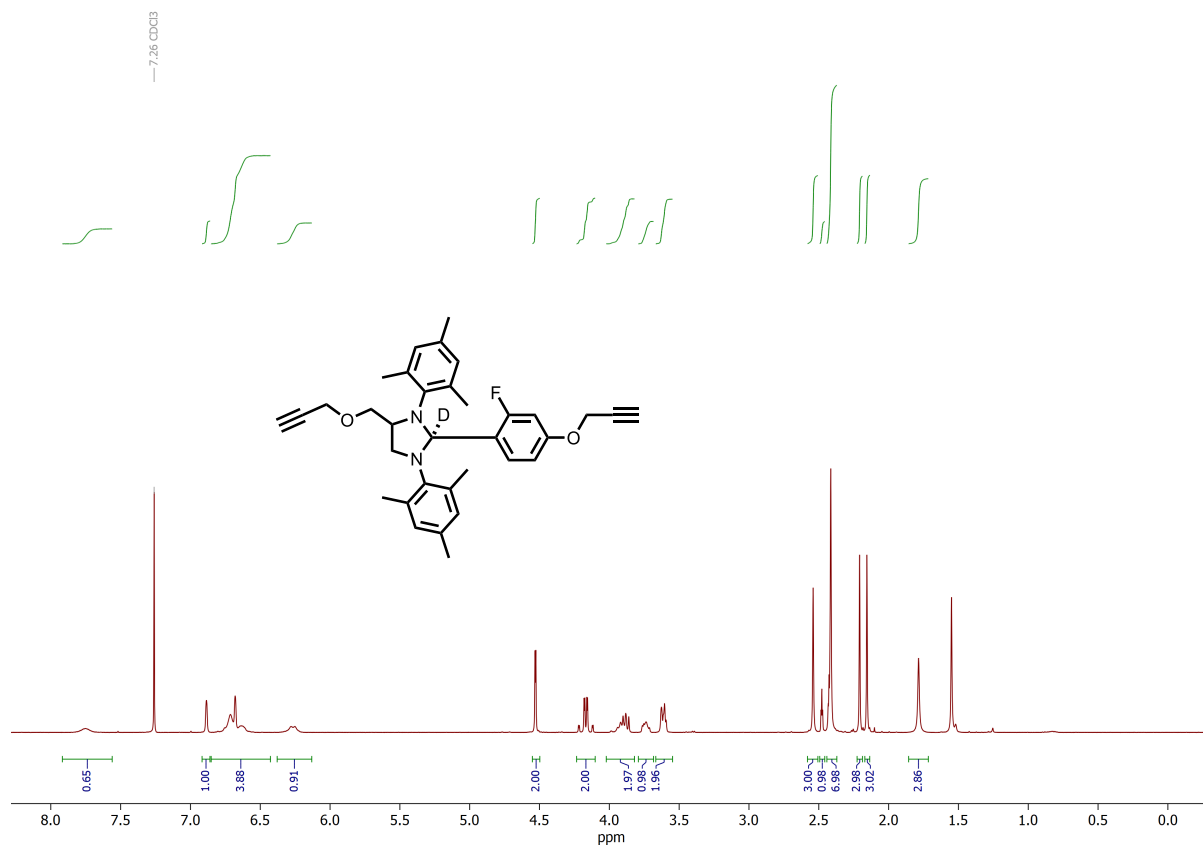


**Spectrum S22.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **S8**.

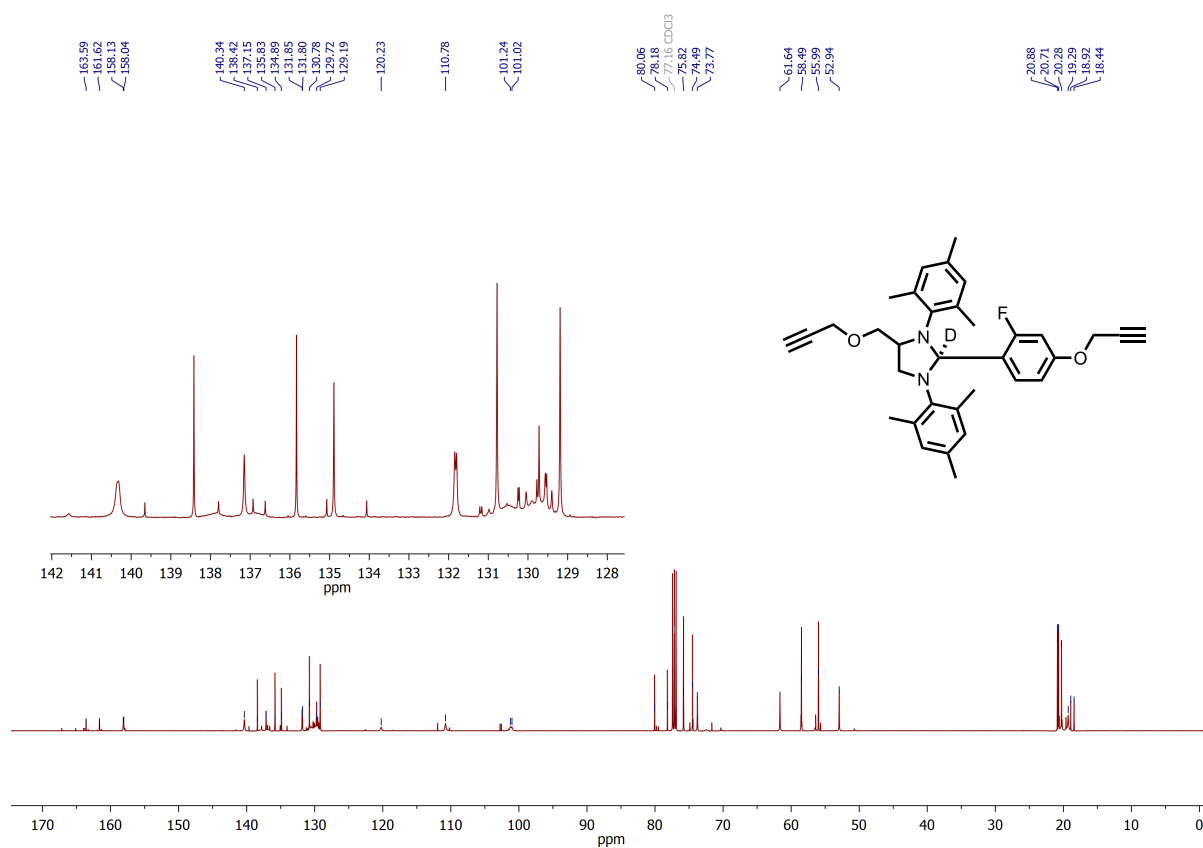


**Spectrum S23.** <sup>2</sup>H NMR (77 MHz, CHCl<sub>3</sub>, 298 K) of compound **58**.

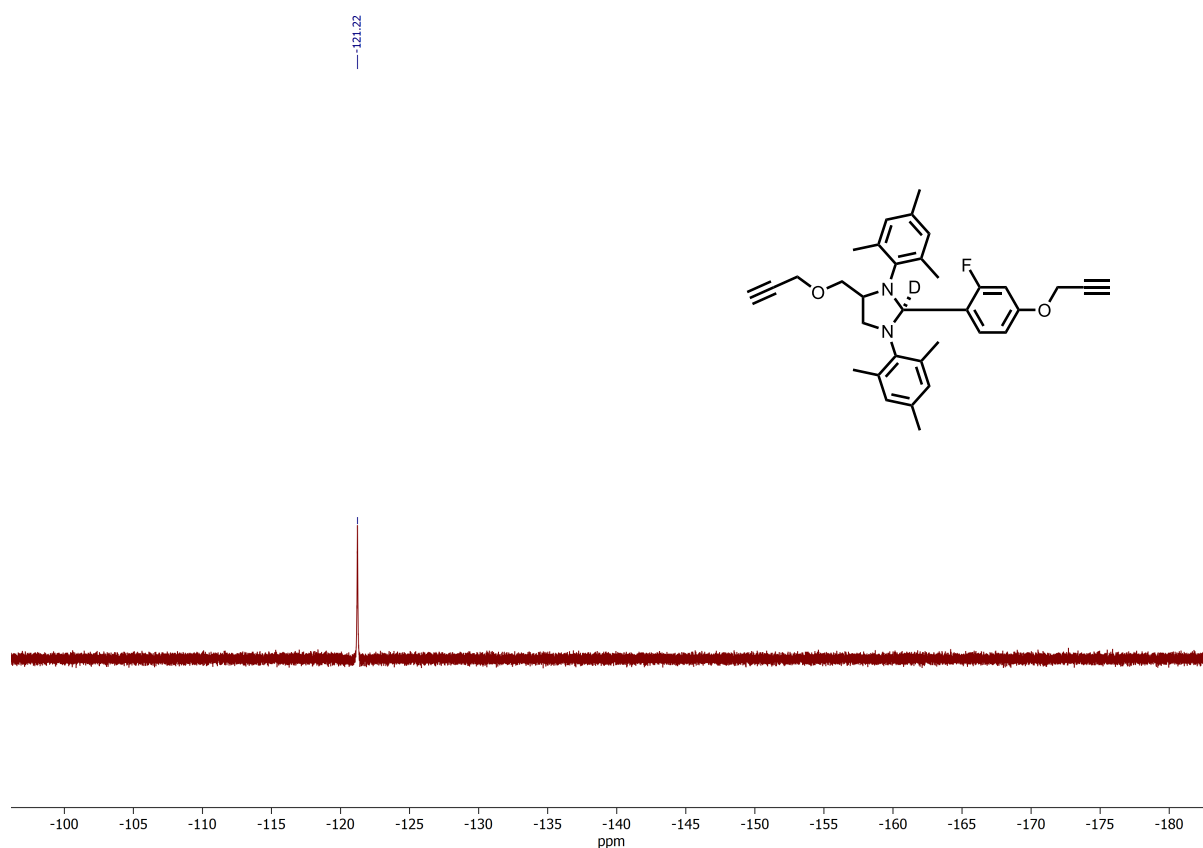
## 5.7 Spectra of S9



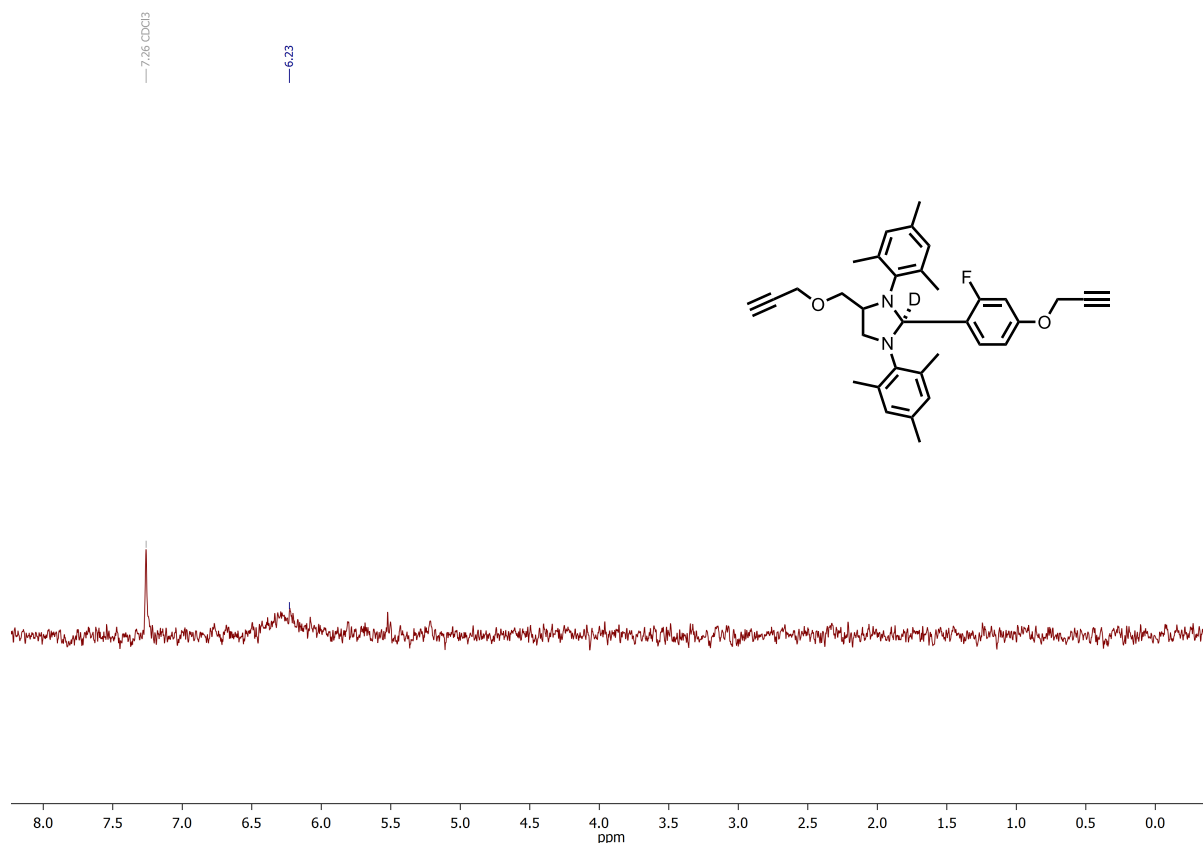
**Spectrum S24.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **S9**.



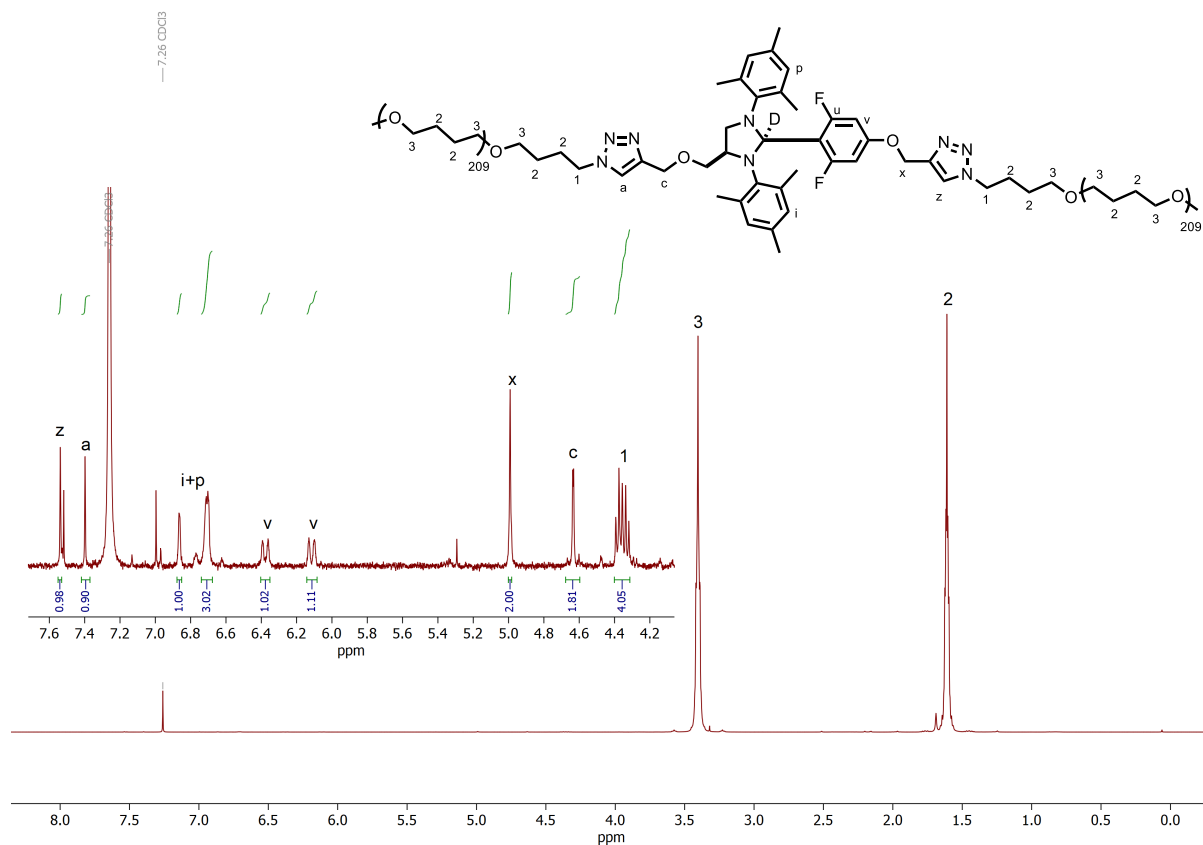
**Spectrum S25.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S9**.

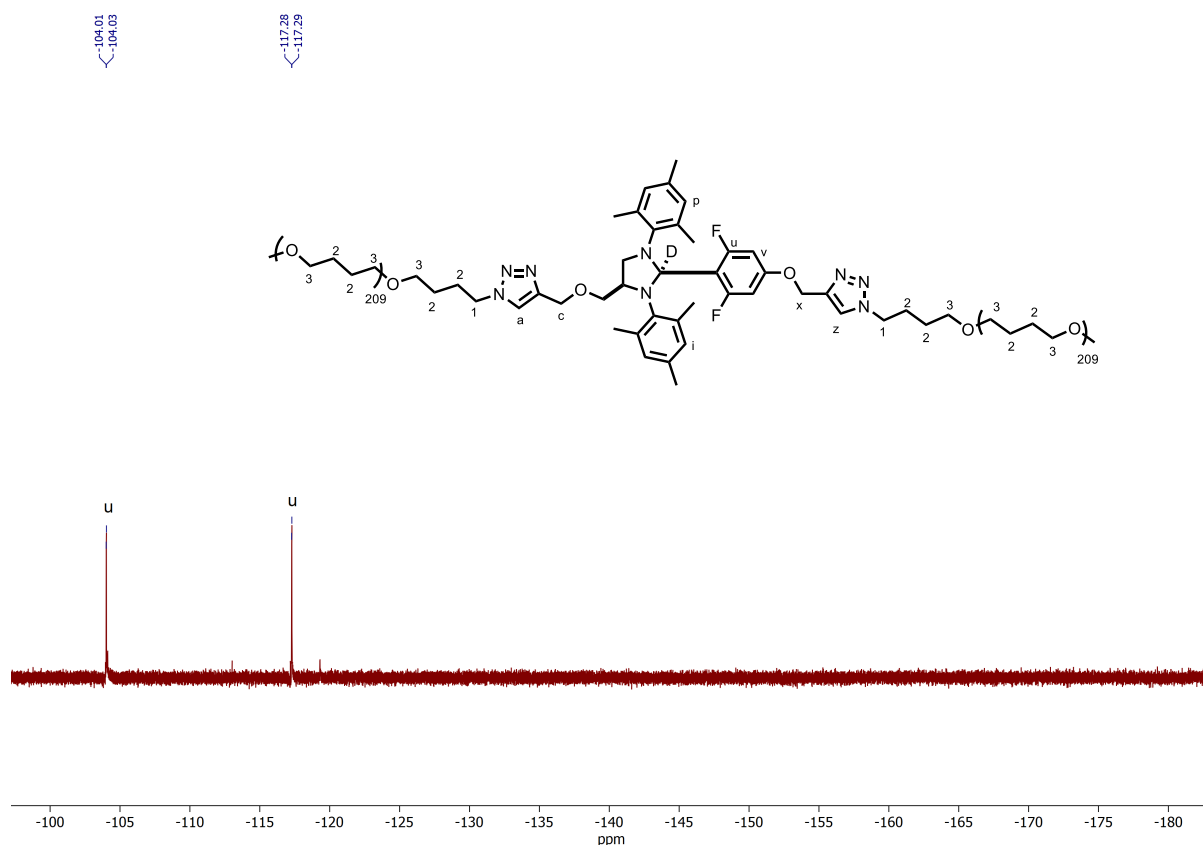


**Spectrum S26.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **S9**.

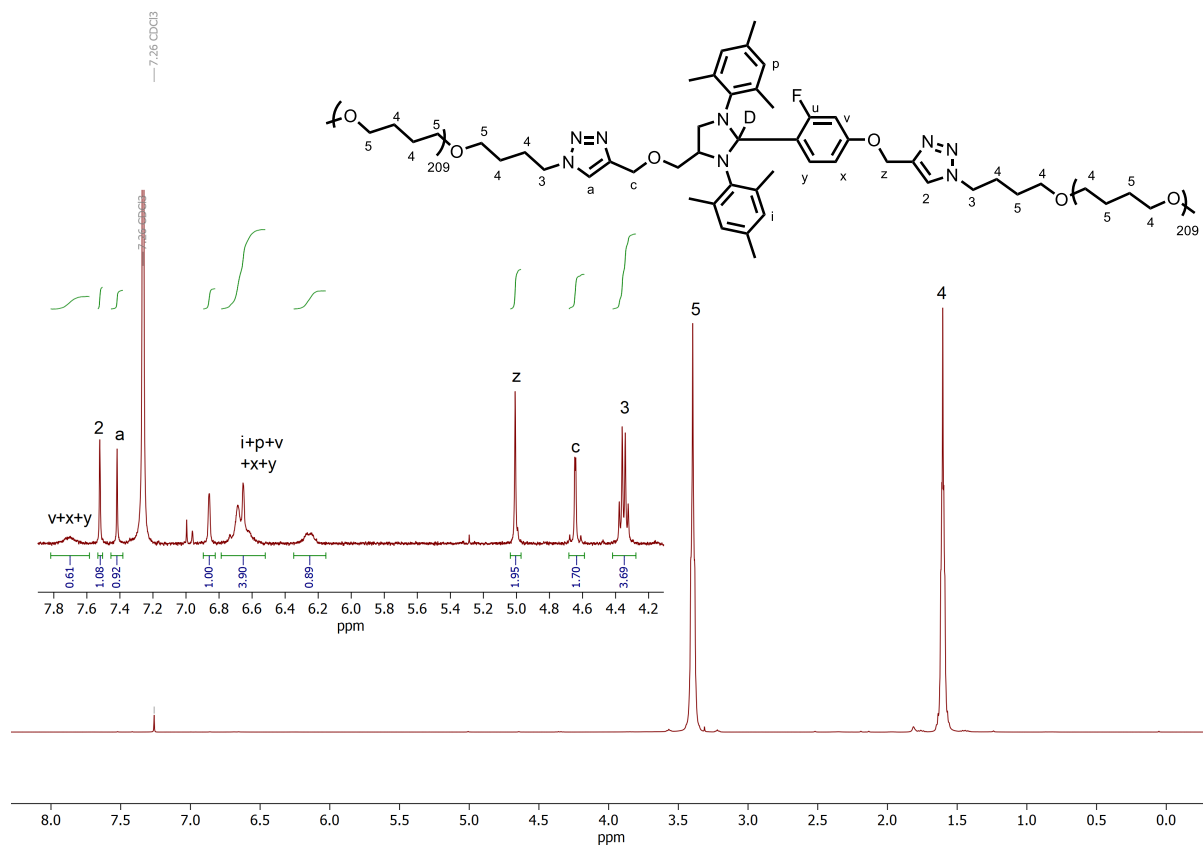


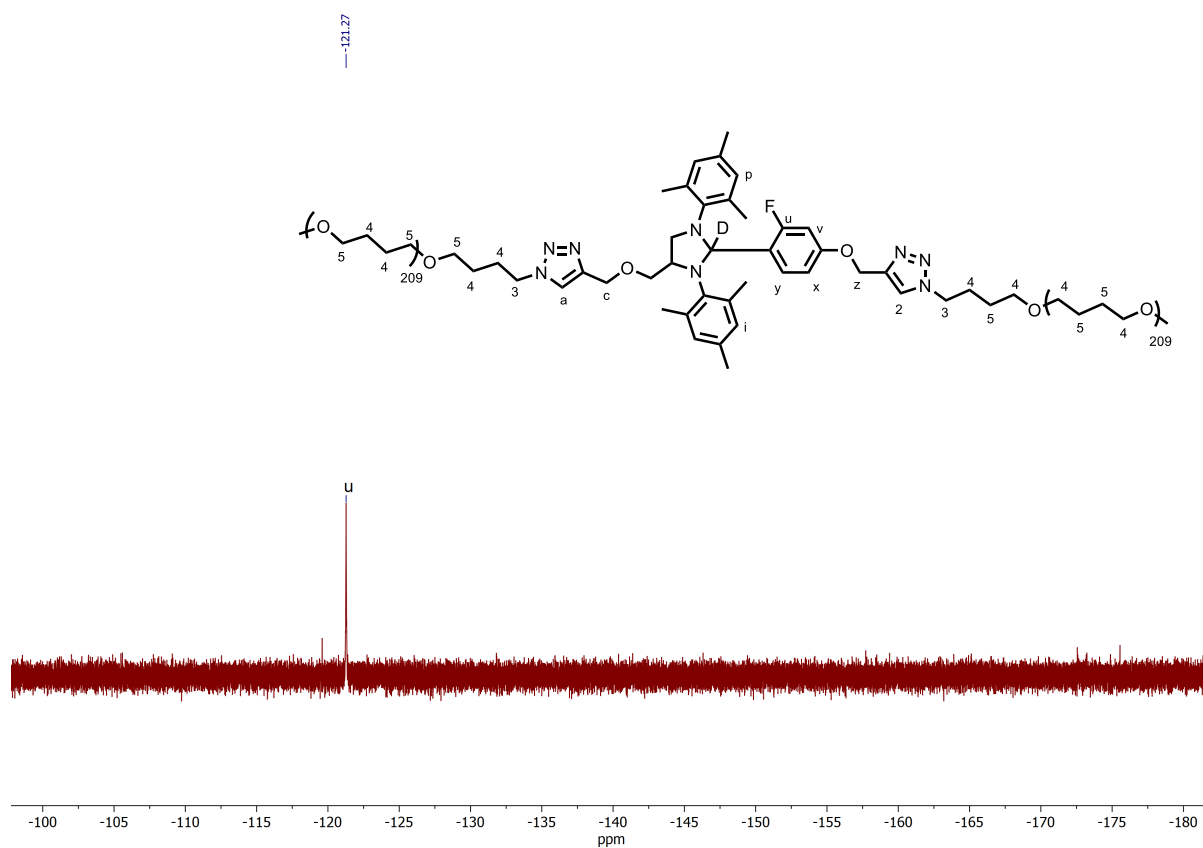
## 5.8 Spectra of **1<sub>D</sub>b**





## 5.9 Spectra of **1dc**





## 6 Sonication Experiments

All experiments were carried out using the same sonication conditions (20 KHz, 15.6 W cm<sup>-2</sup>, 1 s ON / 1 s OFF, 5 – 10 °C). Some experiments previously reported by us,<sup>1</sup> are marked with the corresponding reference and reproduced here to give a complete picture of the mechanophores' reactivity.

### 6.1 Standard Sonication Procedure

The desired polymer (45 mg) was dissolved in the specified solvent mixture (approx. 15 mL) and added to a modified Suslick cell. Nitrogen was gently bubbled through the solution as it was sonicated. After 180 min of sonication time, the mixture was undisturbed for 24 h to allow metal impurities to settle to the bottom of the cell. The solution was then carefully decanted to remove such impurities and condensed to give the crude polymer. After drying under high vacuum for an extended period of time (approximately 24 h), the polymer was washed with acetonitrile (5 mL) before drying again. The ratio of protonated and deuterated fluoroaryl species was determined by <sup>19</sup>F NMR.

### 6.2 Sonication Experiments Overview

Both the protonated and deuterated analogues of polymers **1<sub>xa</sub>**, **1<sub>xb</sub>**, and **1<sub>xc</sub>** were subjected to a series of sonication experiments with varying sources of deuterium present in order to determine the extent of the three potential pathways of cleavage: heterolytic, concerted, and homolytic.

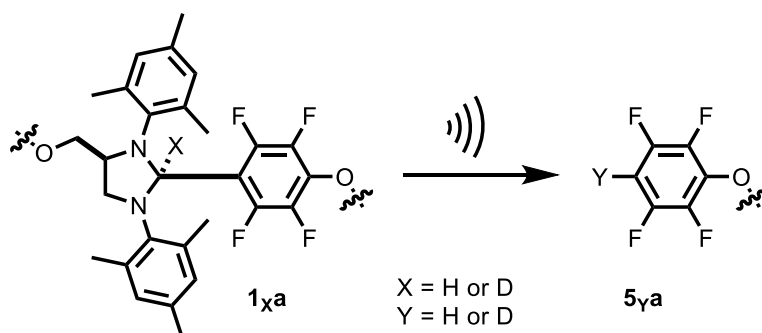
In the case of the protonated analogues, sonication in THF along with added D<sub>2</sub>O reveals the extent of heterolytic cleavage while sonication in THF-d<sub>8</sub>, with benzene making up the remaining solvent, with added H<sub>2</sub>O reveals the extent of homolytic cleavage; the extent of concerted cleavage can then be deduced from the difference between the two.

For the deuterated analogues, sonication in THF with added H<sub>2</sub>O reveals the extent of concerted cleavage while sonication in THF with added D<sub>2</sub>O reveals the extent of homolytic cleavage; the extent of heterolytic cleavage can be deduced from the difference between the two. A summary of the results observed can be seen in *Table S2* below.

**Table S2.** Summary of observed pathways of mechanical cleavage for mechanophore-containing polymers **1<sub>xa</sub>**, **1<sub>xb</sub>**, and **1<sub>xc</sub>** deduced through various sonication experiments. n.o. = not observed. Error: ±1 %

<i>Polymer</i>	<i>% Heterolytic</i>	<i>% Concerted</i>	<i>% Homolytic</i>
<b>1<sub>Ha</sub></b>	68	27	5
<b>1<sub>Da</sub></b>	70	24	6
<b>1<sub>Hb</sub></b>	45	55	n.o.
<b>1<sub>Db</sub></b>	71	26	3
<b>1<sub>Hc</sub></b>	25	75	n.o.
<b>1<sub>Dc</sub></b>	58	39	3

### 6.2.1 Sonication Experiments of Polymers **1<sub>Ha</sub>** and **1<sub>Da</sub>**<sup>1</sup>



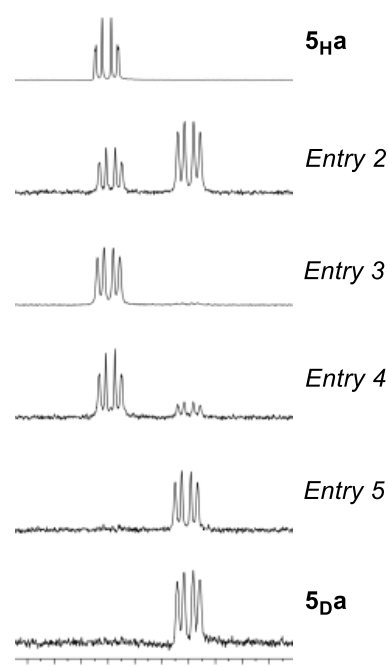
**Scheme S3.** The mechanical activation of polymer **1<sub>xa</sub>** via sonication leads to the formation of a tetrafluorobenzene structure that can be either protonated or deuterated with the ratio of these species depending on the conditions used.

**Table S3.** Summary of sonication experiments carried out using **1<sub>Ha</sub>** and **1<sub>Da</sub>** in various solvent systems along with the resulting ratio of protonated and deuterated tetrafluorobenzene species (**5<sub>ya</sub>**, where the position of Y is shown above in *Scheme S3*) formed. Error:  $\pm 1\%$

Entry	Polymer	Solvent Composition	<b>5<sub>Ha</sub></b> : <b>5<sub>Da</sub></b>
1	<b>1<sub>Ha</sub></b>	THF/H <sub>2</sub> O (15 : 0.2)	100 : 0
2	<b>1<sub>Ha</sub></b>	THF/D <sub>2</sub> O (15 : 0.2)	32 : 68
3	<b>1<sub>Ha</sub></b>	THF-d <sub>8</sub> /benzene/H <sub>2</sub> O (1 : 14 : 0.2)	95 : 5
4	<b>1<sub>Da</sub></b>	THF/H <sub>2</sub> O (15 : 0.2)	76 : 24
5	<b>1<sub>Da</sub></b>	THF/D <sub>2</sub> O (15 : 0.2)	6 : 94

For polymer **1<sub>Ha</sub>**, sonication in THF and D<sub>2</sub>O (*Table S3, Entry 2*) revealed the extent of heterolytic cleavage to be 68% while sonication in THF-d<sub>8</sub>, benzene, and H<sub>2</sub>O (*Table S3, Entry 3*) showed just 5% of cleavage to be homolytic; this leaves the concerted pathway to make up the remaining ~27%. An additional experiment was carried out where **1<sub>Ha</sub>** was sonicated in THF and H<sub>2</sub>O (*Table S3, Entry 1*) to demonstrate sole formation of the protonated tetrafluorobenzene.

For polymer **1<sub>Da</sub>**, sonication in THF and H<sub>2</sub>O (*Table S3, Entry 4*) revealed the extent of concerted cleavage to be 24% while sonication in THF and D<sub>2</sub>O (*Table S3, Entry 5*) showed 6% of cleavage to be homolytic leaving the heterolytic pathway to make up the remaining ~70%. As the deuteration of polymer **1<sub>Da</sub>** is not 100% (approximately 98% D in the precursor small molecule mechanophore) the small amount of **1<sub>Ha</sub>** present must be taken into account. For the experiment shown in *Table S3, Entry 4*, 100% of **1<sub>Ha</sub>** cleavage events will have led to **5<sub>Ha</sub>** meaning the percentage of **5<sub>ya</sub>** that was actually protonated was 75.5%. Similar treatment for the experiment of *Table S3, Entry 5* reveals the true extent of **5<sub>Ha</sub>** formed was 5.5%. The difference this analysis makes to the results here is essentially negligible.

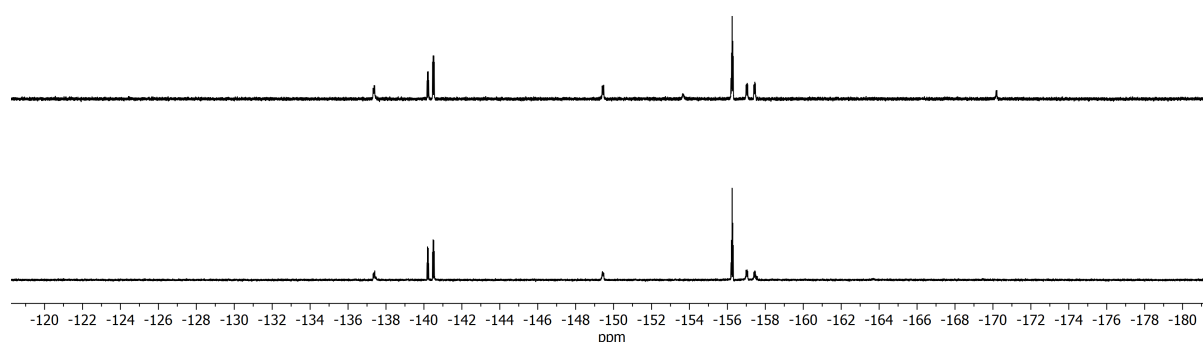


**Figure S1.** <sup>1</sup>H NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectra showing the ratio of **5<sub>Ha</sub>** to **5<sub>Da</sub>** present in the post-sonication polymers reported in *Table S3*.

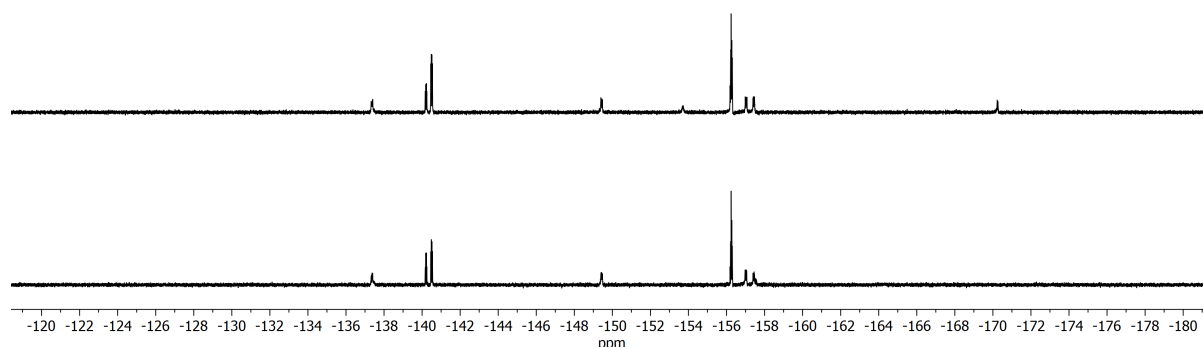


These results show how polymer **1<sub>x</sub>a** demonstrates similar extents of each cleavage mechanism regardless of whether it is protonated or deuterated adjacent to the scissile bond.

It is worth mentioning that in some of the  $^{19}\text{F}$  NMR spectra of post-sonication samples involving polymer **1<sub>H</sub>a** there are unidentified peaks present at -153.7 and -170.2 ppm. A repeat of one of these experiments using a different sample demonstrates no such presence of this species (*Figure S8*) while retaining the ratio of protonated and deuterated **5<sub>y</sub>a** species. A similar result can be observed when the same sample of **1<sub>H</sub>a** is sonicated with methanol- $\text{d}_4$  instead of  $\text{D}_2\text{O}$  (*Figure S9*). This shows that the unidentified peaks are the result of a species that is not involved in the mechanochemical activation of mechanophore **1<sub>x</sub>a** and is likely a simple impurity present in the particular sample discussed here.

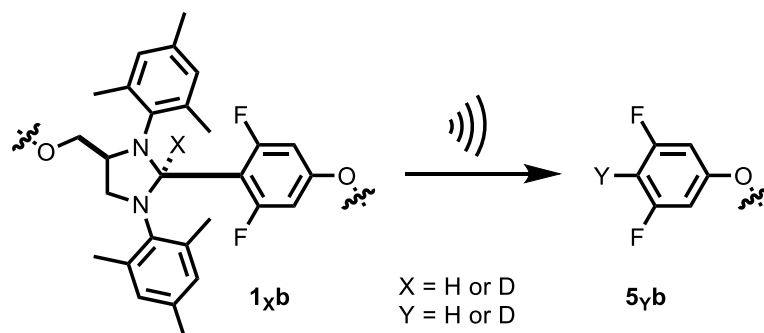


**Figure S8.**  $^{19}\text{F}$  NMR spectra showing (top) the sample of **1<sub>H</sub>a** used elsewhere throughout this work and (bottom) an alternative sample of **1<sub>H</sub>a**, both after 180 min of sonication in THF (15 mL) with added  $\text{D}_2\text{O}$  (0.2 mL). The top spectrum shows 68% of the resulting tetrafluorobenzene species are deuterated while the bottom spectrum shows 69%.



**Figure S9.**  $^{19}\text{F}$  NMR spectra showing (top) the sample of **1<sub>H</sub>a** used elsewhere throughout this work and (bottom) an alternative sample of **1<sub>H</sub>a**, both after 180 min of sonication in THF (15 mL) with added methanol- $\text{d}_4$  (0.2 mL). The top spectrum shows 72% of the resulting tetrafluorobenzene species are deuterated while the bottom spectrum shows 70%.

### 6.2.2 Sonication Experiments of Polymers **1<sub>Hb</sub>** and **1<sub>Db</sub>**



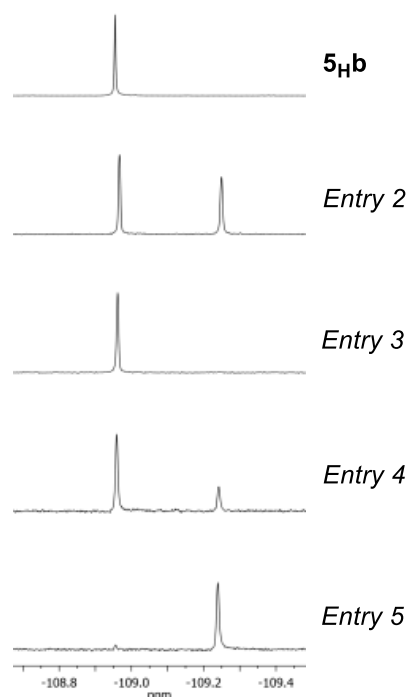
**Scheme S4.** The mechanical activation of polymer **1<sub>x</sub>b** via sonication leads to the formation of a difluorobenzene structure that can be either protonated or deuterated with the ratio of these species depending on the conditions used.

**Table S4.** Summary of sonication experiments carried out using **1<sub>Hb</sub>** and **1<sub>Db</sub>** in various solvent systems along with the resulting ratio of protonated and deuterated difluorobenzene species (**5<sub>y</sub>b**, where the position of Y is shown above in *Scheme S4*) formed. Error:  $\pm 1\%$ .

Entry	Polymer	Solvent Composition	<b>5<sub>Hb</sub></b> : <b>5<sub>Db</sub></b>
1 <sup>1</sup>	<b>1<sub>Hb</sub></b>	THF/H <sub>2</sub> O (15 : 0.2)	100 : 0
2 <sup>1</sup>	<b>1<sub>Hb</sub></b>	THF/D <sub>2</sub> O (15 : 0.2)	55 : 45
3 <sup>1</sup>	<b>1<sub>Hb</sub></b>	THF- <i>d</i> <sub>8</sub> /benzene/H <sub>2</sub> O (1 : 14 : 0.2)	100 : 0
4	<b>1<sub>Db</sub></b>	THF/H <sub>2</sub> O (15 : 0.2)	74 : 26
5	<b>1<sub>Db</sub></b>	THF/D <sub>2</sub> O (15 : 0.2)	4 : 96

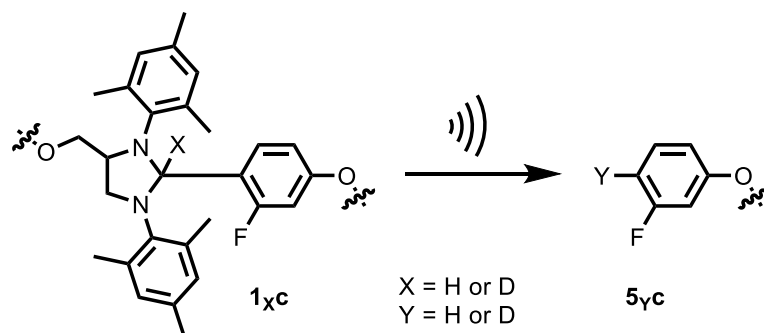
For polymer **1<sub>Hb</sub>**, sonication in THF and D<sub>2</sub>O (*Table S4, Entry 2*) revealed the extent of heterolytic cleavage to be 45% while sonication in THF-*d*<sub>8</sub>, benzene, and H<sub>2</sub>O (*Table S4, Entry 3*) showed no observable amount of cleavage to be homolytic in nature; this leaves the concerted pathway to make up the remaining ~55%. An additional experiment was carried out where **1<sub>Hb</sub>** was sonicated in THF and H<sub>2</sub>O (*Table S4, Entry 1*) to demonstrate sole formation of the protonated difluorobenzene.

For polymer **1<sub>Db</sub>**, sonication in THF and H<sub>2</sub>O (*Table S4, Entry 4*) revealed the extent of concerted cleavage to be just 26%, a substantial decrease from what is expected based on the protonated analogue. Sonication in THF and D<sub>2</sub>O (*Table S4, Entry 5*) showed 4% of **5<sub>Hb</sub>**. Again, we must take into account the incomplete deuteration of polymer **1<sub>Db</sub>** (98% D in **S5**). The extent of protonation for the experiment shown in *Table S4, Entry 4*, was actually 73.5% while for *Table S4, Entry 5* it was 3.0%. This analysis slightly changes the value for the homolytic pathway and leaves the heterolytic pathway to make up the remaining ~71% of cleavage events.



**Figure S2.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectra showing the ratio of **5<sub>Hb</sub>** to **5<sub>Db</sub>** present in the post-sonication polymers reported in *Table S4*.

### 6.2.3 Sonication Experiments of Polymers **1<sub>Hc</sub>** and **1<sub>Dc</sub>**



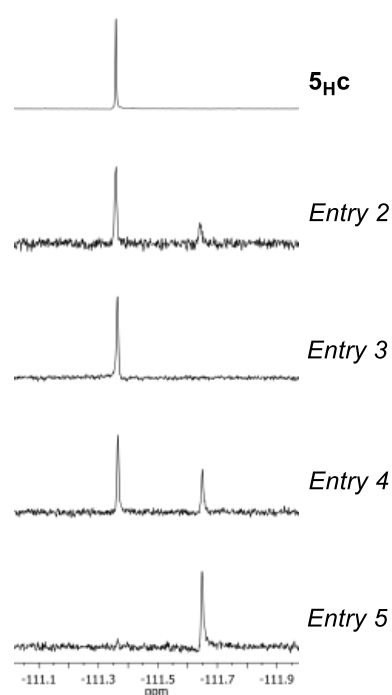
**Scheme S5.** The mechanical activation of polymer **1<sub>xc</sub>** via sonication leads to the formation of a fluorobenzene structure that can be either protonated or deuterated with the ratio of these species depending on the conditions used.

**Table S5.** Summary of sonication experiments carried out using **1<sub>Hc</sub>** and **1<sub>Dc</sub>** in various solvent systems along with the resulting ratio of protonated and deuterated fluorobenzene species (**5<sub>yc</sub>**, where the position of Y is shown above in *Scheme S5*) formed. Error:  $\pm 1\%$ .

Entry	Polymer	Solvent Composition	<b>5<sub>Hc</sub></b> : <b>5<sub>Dc</sub></b>
1 <sup>1</sup>	<b>1<sub>Hc</sub></b>	THF/H <sub>2</sub> O (15 : 0.2)	100 : 0
2 <sup>1</sup>	<b>1<sub>Hc</sub></b>	THF/D <sub>2</sub> O (15 : 0.2)	75 : 25
3 <sup>1</sup>	<b>1<sub>Hc</sub></b>	THF- <i>d</i> <sub>8</sub> /benzene/H <sub>2</sub> O (1 : 14 : 0.2)	100 : 0
4	<b>1<sub>Dc</sub></b>	THF/H <sub>2</sub> O (15 : 0.2)	62 : 38
5	<b>1<sub>Dc</sub></b>	THF/D <sub>2</sub> O (15 : 0.2)	4 : 96

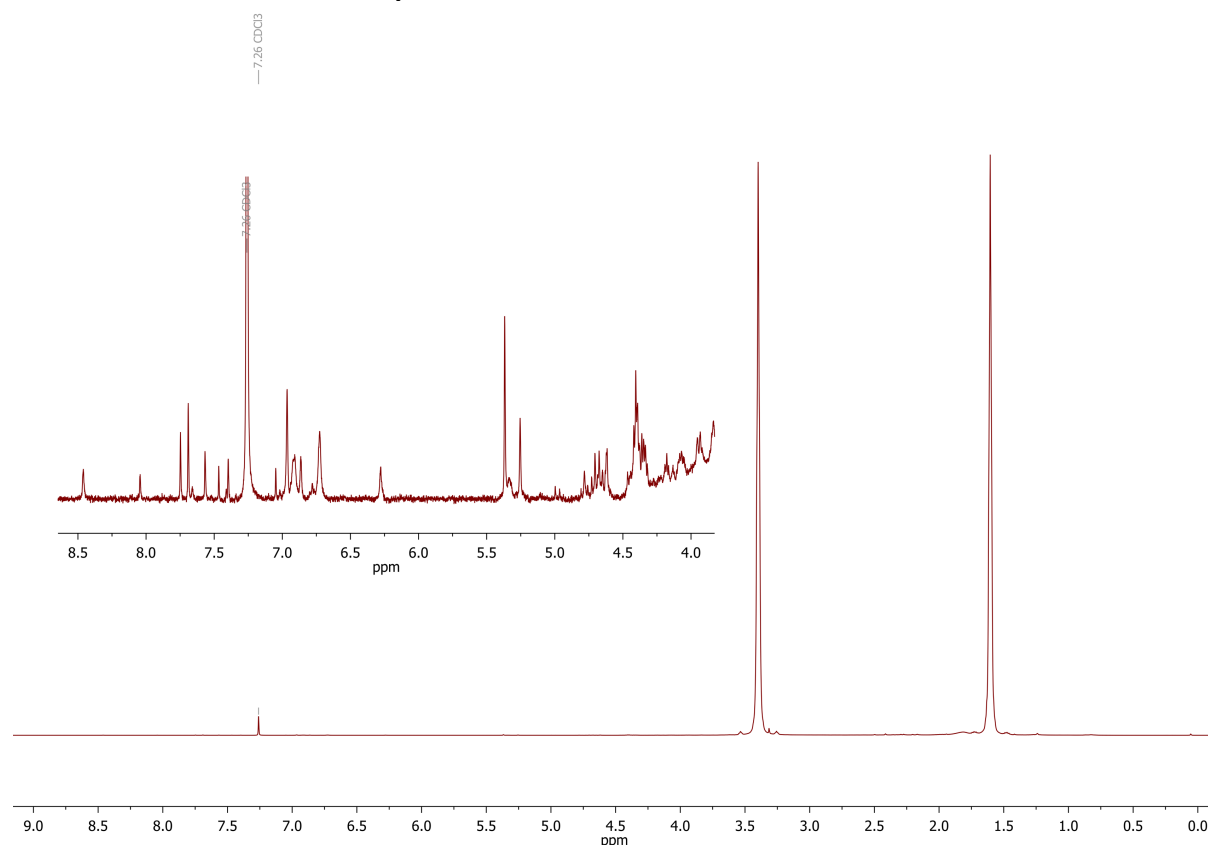
For polymer **1<sub>Hc</sub>**, sonication in THF and D<sub>2</sub>O (*Table S5, Entry 2*) revealed the extent of heterolytic cleavage to be 25% while sonication in THF-*d*<sub>8</sub>, benzene, and H<sub>2</sub>O (*Table S5, Entry 3*) showed no observable amount of cleavage to be homolytic in nature; this leaves the concerted pathway to make up the remaining ~55%. An additional experiment was carried out where **1<sub>Hc</sub>** was sonicated in THF and H<sub>2</sub>O (*Table S5, Entry 1*) to demonstrate sole formation of the protonated fluorobenzene.

For polymer **1<sub>Dc</sub>**, sonication in THF and H<sub>2</sub>O (*Table S5, Entry 4*) revealed the extent of concerted cleavage to be just 38%, a substantial decrease from what is expected based on the protonated analogue. Sonication in THF and D<sub>2</sub>O (*Table S5, Entry 5*) showed 4% of **5<sub>Hc</sub>**. Again, we must take into account the incomplete deuteration of polymer **1<sub>Dc</sub>** (98% D in **S8**). The extent of protonation for the experiment shown in *Table S5, Entry 4*, was actually 61.2% while for *Table S5, Entry 5* it was 2.6%. This analysis slightly changes the values for the concerted and homolytic pathways and leaves the heterolytic pathway to make up the remaining ~59% of cleavage events.

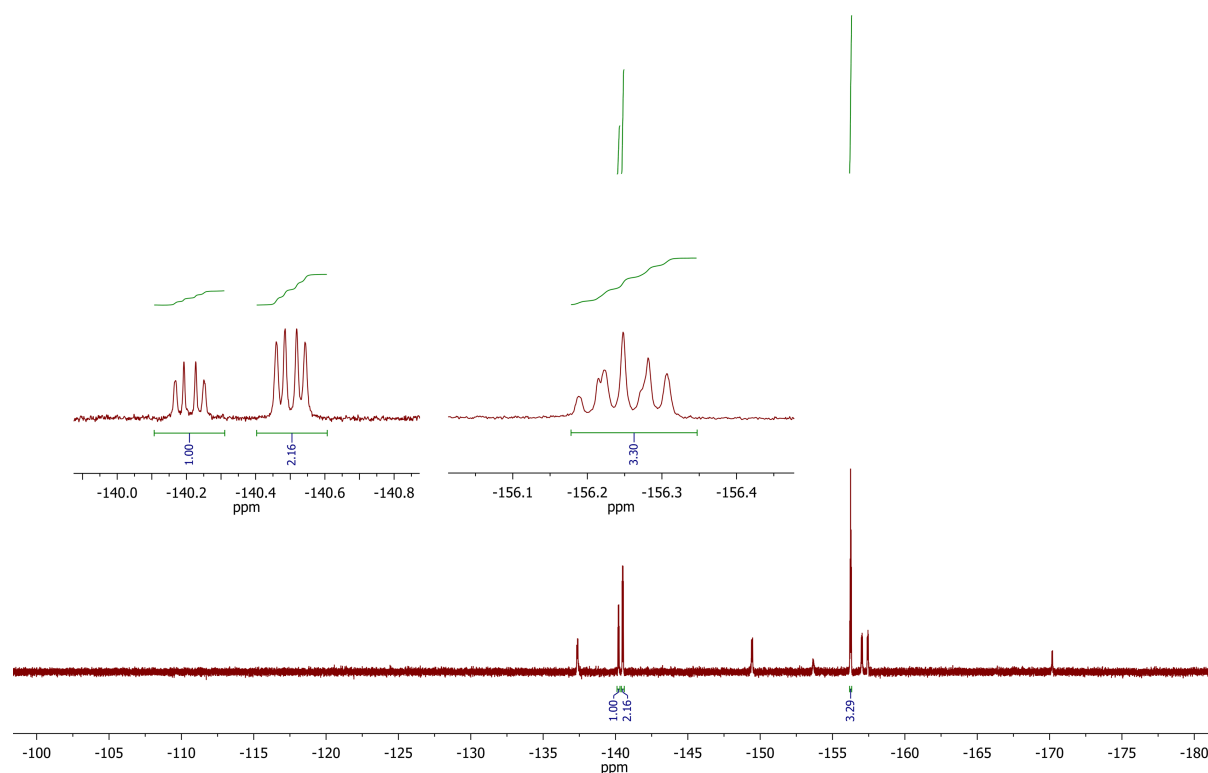


**Figure S3.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectra showing the ratio of **5<sub>Hc</sub>** to **5<sub>Dc</sub>** present in the post-sonication polymers reported in *Table S5*.

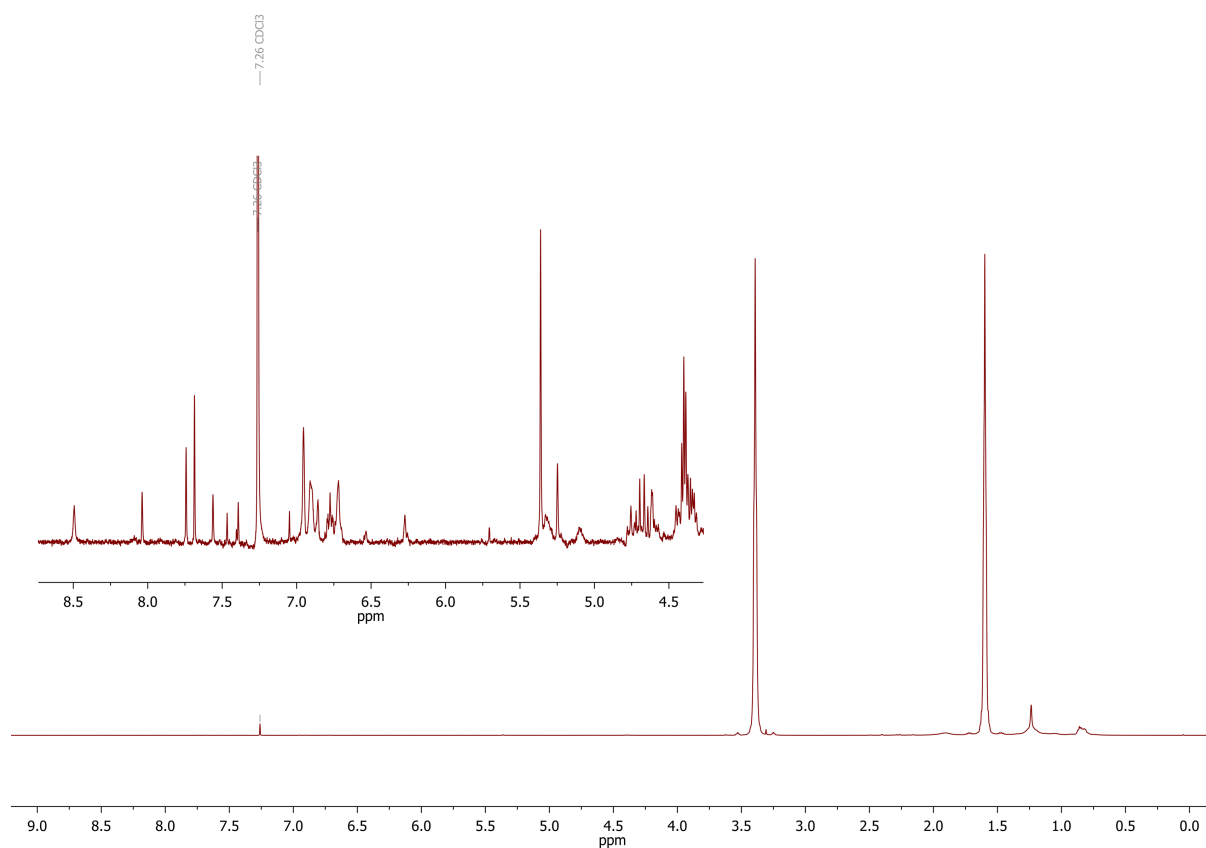
### 6.3 Post-Sonication NMR Spectra



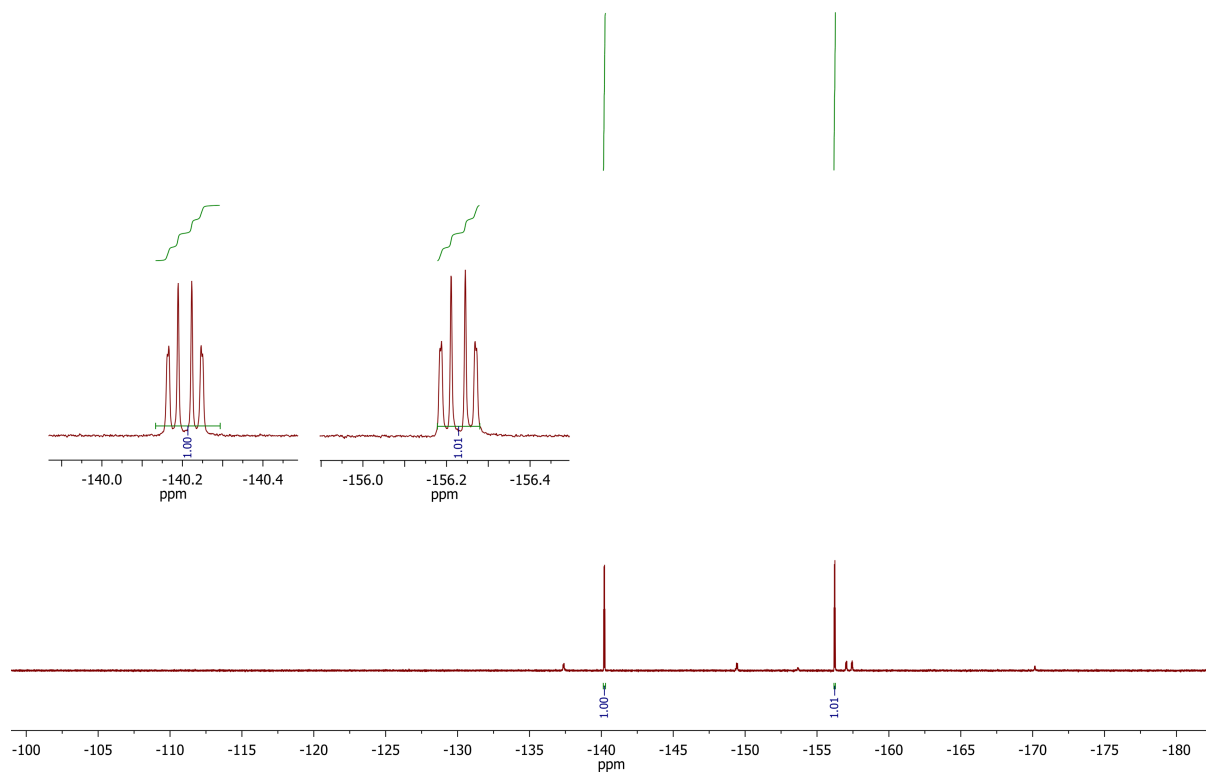
**Spectrum S32.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>Ha</sub>** after 180 min of sonication in THF (15 mL) and  $\text{D}_2\text{O}$  (0.2 mL).



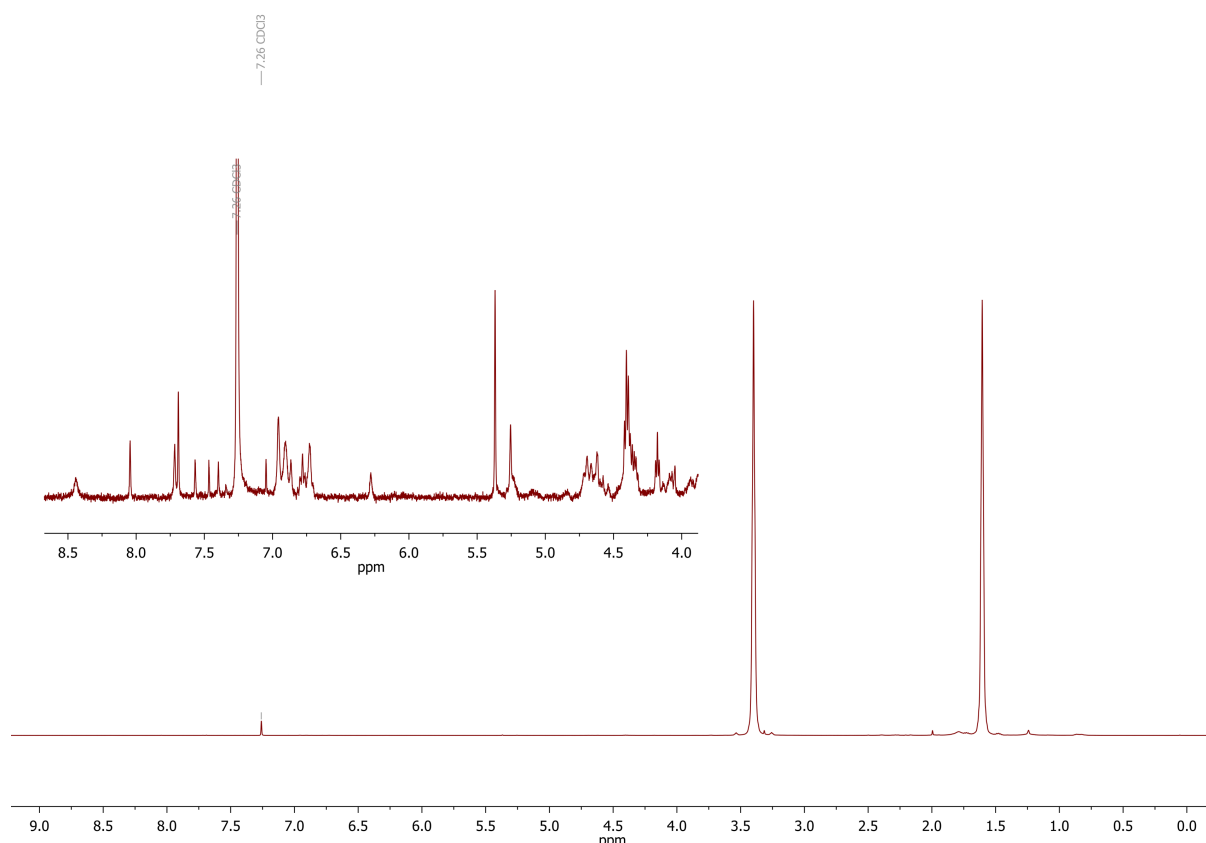
**Spectrum S33.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>Ha</sub>** after 180 min of sonication in THF (15 mL) and  $\text{D}_2\text{O}$  (0.2 mL). Approximately 68% of the tetrafluorobenzene species formed is deuterated.



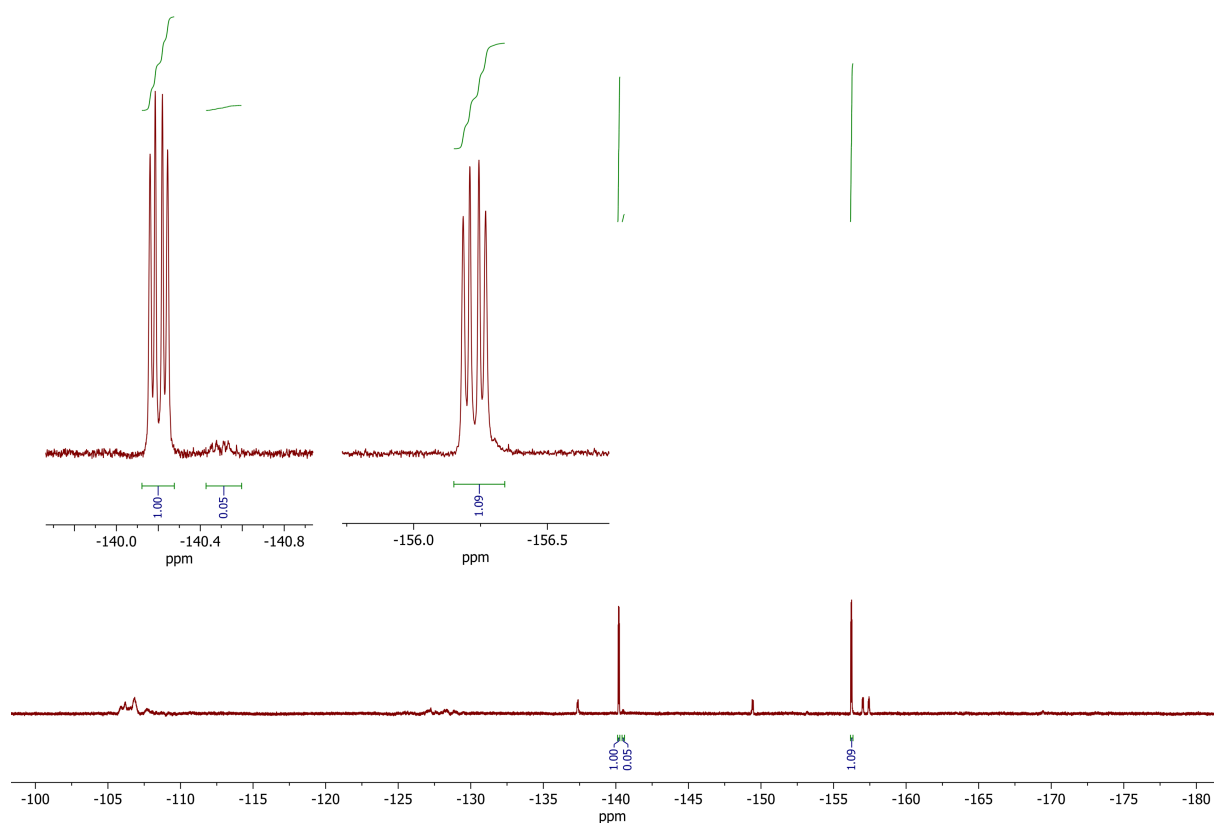
**Spectrum S34.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>Ha</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL).



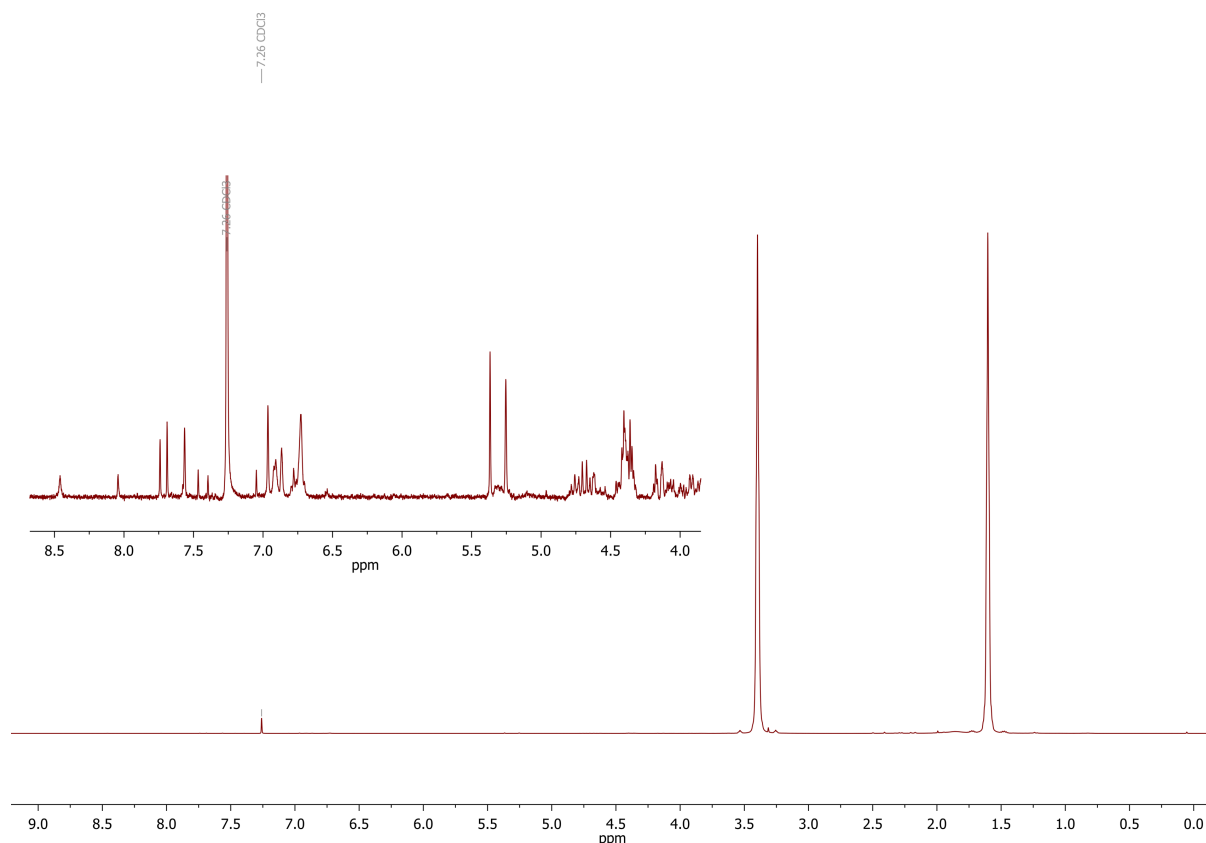
**Spectrum S35.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>Ha</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL). 0% of the tetrafluorobenzene species formed is deuterated.



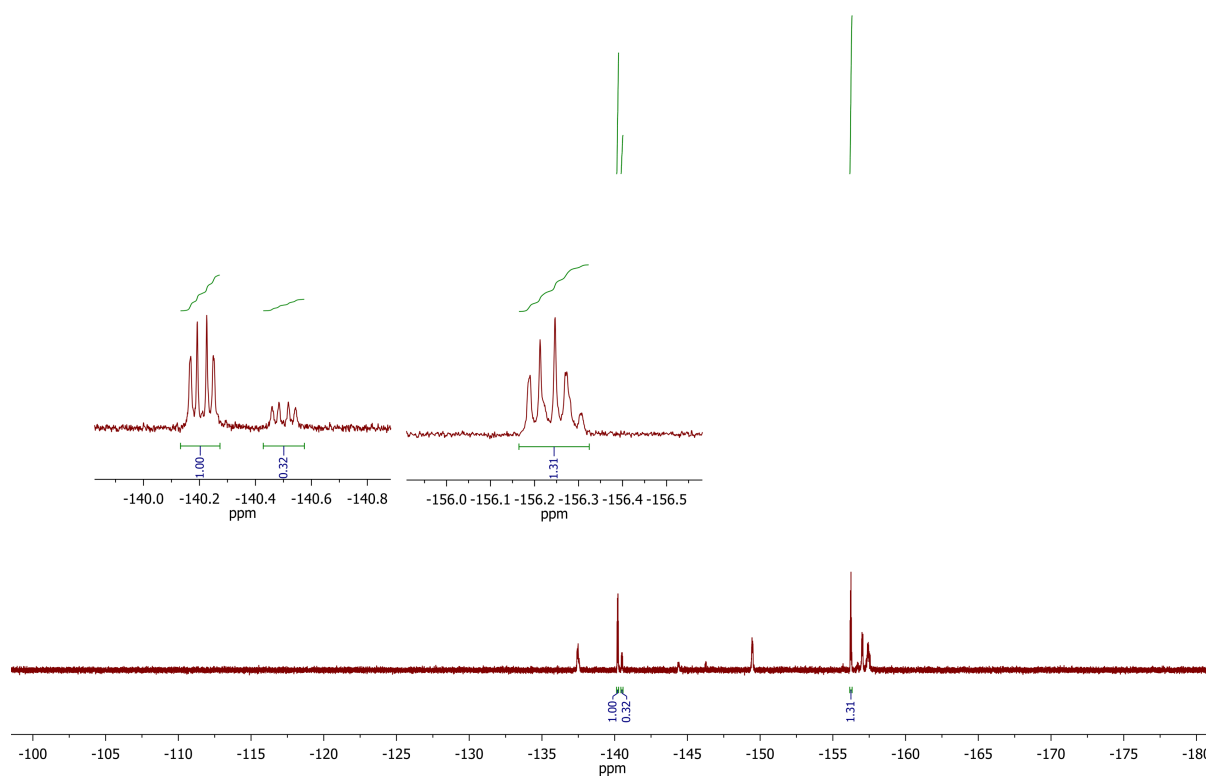
**Spectrum S36.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1Ha** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL).



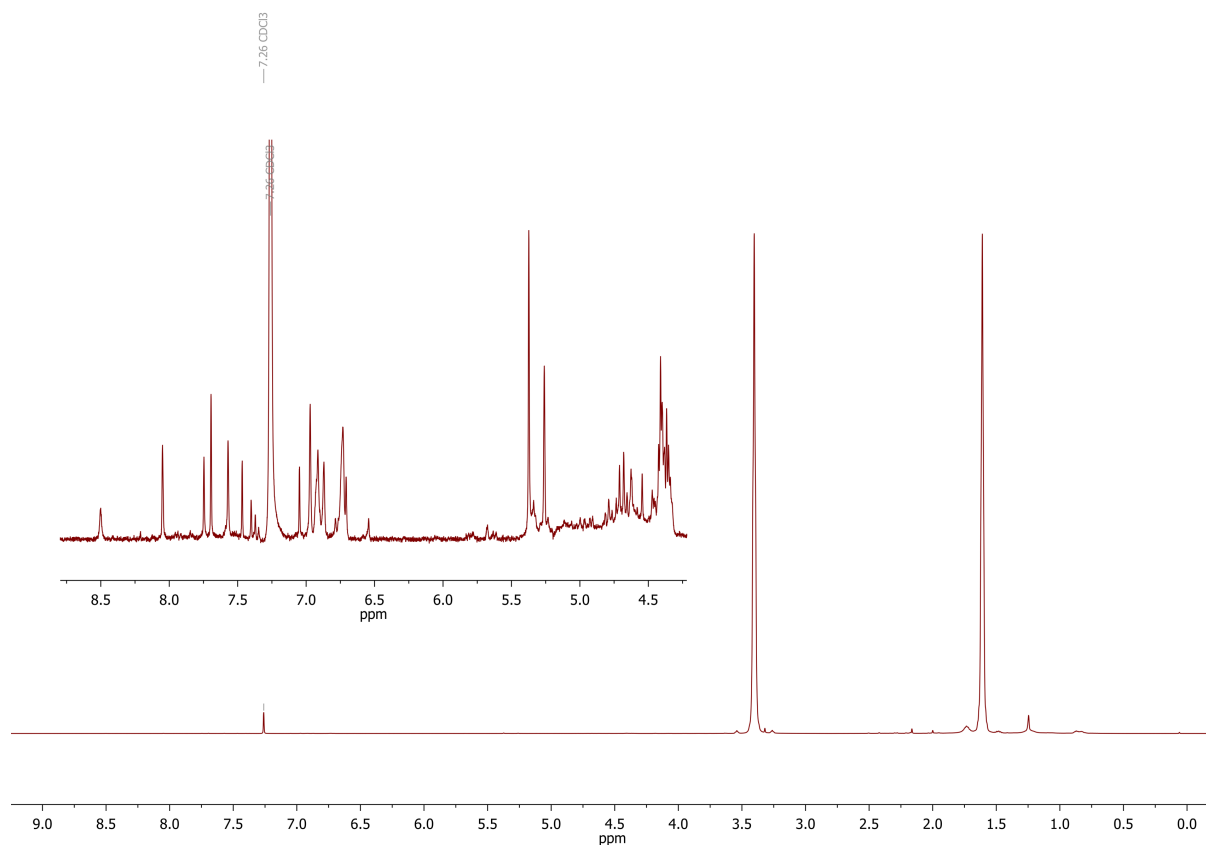
**Spectrum S37.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1Ha** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL). Approximately 5% of the tetrafluorobenzene species formed is deuterated.



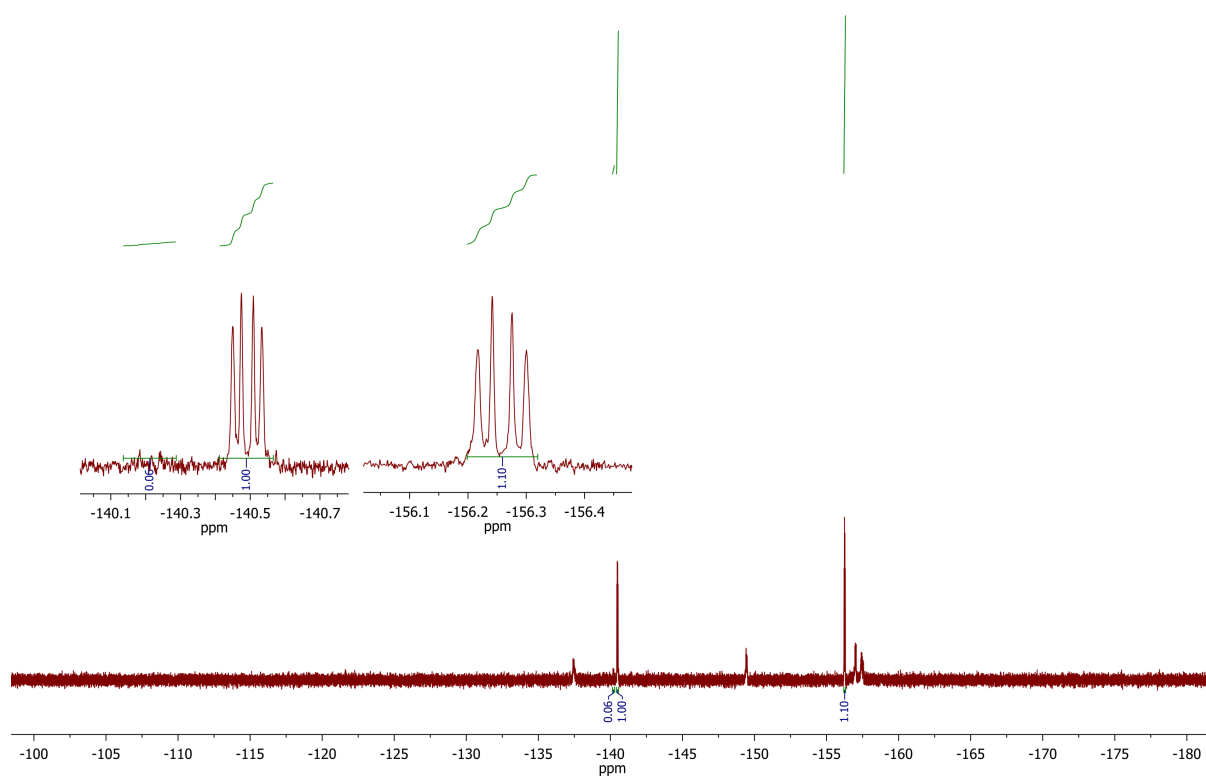
**Spectrum S38.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1Da** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL).



**Spectrum S39.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1Da** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL). Approximately 24% of the tetrafluorobenzene species formed is deuterated.

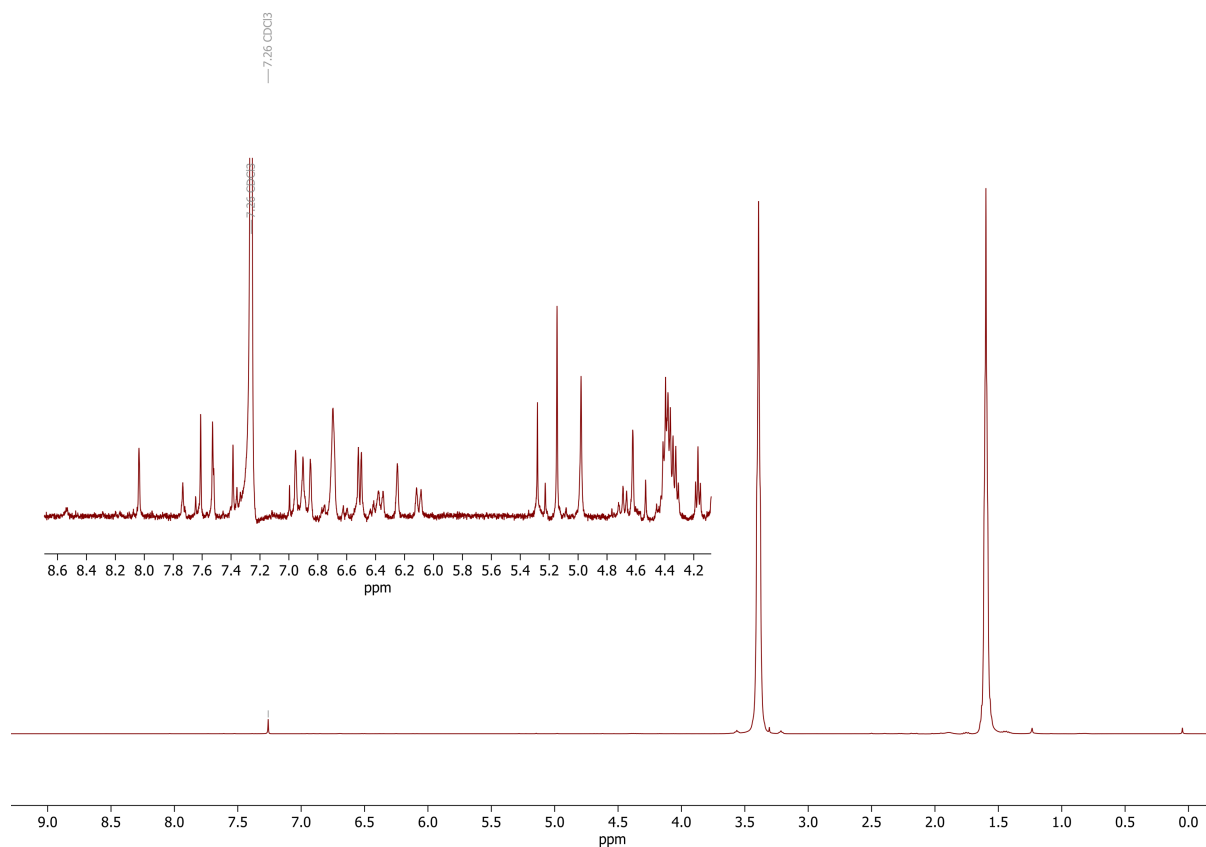


**Spectrum S40.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1ba** after 180 min of sonication in THF (15 mL) and  $\text{D}_2\text{O}$  (0.2 mL).

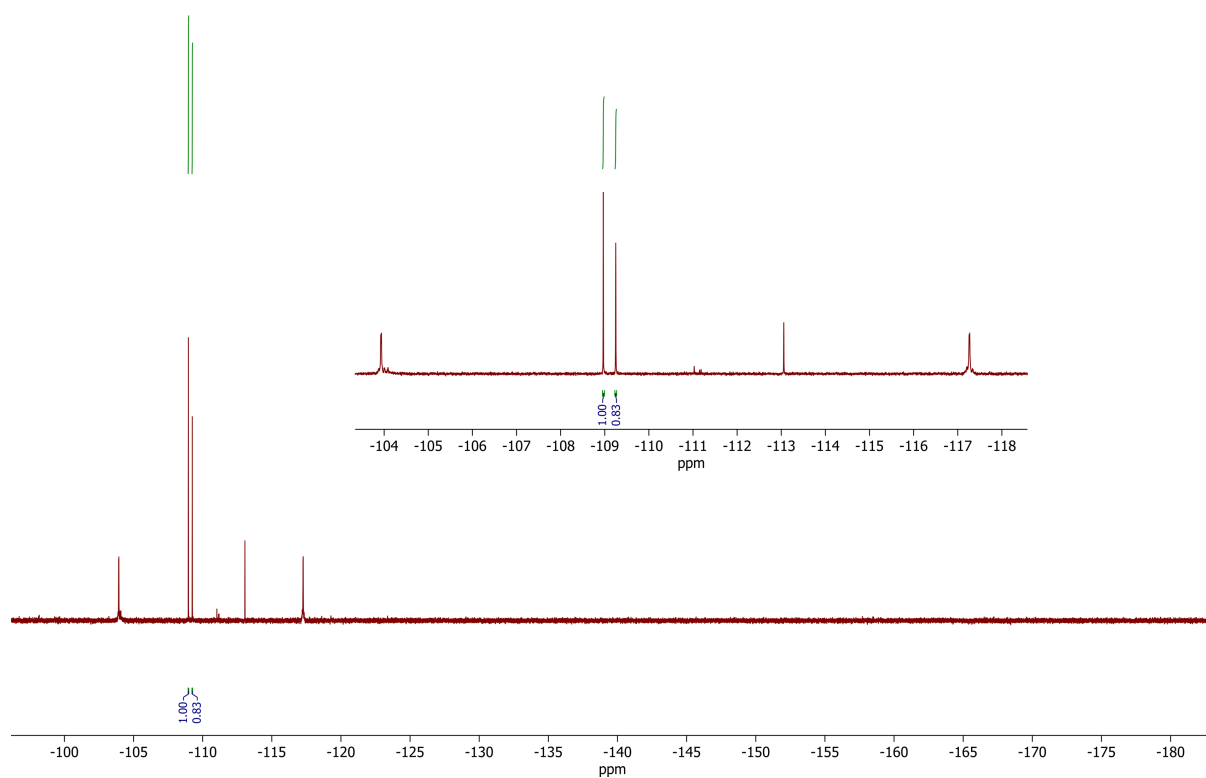


**Spectrum S41.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1ba** after 180 min of sonication in THF (15 mL) and  $\text{D}_2\text{O}$  (0.2 mL). Approximately 94% of the tetrafluorobenzene species formed is deuterated.

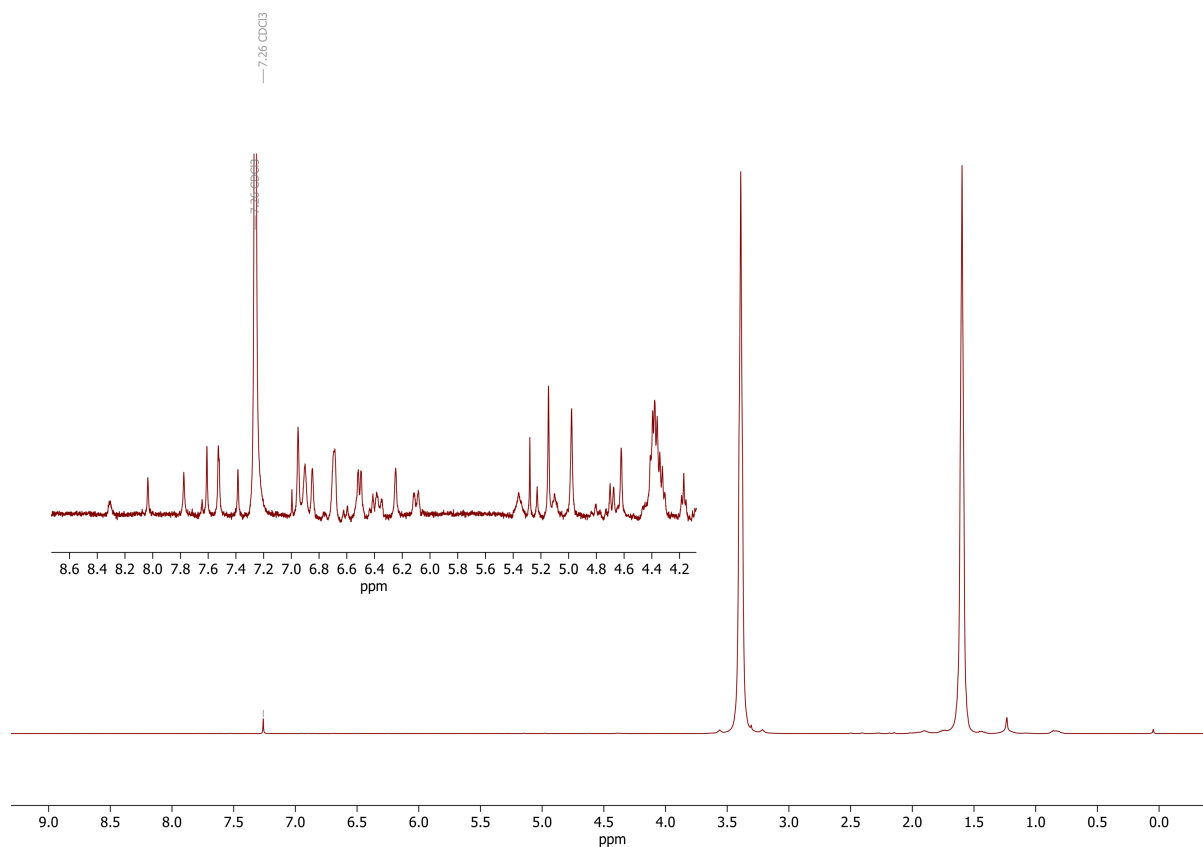




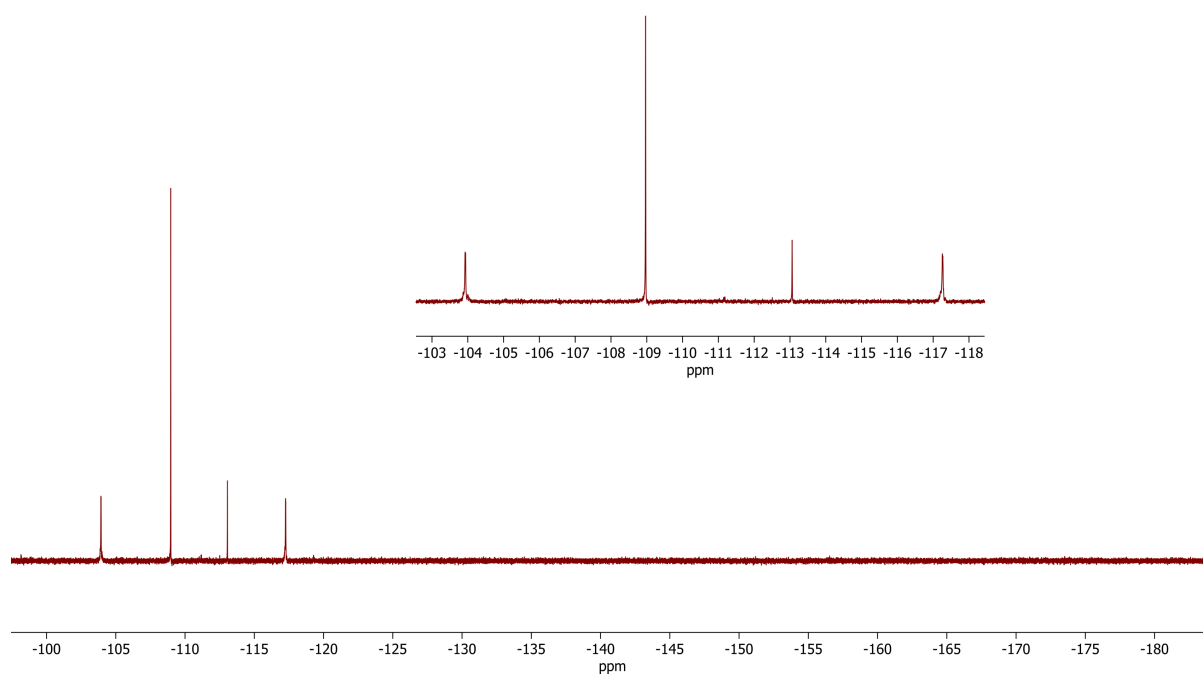
**Spectrum S42.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>H</sub>b** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL).



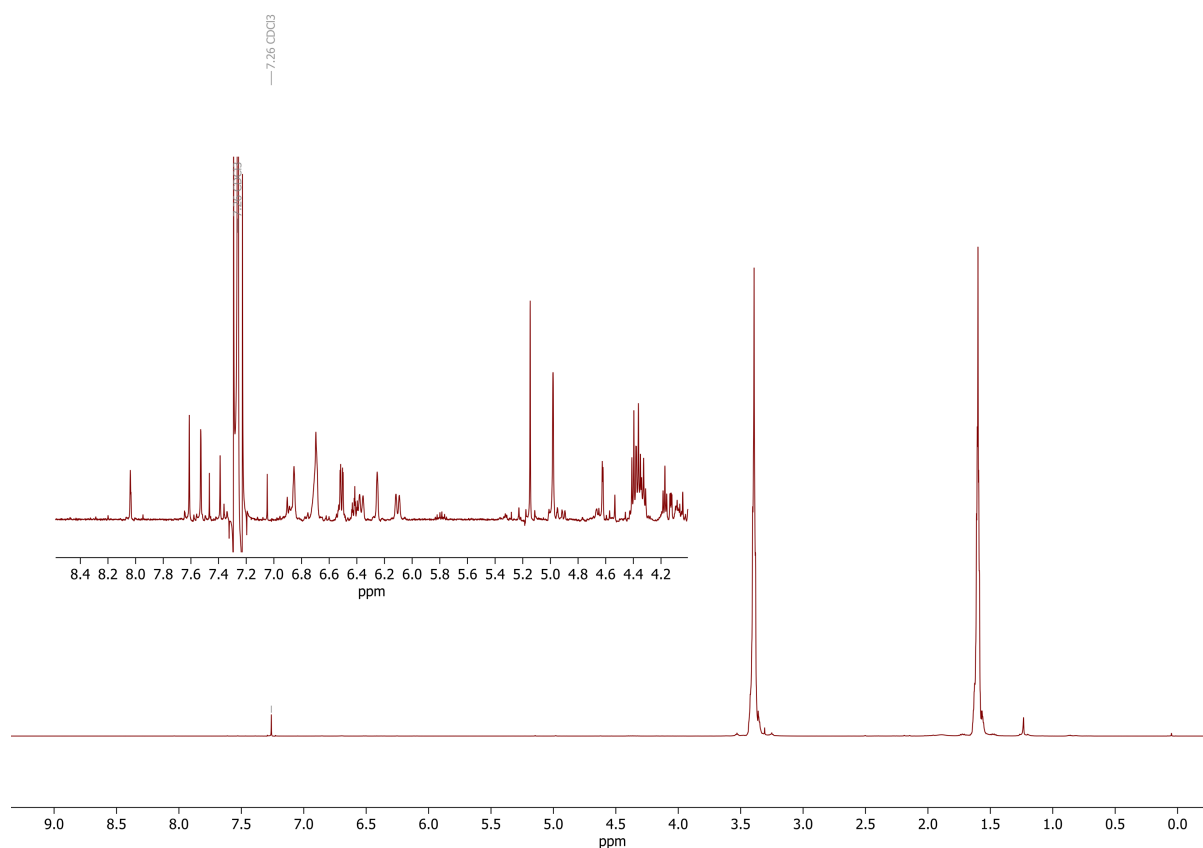
**Spectrum S43.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1<sub>H</sub>b** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL). Approximately 45% of the difluorobenzene species formed is deuterated.



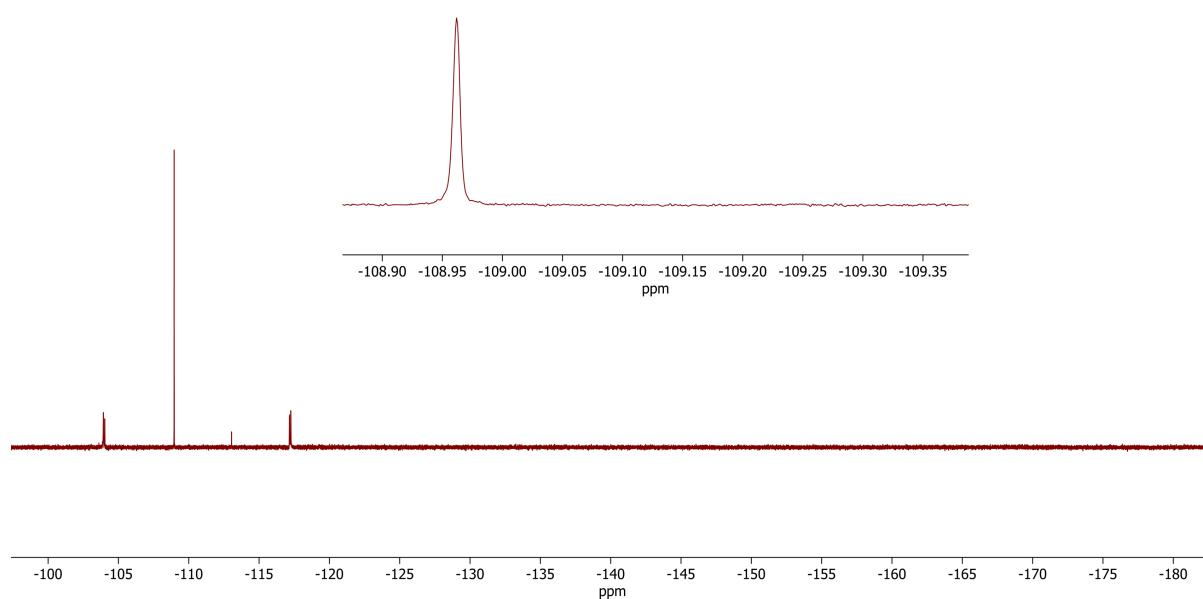
**Spectrum S44.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>h</sub>b** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL).



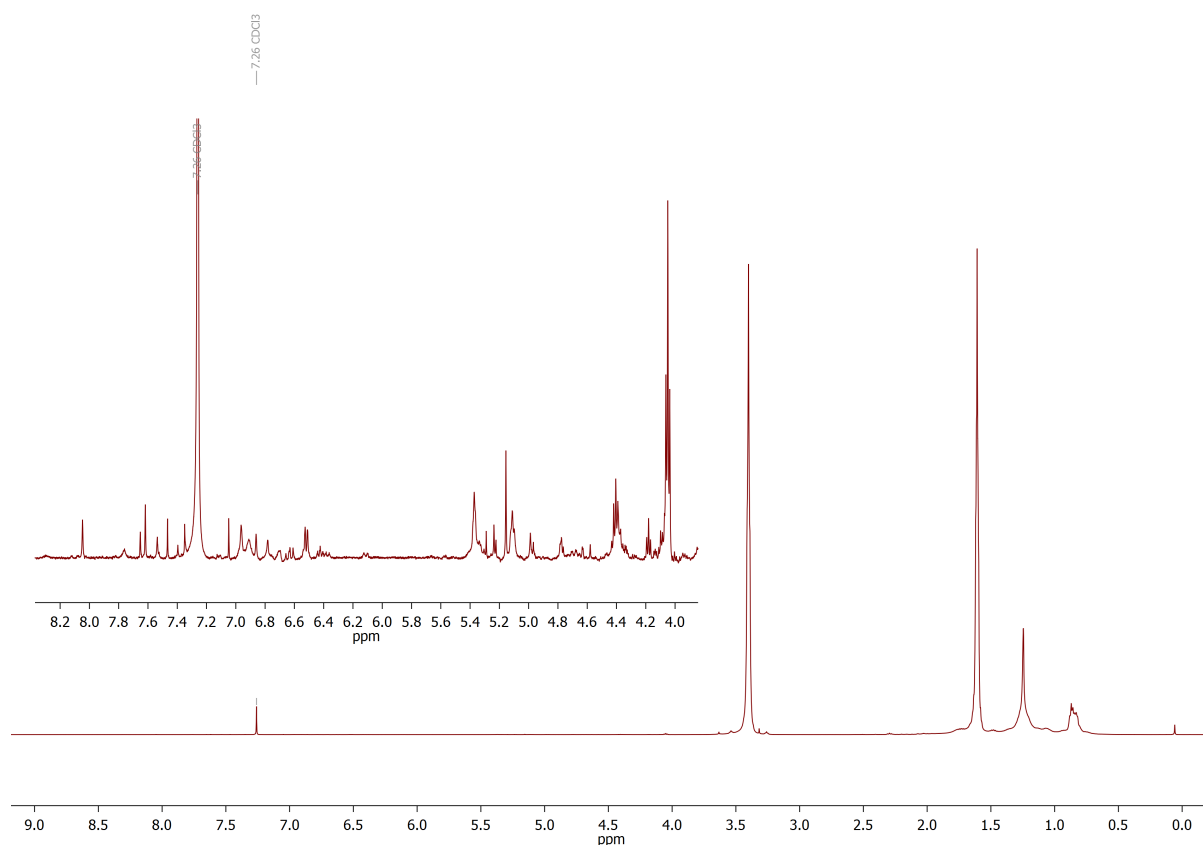
**Spectrum S45.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1<sub>h</sub>b** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL). 0% of the difluorobenzene species formed is deuterated.



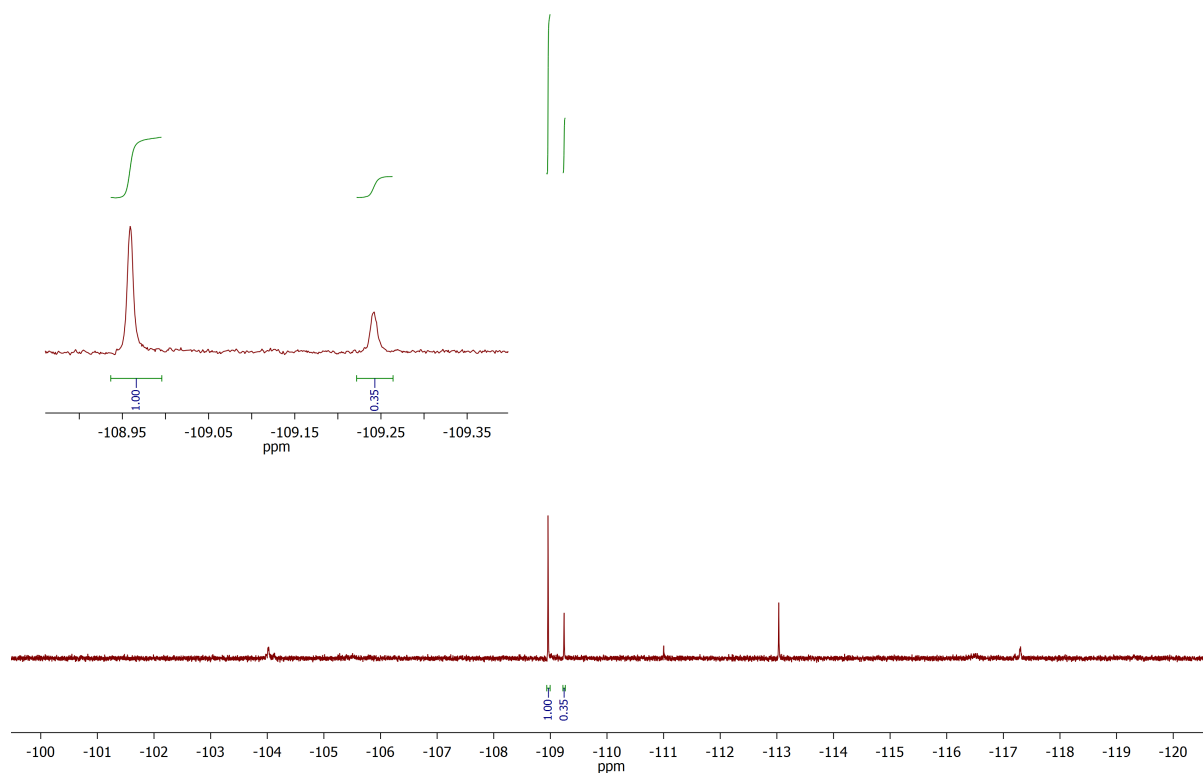
**Spectrum S46.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>Hb</sub>** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL).



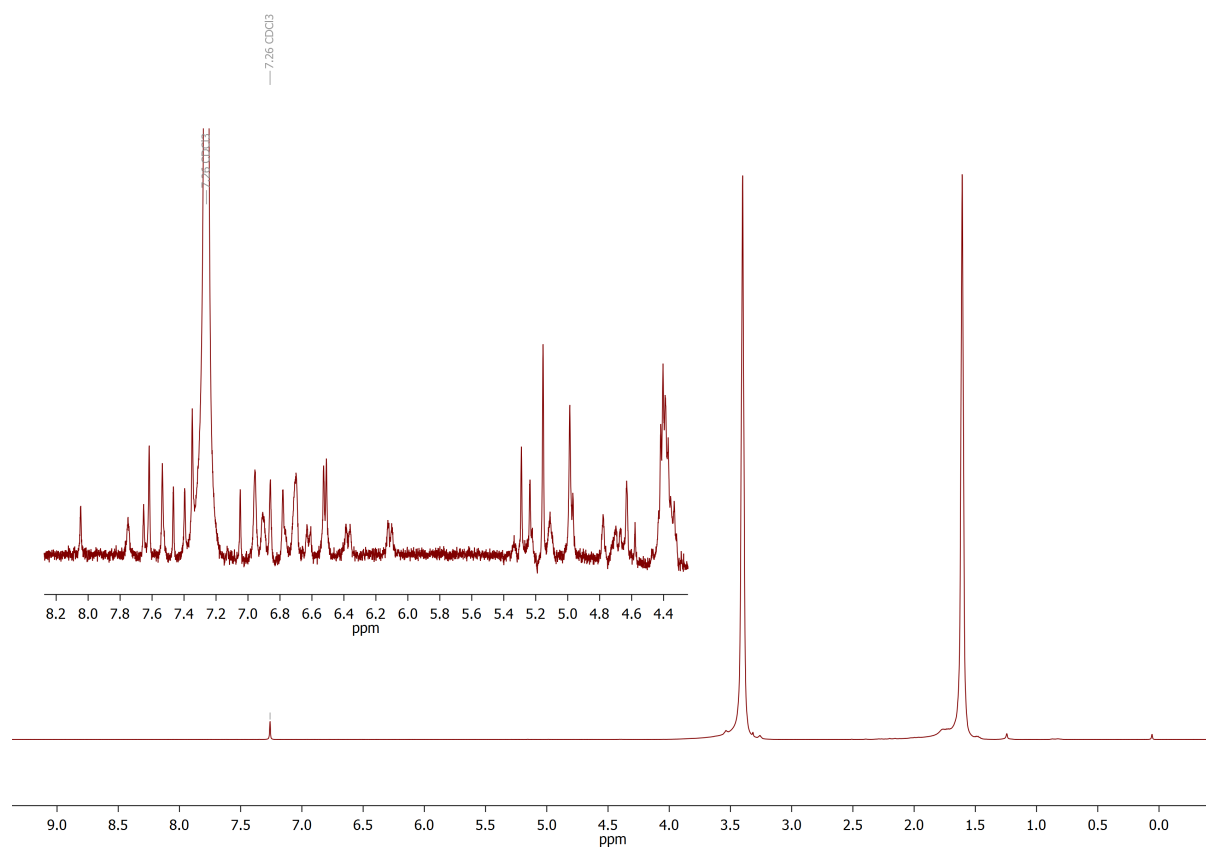
**Spectrum S47.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>Hb</sub>** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL). There is no observable deuteration of the difluorobenzene species formed.



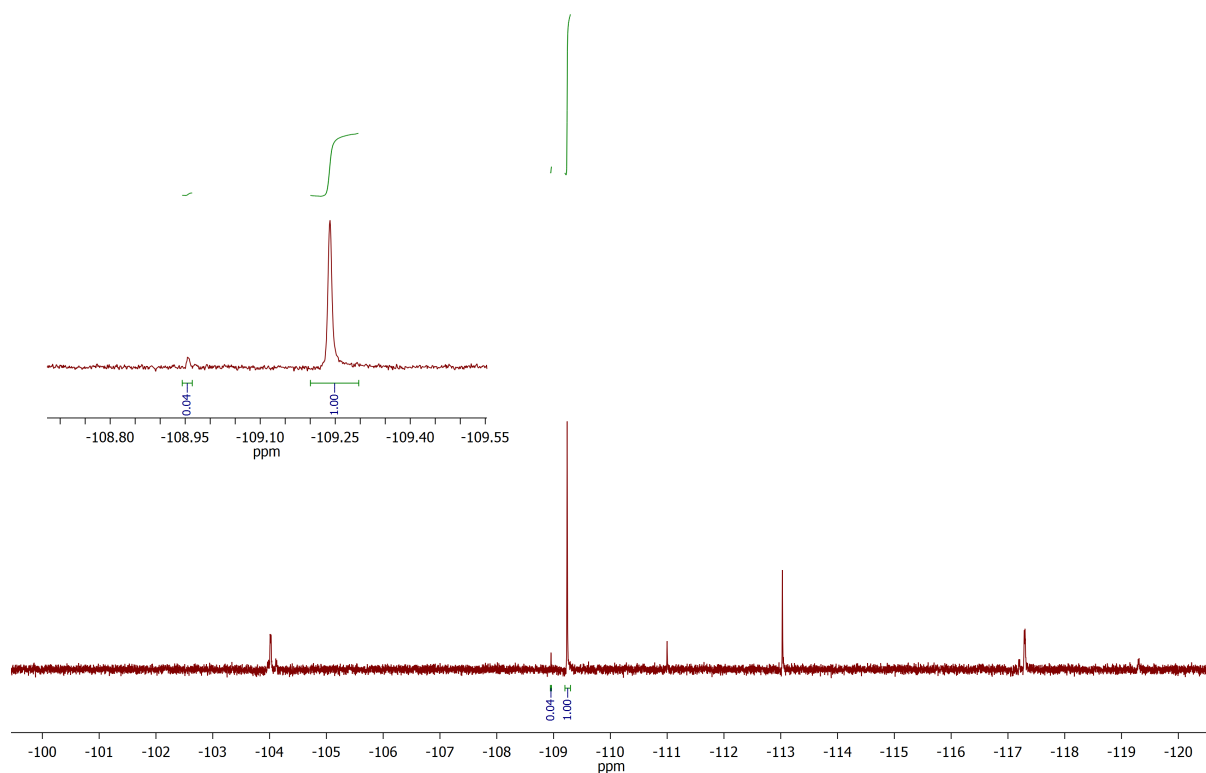
**Spectrum S48.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1b** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL).



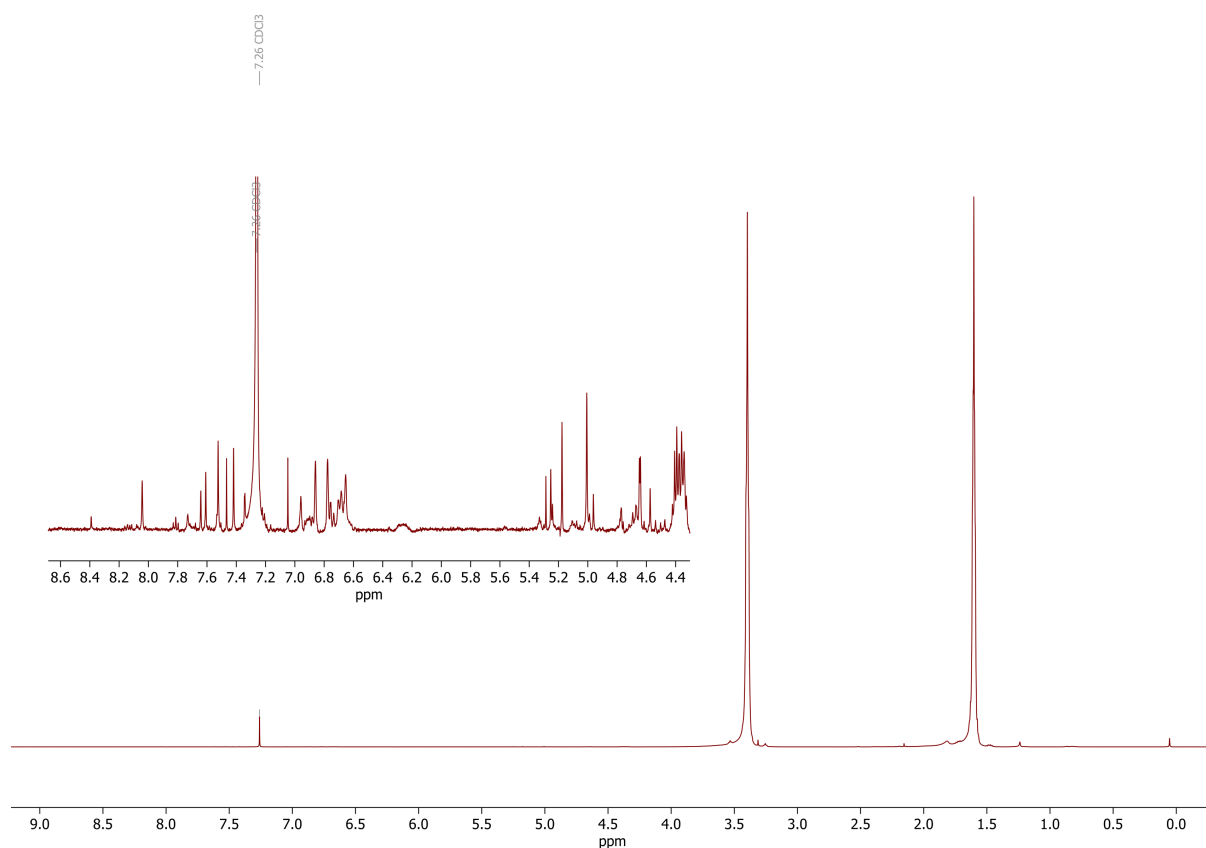
**Spectrum S49.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1b** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL). Approximately 26% of the difluorobenzene species formed is deuterated.



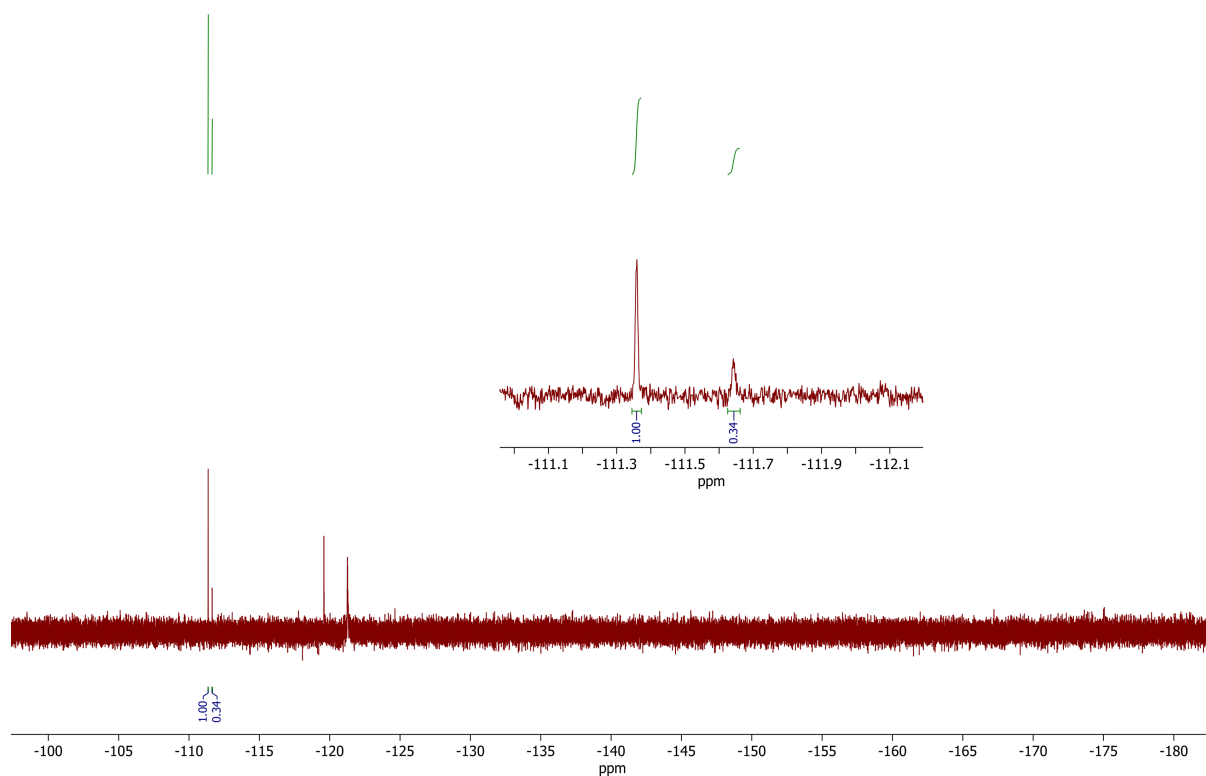
**Spectrum S50.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>b</sub>** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL).



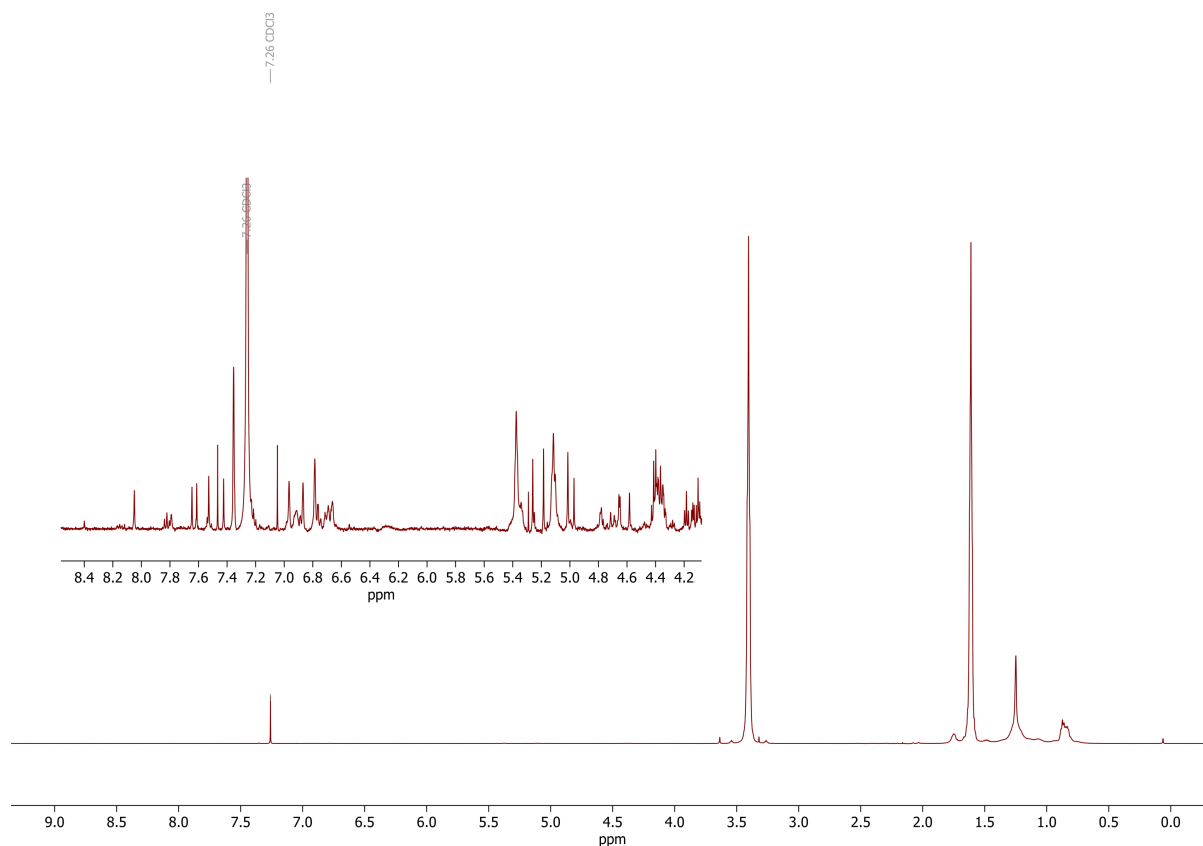
**Spectrum S51.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1<sub>b</sub>** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL). Approximately 96% of the difluorobenzene species formed is deuterated.



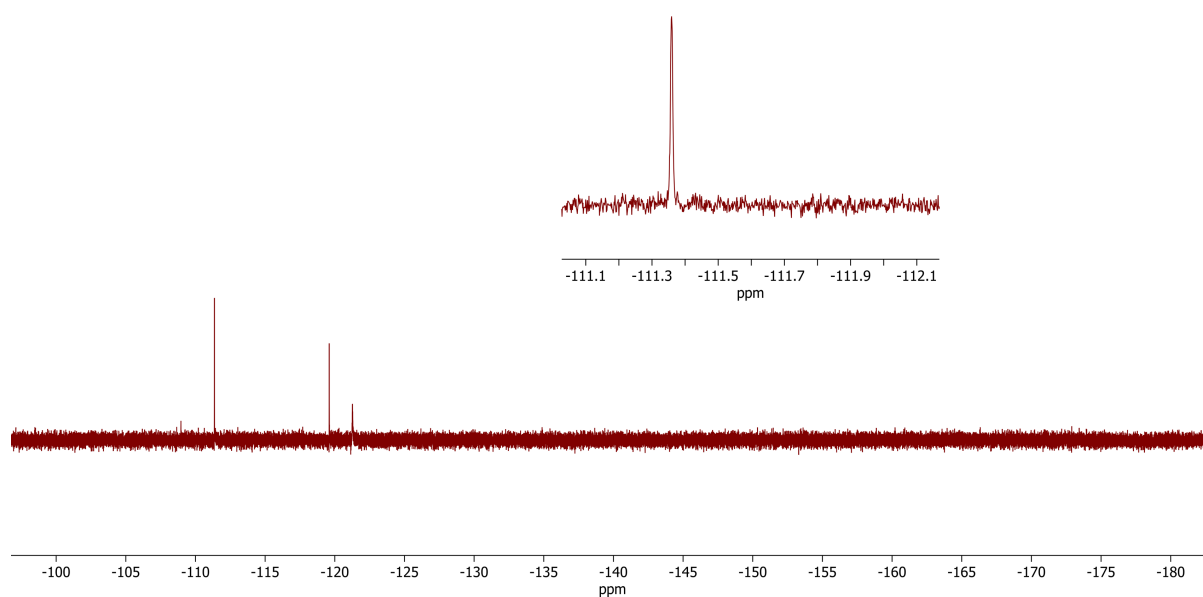
**Spectrum S52.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>Hc</sub>** after 180 min of sonication in THF (15 mL) and  $\text{D}_2\text{O}$  (0.2 mL).



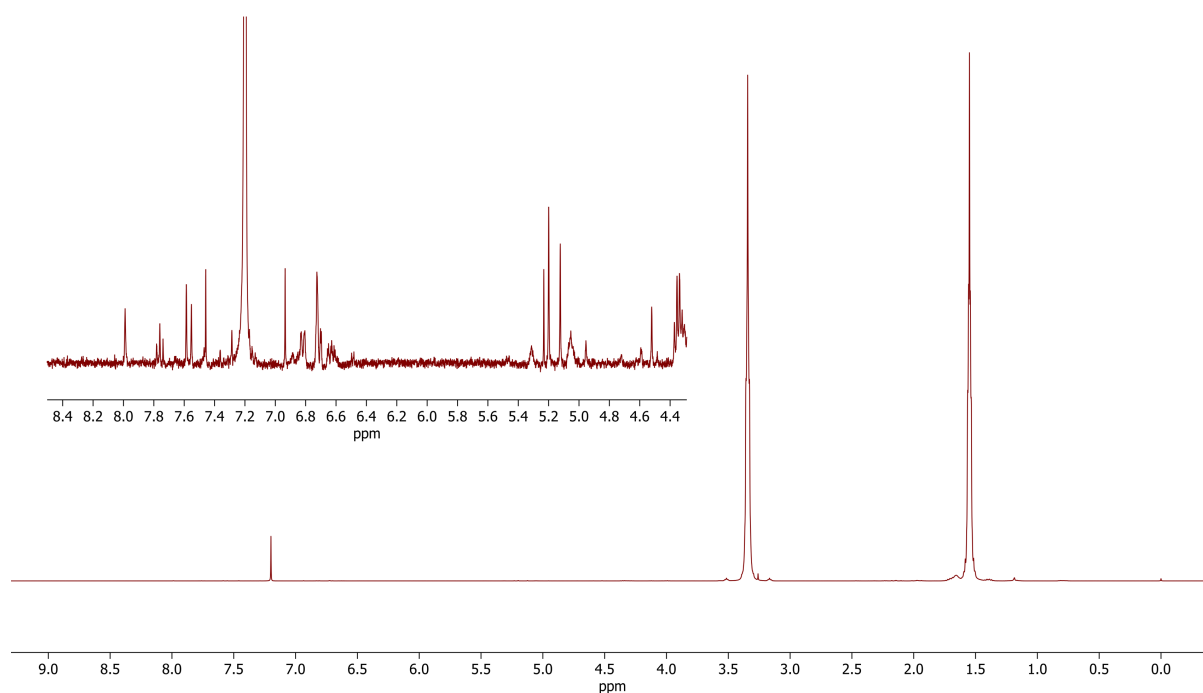
**Spectrum S53.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>Hc</sub>** after 180 min of sonication in THF (15 mL) and  $\text{D}_2\text{O}$  (0.2 mL). Approximately 25% of the fluorobenzene species formed is deuterated.



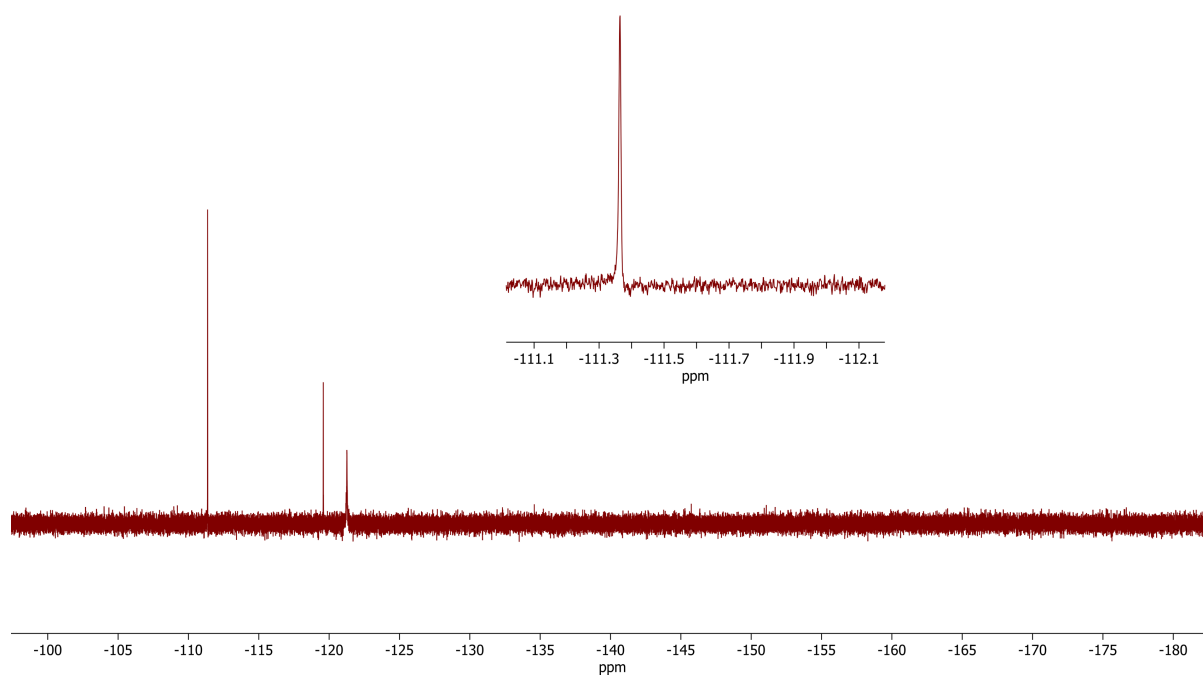
**Spectrum S54.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>Hc</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL).



**Spectrum S55.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>Hc</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL). 0% of the fluorobenzene species formed is deuterated.

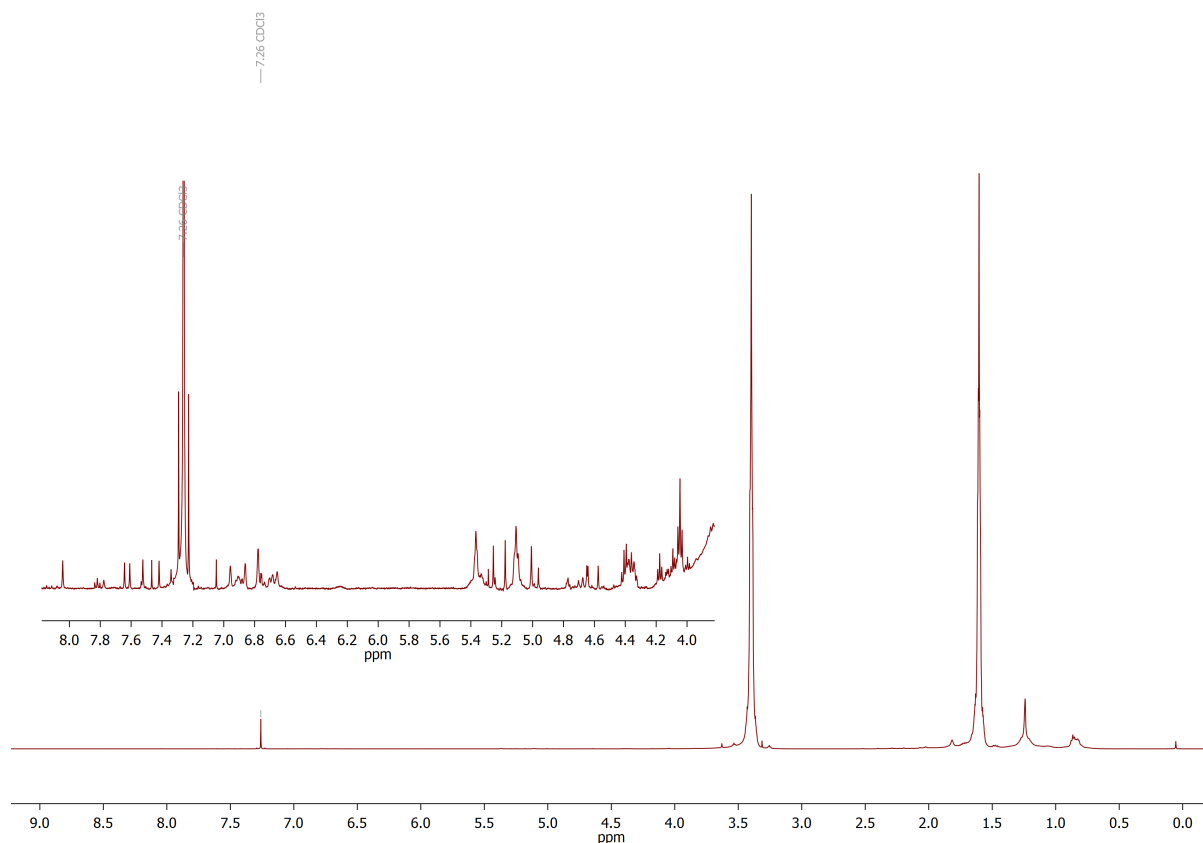


**Spectrum S56.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>Hc</sub>** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL).

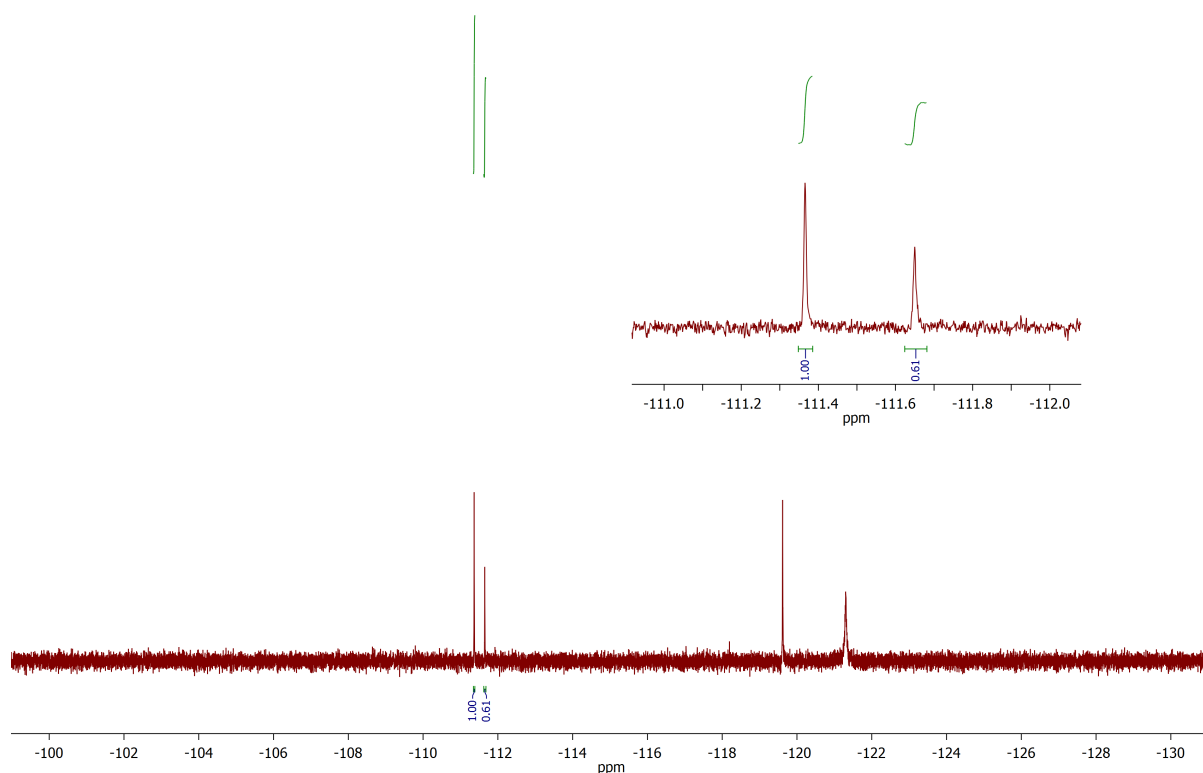


**Spectrum S57.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>Hc</sub>** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL). There is no observable deuteration of the fluorobenzene species formed.

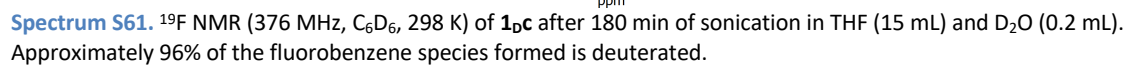
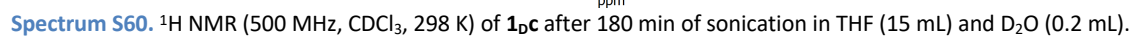




**Spectrum S58.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1b** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL).



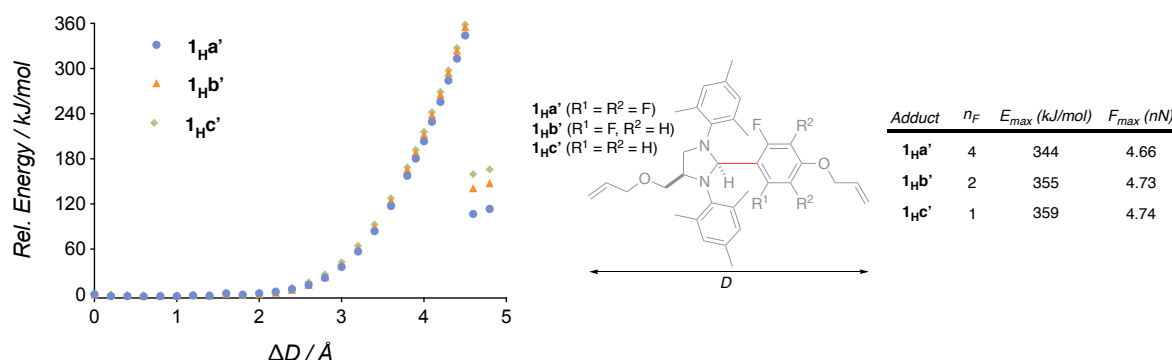
**Spectrum S59.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1b** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL). Approximately 38% of the fluorobenzene species formed is deuterated.



## 7 Calculations

### 7.1 CoGEF

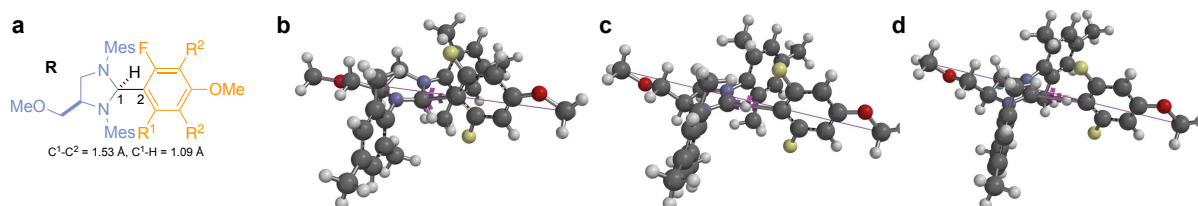
CoGEF calculations were performed on Spartan '14 following Beyer's method.<sup>3</sup> The structure of the mechanophore was built in Spartan '14 and minimized using molecular mechanics (MMFF). The distance between the terminal methylene groups was constrained and increased by increments of 0.2 Å. At each step, the energy was minimized by molecular mechanics (MMFF) then DFT (B3LYP/6-31G\*/SM8=THF). The relative energy of each intermediate was determined by setting the energy of the initial state at 0 kJ/mol.  $F_{\max}$  values were determined from the slope of the final 40% of the energy/elongation curve (i.e. from 0.6  $E_{\max}$  to  $E_{\max}$ ).



**Figure S12.** Evolution of energy of model mechanophores **1Ha-c'** upon simulated elongation (CoGEF, DFT B3LYP/6-31G\*/SM8=THF).  $F_{\max}$  values determined from the slope of the final 40% of the energy/elongation curve.

### 7.2 Force-modified potential energy surfaces

PES calculations were performed on Spartan '14. The structure of the model mechanophore **R** was built in Spartan '14 and minimized using molecular mechanics (MMFF). The distance between the terminal methyl groups was constrained at 13.839 Å to mimic the  $E_{\max}$  structures found in the CoGEF calculations, and C<sup>1</sup>-C<sup>2</sup> and C<sup>1</sup>-H bond lengths were increased by increments of 0.1 Å from 1.805 Å to 3.405 Å, and 0.99 Å to 2.09 Å respectively. At each step, the energy was minimized by molecular mechanics (MMFF) then DFT (B3LYP/6-31G\*/SM8=THF). The relative energy of each intermediate was determined by setting the energy of the force-free state at 0 kJ/mol.



**Figure S13.** Structure of model mechanophore **R** used in the PES calculations (a) and structures of **TS** (b), **P<sub>hetero</sub>** (c), **P<sub>conc</sub>** (d) for **R** where  $n_F = 2$  ( $R^1=F$ ,  $R^2=H$ ) as noted in Figure 2c given as examples.

**Table S6.** Energy values (kJ/mol) calculated for PES of **R** where  $n_F = 4$  ( $R^1=R^2=F$ )

$\downarrow C^1-C^2/C^1-H \rightarrow (\text{\AA})$	0.99	1.09	1.19	1.29	1.39	1.49	1.59	1.69	1.79	1.89	1.99	2.09
1.805	225.985871	206.06041	218.643916	247.765458								
1.905	231.175438	212.180195	225.734607	256.037362								
2.005	233.941407	216.110568	230.906583	262.385039								
2.105	233.959256	216.553753	232.425701	265.131842								
2.205	228.272945	212.751504	229.976634	264.114457								
2.305	219.122284	204.692263	223.240906	258.626895								
2.405	207.194891	193.977063	206.024705	199.611654	198.442257							
2.505	193.06943	180.790481	162.314299	153.71342	147.894779							
2.605	177.927635	142.473907	132.464707	125.298136	116.160342	109.695565	111.183438	114.97309	117.468366	118.888498	119.520721	120.267149
2.705	144.3879	120.657563	113.118434	109.568229	101.754735	89.9032212	81.9274739	83.79709	88.3292334	91.6735968	94.1213534	96.4428208
2.805	133.706306	105.905654	101.389531	101.656805	98.0937392	86.8350614	71.796713	62.0214435	64.0653967	68.8107263	72.5617834	76.0663018
2.905	125.386878	96.6247674	94.1940782	99.2016984	100.596366	93.3914644	78.0018206	59.4261344	48.0955192	50.4411402	55.0741037	59.127616
3.005	119.154463	91.8203619	91.9500646	101.007255	107.077418	104.98752	93.0010509	73.1614464	51.7208104	38.8915583	41.2605505	45.9281671
3.105	116.42368	90.0436875	92.2866546	104.601043	115.795921	119.229812	112.037777	95.0641694	71.3422355	48.0650619	33.6518457	35.4335083
3.205	115.811938	90.1384679	94.8496676	109.968096	123.764318	134.147129	132.686035	120.533113	98.8637977	71.1232688	44.8007736	29.8860881
3.305	116.319447	92.4221279	97.1966042	115.318082	134.80954	148.823423	151.243872	145.919091	128.24185	103.006315	73.0679766	43.3087045
3.405	119.826068	94.1940782	100.43805	122.04199	145.471181	163.959701	173.427786	171.773459	159.198355	136.860848	107.297959	74.817353

**Table S7.** Energy values (kJ/mol) calculated for PES of **R** where  $n_F = 2$  ( $R^1=F$ ,  $R^2=H$ )

$\downarrow C^1-C^2/C^1-H \rightarrow (\text{\AA})$	0.99	1.09	1.19	1.29	1.39	1.49	1.59	1.69	1.79	1.89	1.99	2.09
1.805	241.3805	221.537482	234.194762	263.465436								
1.905	248.537618	229.566267	243.093377	273.333647								
2.005	253.728498	235.743023	250.274912	281.541751								
2.105	255.195891	238.064491	253.654198	286.161584								
2.205	251.932129	236.429329	253.319447	287.152189								
2.305	245.352884	230.523787	248.584353	283.618524								
2.405	235.876136	222.18992	232.665673	222.643082	218.753138							
2.505	223.786225	211.012108	188.987562	176.654268	167.317455							
2.605	209.894957	172.263639	159.52208	148.744654	135.714026	125.471422	125.951362	129.177317	131.7209	133.23713	134.59	136.268271
2.705	175.17217	150.453333	140.342261	133.466863	121.838253	106.21389	94.6874111	96.1495553	100.676182	104.229798	107.15	109.949716
2.805	164.18103	136.495377	129.012173	126.531598	119.107201	104.13344	85.4157139	72.5851503	74.6558831	79.6543127	83.66	87.4352499
2.905	156.688112	127.783437	123.313782	125.4365	123.261274	112.189008	92.9396145	71.0539582	56.9263938	59.5518953	64.46	68.9417402
3.005	152.437162	123.83442	122.072971	128.425895	131.652112	125.888875	109.819491	86.4294199	62.0046408	46.6331158	49.05	53.8892146
3.105	150.51687	125.01222	124.878058	134.730253	142.925231	142.910531	132.044627	111.304999	84.3657781	56.2920722	40.33	42.131428
3.205	152.335555	124.041047	127.107107	140.37062	151.793913	158.92425	153.798484	137.736975	112.837242	82.6896554	54.04	37.103592
3.305	152.303524	126.753978	130.607165	146.848258	164.007222	174.80591	173.671958	165.055587	143.854134	114.930555	81.83	51.9975388
3.405	155.450713	128.695272	134.462974	153.36948	174.440443	190.279571	196.43532	191.723333	175.675478	149.843166	117.38	82.2672121

**Table S8.** Energy values (kJ/mol) calculated for PES of **R** where  $n_F = 1$  ( $R^1=R^2=H$ )

$\downarrow C^1-C^2/C^1-H \rightarrow (\text{\AA})$	0.99	1.09	1.19	1.29	1.39	1.49	1.59	1.69	1.79	1.89	1.99	2.09
1.805	248.593277	226.114256	235.294848	260.863823								
1.905	256.799546	234.682056	244.653712	270.69974								
2.005	263.512954	242.208582	253.045078	279.702061								
2.105	266.283909	247.040293	258.828271	286.909589								
2.205	266.574814	248.50086	261.598701	290.98253								
2.305	263.645542	245.981953	260.444793	290.866745								
2.405	257.575382	241.508098	258.07344	243.636067	236.251844							
2.505	248.767611	234.24701	215.521406	198.739723	185.055083							
2.605	237.37267	201.621737	185.93095	171.337098	154.06996	140.154013	138.795576	140.650233	141.200537	140.877337	141.174022	142.03676
2.705	201.261781	179.167918	166.544507	156.453128	141.237295	121.575699	107.061137	106.919098	109.958379	111.92593	113.432705	115.157397
2.805	190.735883	164.000131	154.653347	149.493185	138.842312	120.209651	98.1184156	82.8779025	83.5841625	87.1842504	89.8349573	92.1299095
2.905	184.043739	154.531786	148.113747	147.732524	142.634324	128.395178	105.998859	81.4798247	65.1870086	66.9804889	70.5503838	73.4704669
3.005	179.161619	148.983838	145.447812	149.685372	150.353825	141.631383	122.832002	96.5601803	69.9171127	53.0469503	54.7243838	58.4709764
3.105	175.37512	146.167987	144.993863	153.474234	159.857354	157.361289	143.715506	120.08599	90.5023599	61.8891157	44.5521394	46.7402304
3.205	173.381576	145.414992	147.096627	159.148468	176.452101	173.370812	165.730076	146.798108	119.159975	86.9650213	57.0826095	39.0026152
3.305	173.102486	146.358074	149.994656	165.251973	180.865044	189.630807	193.716088	174.659671	150.827728	119.729709	84.8756469	53.6434639
3.405	177.744109	148.120311	153.539084	171.697842	191.383592	205.126257	208.972092	201.618849	183.035022	154.99755	120.454085	84.3983291

### 7.3 Zoom on the force-modified potential energy surface of **R** ( $n_F = 1$ )

Calculations were performed on Spartan '18. The structure of the model mechanophore **R** was built in Spartan '18 and minimized using molecular mechanics (MMFF). The distance between the terminal methyl groups was constrained at 13.839Å to mimic the  $E_{max}$  structures found in the CoGEF calculations. An energy profile was built (MMFF) by increasing C<sup>1</sup>-C<sup>2</sup> bond length by increments of 0.025 Å from 2.205 Å to 2.705 Å, and the C<sup>1</sup>-H by increments of 0.01 Å from 1.04 Å to 1.14 Å. The equilibrium geometry of each structure was then recalculated by DFT (B3LYP/6-31G\*). The relative energy of each intermediate was determined by setting the energy of the force-free state at 0 kJ/mol.

**Table S9.** Energy values (kJ/mol) calculated for zoom of PES of **R** where  $n_F = 1$  ( $R^1=R^2=H$ )

$\downarrow C^1-C^2/C^1-H \rightarrow$ (Å)	1.04	1.05	1.06	1.07	1.08	1.09	1.10	1.11	1.12	1.13	1.14
2.205	263.60	261.94	260.70	259.83	259.33	259.21	259.38	259.79	260.54	261.54	262.75
2.230	264.19	262.6	261.37	260.54	260.07	259.94	260.12	260.61	261.37	262.41	263.65
2.255	263.2	261.62	260.44	259.61	259.15	260.53	259	259.5	260.24	261.27	262.51
2.280	263.25	261.65	260.48	259.68	259.24	259.28	259.37	259.9	260.71	261.78	263.06
2.305	263.52	261.95	260.8	260.02	259.62	259.56	259.79	260.35	261.19	262.29	263.6
2.330	265.79	264.27	263.19	262.44	262.06	262.03	262.32	262.92	263.82	264.92	266.27
2.355	265.67	264.19	263.13	262.41	262.06	262.06	262.38	263.02	263.95	265.09	266.47
2.380	265.63	264.16	263.11	262.45	262.14	262.16	262.51	263.17	264.13	265.3	266.72
2.405	265.45	264.01	262.99	262.36	262.08	262.13	262.52	263.21	264.2	265.4	266.85
2.430	263.38	261.99	261.03	260.39	260.13	260.22	260.62	261.34	262.35	263.55	265.01
2.455	263.09	261.73	260.8	260.2	259.97	260.09	260.53	261.28	262.28	263.57	265.07
2.480	262.75	261.42	260.52	259.94	259.75	259.9	260.37	261.16	262.23	259.88	257.23
2.505	262.35	261.1	260.2	259.69	259.53	259.7	260.18	257.4	254.71	252.01	249.4
2.530	261.82	260.68	259.73	259.27	258.7	255.75	252.92	250.19	247.52	244.87	242.33
2.555	261.37	261.59	258.23	255.03	251.99	249.11	246.29	243.61	241.02	238.45	235.97
2.580	258.86	255.43	252.14	249.03	246.37	243.08	240.36	237.77	235.22	232.76	230.28
2.605	253.47	249.99	246.66	243.5	240.51	237.72	235	232.43	229.98	227.53	225.17
2.630	248.32	244.89	241.64	238.58	235.66	232.88	230.26	227.72	225.34	222.98	220.71
2.655	244.04	240.43	237.22	234.21	231.34	228.64	226.08	223.64	221.26	218.98	216.8
2.680	239.86	236.5	233.33	230.36	227.72	225.08	222.57	219.94	217.94	215.77	213.59
2.705	236.33	233.07	229.94	226.98	224.44	221.85	219.42	216.84	214.94	212.83	210.53

**Table S10.** C<sup>2</sup>-C<sup>1</sup>-H bond angle measured from the structures calculated for zoom of PES of **R** where  $n_F = 1$  ( $R^1=R^2=H$ )

$\downarrow C^1-C^2/C^1-H \rightarrow$ (Å)	1.04	1.05	1.06	1.07	1.08	1.09	1.10	1.11	1.12	1.13	1.14
2.205	82.4	82.4	82.5	82.4	82.4	82.5	82.6	82.6	82.6	82.6	82.7
2.230	81.4	81.5	81.5	81.5	81.5	81.5	81.7	81.7	81.7	81.7	81.8
2.255	80.1	80.3	80.4	80.5	80.5	80.6	80.7	80.7	80.8	80.9	81.4
2.280	79.4	79.4	79.5	79.5	79.4	79.5	79.7	79.7	79.7	79.7	79.9
2.305	78.5	78.5	78.6	78.6	78.6	78.8	78.8	78.8	78.8	78.9	79.0
2.330	77.7	77.8	78.0	78.0	78.0	78.0	78.0	78.0	78.0	78.2	78.4
2.355	76.7	76.8	76.9	76.9	76.9	76.9	76.9	77.0	77.0	77.1	77.3
2.380	75.8	75.8	75.9	76.0	76.1	76.1	76.0	76.1	76.1	76.2	76.4
2.405	74.8	74.8	74.9	75.0	75.1	75.1	75.0	75.1	75.1	75.2	75.5
2.430	73.5	73.7	73.9	73.9	74.0	74.0	74.0	74.0	74.0	74.3	74.6
2.455	72.4	72.6	72.8	72.8	72.9	72.9	72.9	73.0	73.1	73.2	73.5
2.480	71.3	71.6	71.8	71.8	71.9	71.9	71.9	71.9	72.0	7.9	7.5
2.505	69.9	70.4	70.5	70.7	70.7	70.7	9.3	8.9	8.5	7.8	7.4
2.530	68.0	68.2	68.5	68.8	10.2	9.9	9.3	8.8	8.2	7.6	7.3
2.555	66.7	66.8	11.6	11.1	10.3	9.4	9.0	8.6	8.2	7.6	7.2
2.580	14.4	12.9	11.8	10.9	10.9	9.6	9.3	8.8	8.2	7.7	7.2
2.605	13.3	11.9	11.3	10.9	10.0	9.1	8.7	8.4	8.1	7.4	7.0
2.630	13.7	12.6	11.6	10.7	10.0	9.4	8.8	8.3	7.8	7.4	7.0
2.655	12.8	12.4	11.6	10.6	10.0	9.4	8.8	8.4	7.8	7.3	6.8
2.680	13.6	12.4	11.4	10.6	9.9	9.2	8.6	8.3	7.6	7.1	6.6
2.705	13.7	11.5	11.3	10.5	9.8	9.2	8.6	8.4	7.5	7.1	6.8

Force free

104.7

## 7.4 Vibration of the C-X bond along the heterolytic pathway

Calculations were performed on Spartan '18. The structure of the model mechanophore **R** was built in Spartan '18 and minimized using molecular mechanics (MMFF). The distance between the terminal methyl groups was constrained at 13.839 Å to mimic the  $E_{max}$  structures found in the CoGEF calculations. An energy profile was built (MMFF) by increasing C<sup>1</sup>-C<sup>2</sup> bond length by increments of 0.1 Å from 2.205 Å to 3.205 Å, at a fixed C<sup>1</sup>-H bond length of 1.090 Å. The equilibrium geometry and the IR spectrum of each structure was then recalculated by DFT (B3LYP/6-31G\*/SM8=THF). The relative energy of each intermediate was determined by setting the energy of the force-free state at 0 kJ/mol.

**Table S10.** C-H bond vibration calculated for **R** where  $n_F = 1$  ( $R^1=R^2=H$ ) along the heterolytic pathway (C<sup>1</sup>-H = 1.090 Å)

C <sup>1</sup> -C <sup>2</sup> (Å)	Rel. energy (kJ/mol)	$\bar{\nu}_{C1-H}$ (cm <sup>-1</sup> )	$\nu_{C1-H}$ (THz)	$\nu_{C1-H}$ (fs)
2.205	259.136244	2947	88.3488374	11.32
2.305	259.522457	2967	88.9484223	11.24
2.405	260.231606	2979	89.3081732	11.20
2.505	259.791834	2997	89.8477997	11.13
2.605	237.75127	2582	77.4064127	12.92
2.705	221.529607	2612	78.30579	12.77
2.805	212.632043	2645	79.2951051	12.61
2.905	209.90152	2622	78.6055825	12.72
3.005	209.085775	2664	79.8647108	12.52
3.105	210.951724	2716	81.4236316	12.28
3.205	214.63189	2768	82.9825524	12.05
Force free	0	2854	85.5607675	11.68

**Table S11.** C-D bond vibration calculated for **R** where  $n_F = 1$  ( $R^1=R^2=H$ ) along the heterolytic pathway (C<sup>1</sup>-D = 1.090 Å)

C <sup>1</sup> -C <sup>2</sup> (Å)	Rel. energy (kJ/mol)	$\bar{\nu}_{C1-D}$ (cm <sup>-1</sup> )	$\nu_{C1-D}$ (THz)	$\nu_{C1-D}$ (fs)
2.205	259.23	2181	65.3847351	15.29
2.305	259.44	2191	65.6845275	15.22
2.405	260.19	2203	66.0442785	15.14
2.505	259.8	2219	66.5239464	15.03
2.605	237.74	1964	58.8792388	16.98
2.705	221.53	1988	59.5987407	16.78
2.805	213.09	2005	60.1083878	16.64
2.905	210.02	2013	60.3482218	16.57
3.005	209.13	2044	61.2775784	16.32
3.105	211.22	2074	62.1769558	16.08
3.205	215.01	2098	62.8964577	15.90
Force free	0	2099	62.9264369	15.8915719

**Table S12.** C-H bond vibration calculated for **R** where  $n_F = 2$  ( $R^1=F$ ,  $R^2=H$ ) along the heterolytic pathway (C<sup>1</sup>-H = 1.090 Å)

C <sup>1</sup> -C <sup>2</sup> (Å)	Rel. energy (kJ/mol)	$\bar{\nu}_{C1-H}$ (cm <sup>-1</sup> )	$\nu_{C1-H}$ (THz)	$\nu_{C1-H}$ (fs)
2.205	244.511935	2995	89.7878412	11.14
2.305	241.332715	3009	90.2075506	11.08
2.405	237.197812	3021	90.5673016	11.04
2.505	231.537492	3037	91.0469695	10.98
2.605	198.416789	2577	77.2565164	12.94
2.705	180.579917	2602	78.0059976	12.82
2.805	170.635303	2634	78.9653334	12.66
2.905	166.130727	2689	80.614192	12.40
3.005	166.126526	2735	81.9932373	12.20
3.105	169.260325	2779	83.3123241	12.00
3.205	174.060006	2822	84.6014316	11.82
Force free	0	2809	84.2144268	11.92

**Table S13.** C-D bond vibration calculated for **R** where  $n_F = 2$  ( $R^1=F$ ,  $R^2=H$ ) along the heterolytic pathway ( $C^1-D = 1.090$  Å)

$C^1-C^2$ (Å)	Rel. energy (kJ/mol)	$\bar{\nu}_{C1-D}$ (cm <sup>-1</sup> )	$\nu_{C1-D}$ (THz)	$\nu_{C1-D}$ (fs)
2.205	244.511935	2215	66.4040294	15.06
2.305	241.332715	2226	66.7338012	14.98
2.405	237.197812	2238	67.0935521	14.90
2.505	231.537492	2252	67.5132615	14.81
2.605	198.416789	1977	59.2689689	16.87
2.705	180.579917	1998	59.8985331	16.69
2.805	170.635303	2022	60.618035	16.50
2.905	166.130727	2056	61.6373294	16.22
3.005	166.126526	2084	62.4767482	16.00
3.105	169.260325	2111	63.2861879	15.80
3.205	174.060006	2136	64.035669	15.62
Force free	0	2119	63.5423742	15.77

**Table S14.** C-H bond vibration calculated for **R** where  $n_F = 4$  ( $R^1=R^2=F$ ) along the heterolytic pathway ( $C^1-H = 1.090$  Å)

$C^1-C^2$ (Å)	Rel. energy (kJ/mol)	$\bar{\nu}_{C1-H}$ (cm <sup>-1</sup> )	$\nu_{C1-H}$ (THz)	$\nu_{C1-H}$ (fs)
2.205	222.407048	2998	89.8777789	11.13
2.305	217.592926	3005	90.0876336	11.10
2.405	210.869018	3021	90.5673016	11.04
2.505	203.183387	3042	91.1968657	10.96
2.605	169.128529	2578	77.2864957	12.94
2.705	151.074001	2604	78.0659561	12.81
2.805	139.97942	2655	79.5948976	12.56
2.905	134.544102	2709	81.2137769	12.31
3.005	132.723316	2757	82.6527807	12.10
3.105	135.432835	2798	83.8819297	11.92
3.205	138.987504	2839	85.1110788	11.75
Force free	0	2941	88.1689619	11.34

**Table S15.** C-D bond vibration calculated for **R** where  $n_F = 2$  ( $R^1=F$ ,  $R^2=H$ ) along the heterolytic pathway ( $C^1-D = 1.090$  Å)

$C^1-C^2$ (Å)	Rel. energy (kJ/mol)	$\bar{\nu}_{C1-D}$ (cm <sup>-1</sup> )	$\nu_{C1-D}$ (THz)	$\nu_{C1-D}$ (fs)
2.205	222.407048	2216	66.4340087	15.05
2.305	217.592926	2225	66.7038219	14.99
2.405	210.869018	2239	67.1235313	14.90
2.505	203.183387	2257	67.6631578	14.78
2.605	169.128529	1981	59.3888859	16.84
2.705	151.074001	2003	60.0484293	16.65
2.805	139.97942	2036	61.0377444	16.38
2.905	134.544102	2069	62.0270596	16.12
3.005	132.723316	2098	62.8964577	15.90
3.105	135.432835	2121	63.5859803	15.73
3.205	138.987504	2147	64.3654407	15.54
Force free	0	2163	64.8451087	15.42

## 7.5 Amplitude of the C-X bond stretching along the heterolytic pathway for **R** ( $n_F = 1$ )

The amplitude was calculated by treating the C-X bond as a harmonic oscillator with the following equation:  $x = \sqrt{k/2E}$ , where  $x$  is the amplitude,  $k$  the force constant of the oscillator (C-X bond), and  $E$  the thermal energy ( $3.866 \times 10^{-21}$  J at 280 K). The force constant can be calculated with the following equation:  $k_X = m_X \cdot (2\pi \cdot \nu_X)^2$  where  $m_X$  is the mass of X ( $m_H = 1.6726 \times 10^{-27}$  kg,  $m_D = 3.3435 \times 10^{-27}$  kg), and  $\nu_X$  the C-X vibration frequency. We used the average over the pre-VRI range (i.e. from 2.205 Å to 2.505 Å) for  $\nu_X$  ( $\nu_H = 8.91 \times 10^{13}$  Hz,  $\nu_D = 6.59 \times 10^{13}$  Hz). Results are presented in Table S16.

**Table S1.** Parameters for the determination of the C-X bond vibration amplitude for **R** ( $n_F = 1$ )

	X = H	X = D
$m_X$	$1.6726 \times 10^{-27}$ kg	$3.3435 \times 10^{-27}$ kg
$\nu_X$	$8.91 \times 10^{13}$ Hz	$6.59 \times 10^{13}$ Hz
$k_X$	524 N/m	573 N/m
$x_X$	0.0384 Å	0.0367 Å

## 8 References

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