

Supporting Information

**Borazine- $\text{CF}_3^-$  Adducts for Rapid, Room Temperature, and Broad Scope Trifluoromethylation**

*Jacob B. Geri, Michael M. Wade Wolfe, and Nathaniel K. Szymczak\**

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## General Considerations:

Hexamethylborazine,<sup>[1]</sup> 1-Chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole,<sup>[2]</sup> 6-chloro-9-tosyl-9*H*-purine,<sup>[3]</sup> 2-fluoroquinoline,<sup>[4]</sup> benzylpotassium,<sup>[5]</sup> dimsyl potassium,<sup>[6]</sup> dimsyl sodium,<sup>[7]</sup> 2-nitro-5-phenylpyridine,<sup>[8]</sup> Pd(TMEDA)(Tol)I,<sup>[9]</sup> diphenoxy-chloro-triazine,<sup>[10]</sup> and K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF),<sup>[11]</sup> K(BOCH<sub>2</sub>CH<sub>2</sub>N)<sub>3</sub>CF<sub>3</sub>,<sup>[11]</sup> and N-tosylbenzaldimine<sup>[12]</sup> were prepared according to literature procedures. DMSO, THF, and DMF were purified using a Glass Contour solvent purification system through percolation through a Cu catalyst, molecular sieves, and alumina and finally stored over activated molecular sieves for a minimum of 48 hours. All other reagents were used from commercial sources without further purification. Unless otherwise noted, all manipulations were performed under an inert nitrogen atmosphere.

NMR spectra were recorded on a Varian Vnmrs 700, Varian Vnmrs 500, or Varian MR400 spectrometer. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, <sup>11</sup>B, and <sup>31</sup>P shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. <sup>31</sup>P, <sup>11</sup>B, <sup>77</sup>Se, <sup>127</sup>Te, <sup>29</sup>Si, and <sup>19</sup>F NMR spectra are referenced to fluorobenzene or, in spectra lacking internal standard, on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the <sup>1</sup>H NMR spectrum. Peaks not listed in the peak assignment correspond to residual solvent.<sup>[13]</sup> Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), septet (sp), and multiplet (m). Mass spectra were obtained on an electrospray Agilent Q-TOF mass spectrometer or a Micromass AutoSpec Ultima Magnetic Sector Mass Spectrometer electron ionization mass spectrometer. NMR spectra were processed using MestReNova version 10.0.2. For the purpose of labeling atoms for spectral assignments, hydrogen atoms are labeled with greek letters while carbon atoms are labeled with numbers. In spectra of *in-situ* reactions, HCF<sub>3</sub> and fluorobenzene (internal standard) appear at -78.52 and -113.15 ppm, respectively

## Preparation of CF<sub>3</sub><sup>-</sup> Reagent Stock Solutions

### K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>)CF<sub>3</sub>(THF) in THF:

Hexamethylborazine (2.70 mmol, 0.443 g) and 18-crown-6 (2.70 mmol, 0.712 g) were dissolved in 11 mL THF in a 20 mL single-neck conical flask equipped with a large Teflon-coated magnetic stirbar. The vessel was then cooled to 0 °C for one hour with gentle stirring. Benzylpotassium (2.70 mmol, 0.350 g) was quickly added to this cold solution, and the initial deep red color of dissolved benzylpotassium quickly changed to light purple. The flask was then sealed with a belt-clamped septum. HCF<sub>3</sub> was added to the sealed vessel with a 60 mL syringe (3.3 mmol, 75 mL) and continuously stirred for 10 minutes. <sup>19</sup>F NMR showed >99% yield of K(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>).

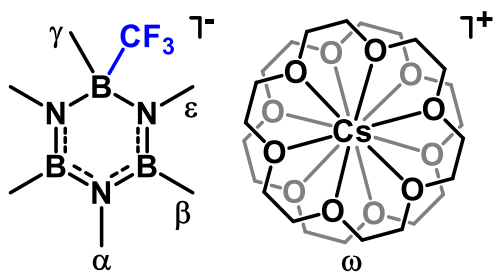
### K(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>)CF<sub>3</sub> in DMSO:

Hexamethylborazine (2.70 mmol, 0.443 g) was suspended in 13 mL DMSO in a 20 mL single-neck conical flask equipped with a large Teflon-coated magnetic stirbar, which was then sealed with a belt-clamped septum. Dimsyl potassium (1.80 M, 2.70 mmol, 1.50 mL) was then rapidly added via syringe, and the mixture was stirred for 30 minutes at 2000 rpm, which afforded a homogeneous solution. HCF<sub>3</sub> was added to the sealed vessel with a 60 mL syringe (12.0 mmol, 297 mL) and continuously stirred for 10 minutes. <sup>19</sup>F NMR showed >99% yield of K(BOCH<sub>2</sub>CH<sub>2</sub>N)<sub>3</sub>CF<sub>3</sub>. The t<sub>1/2</sub> of this solution (<sup>19</sup>F NMR, 25 °C): 17 days

### K(BOCH<sub>2</sub>CH<sub>2</sub>N)<sub>3</sub>CF<sub>3</sub> in DMSO:

Trisethyleneoxyborazine (10.5 mmol, 2.17 g) was suspended in 43 mL DMSO in a 100 mL single-neck round bottom flask equipped with a large Teflon-coated magnetic stirbar, which was then sealed with a belt-clamped septum. Dimsyl potassium (1.93 M, 10.0 mmol, 5.18 mL) was then rapidly added via syringe, and the mixture vigorously stirred for 30 minutes. HCF<sub>3</sub> was added to the sealed vessel with a 60 mL syringe (12.0 mmol, 297 mL) and continuously stirred for 10 minutes. <sup>19</sup>F NMR showed 99% yield of K(BOCH<sub>2</sub>CH<sub>2</sub>N)<sub>3</sub>CF<sub>3</sub> (based on KDMSO). The t<sub>1/2</sub> of this solution (<sup>19</sup>F NMR, 25 °C): >5 months

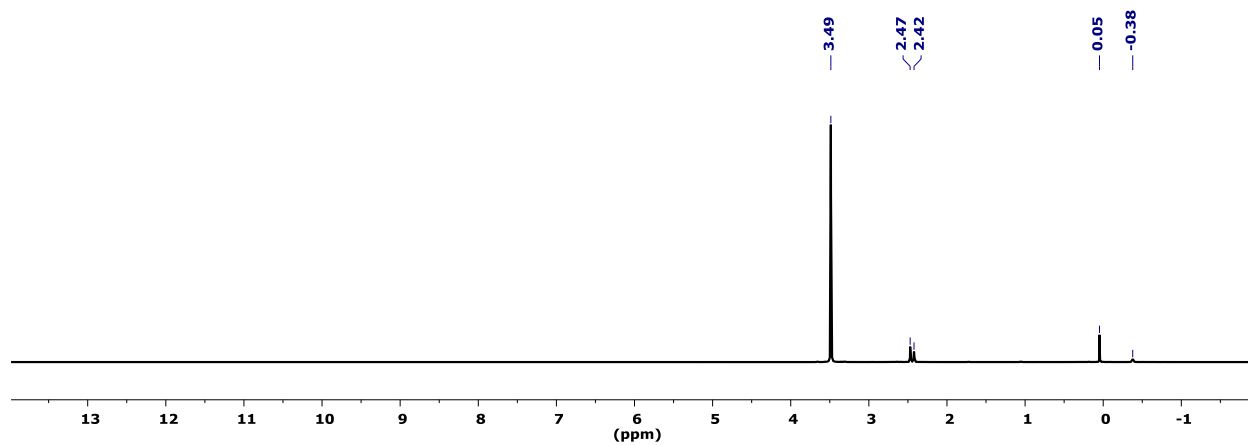
## Preparation of 2b:



Hexamethylborazine (3.15 mmol, 0.518 g), 18-crown-6 (6.30 mmol, 1.668 g) and cesium fluoride (3.00 mmol, 0.455 g) were combined in 10 mL THF. The mixture was stirred at 0 °C for 50 minutes. SiMe<sub>3</sub>CF<sub>3</sub> (3.6 mmol, 0.53 mL), cooled to 0 °C, was slowly added to the mixture and the reaction stirred for 1.5 hours. Volatiles were removed under vacuum, and the resulting solid dissolved in 10 mL of THF and filtered. The filtrate was layered with 115 mL of Et<sub>2</sub>O, and allowed to stand for 3 days at -30 °C to afford large crystals. Solvent was decanted from the crystals, which

were then washed with pentane (5x 15 mL). The residual solvent was allowed to evaporate at ambient pressure for 90 minutes to afford crystalline **2b** (1.215g, 45%). A single crystal for structural analysis was prepared by layering Et<sub>2</sub>O on a concentrated THF solution of **2b** at -30 °C. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): 3.49 (ω, 48H, s), 2.47 (α, 3H, s), 2.42 (ε, 6H, s), -0.05 (β, 6H, s), -0.38 (γ, 3H, s). <sup>11</sup>B-NMR: 32.94 (2B), -5.77 (1B). <sup>19</sup>F-NMR: -64.50 (3F (dd, *J*<sub>11B-19F</sub>: 56, 22)). HRMS (ES<sup>+</sup>): 191.0195 (M<sup>+</sup>: 191.0194). Anal. Calcd for C<sub>31</sub>H<sub>66</sub>B<sub>3</sub>CsF<sub>3</sub>N<sub>3</sub>O<sub>12</sub>: C, 41.59; H, 7.43; N, 4.69. Found: C, 41.09; H, 6.95; N, 4.46. Samples were aged for 30 days at either 25 °C, during which time greater than 80% of the sample decomposed, or at or -30 °C, during which no decomposition was observed. The samples were subjected to elemental analysis (Anal. Calcd for C<sub>31</sub>H<sub>66</sub>B<sub>3</sub>CsF<sub>3</sub>N<sub>3</sub>O<sub>12</sub>: C, 41.59; H, 7.43; N, 4.69. Found (30 days at 25 °C): C, 41.67; H, 7.62; N, 4.45), found (30 days at -30 °C): C, 41.42; H, 7.24; N, 4.66). Elemental analysis of the decomposed sample still closely matched the expected values for pure **2b**, indicating that HCF<sub>3</sub> gas is not a decomposition product.

**Fig. S1. <sup>1</sup>H NMR Spectrum:**



**Fig. S2. <sup>13</sup>C NMR Spectrum:**

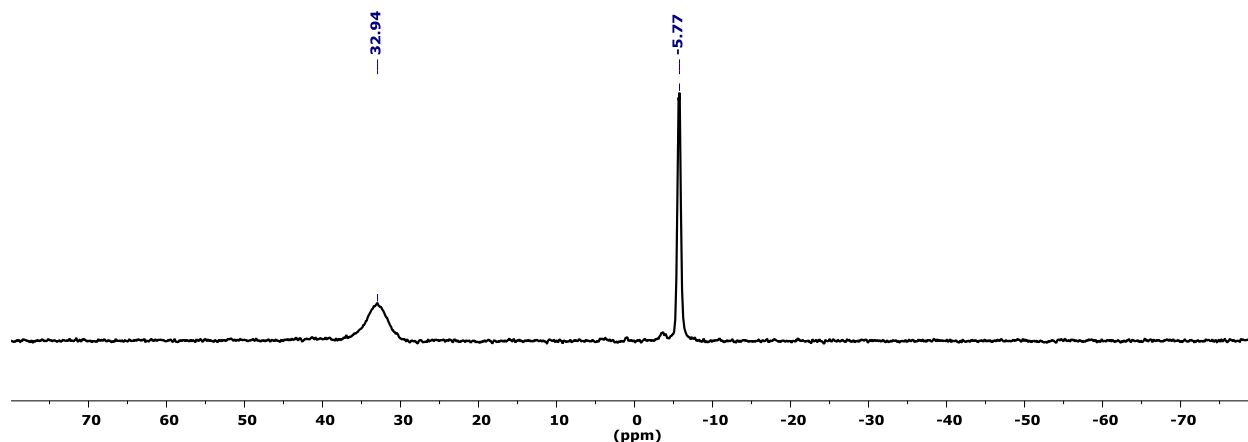


Fig. S3.  $^{19}\text{F}$  NMR Spectrum:

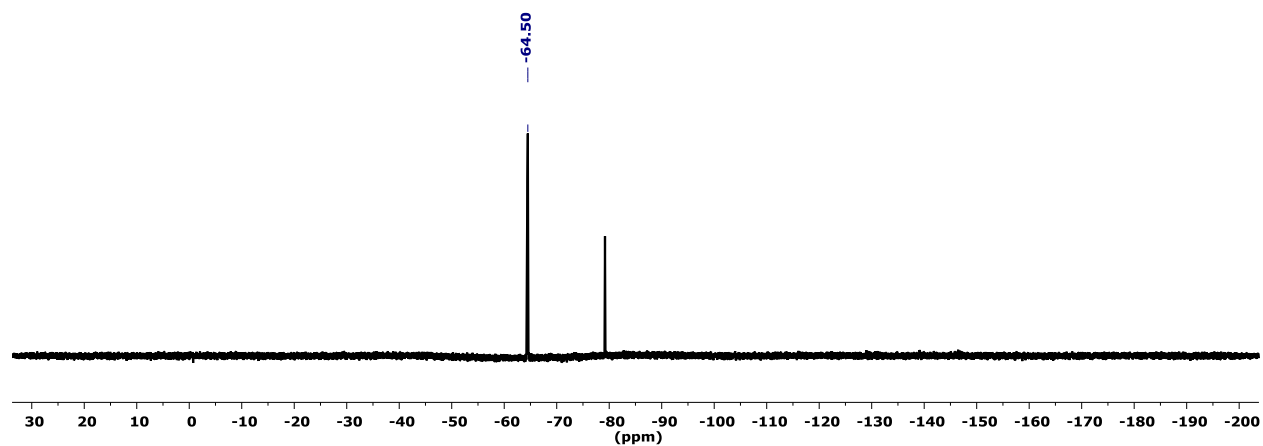
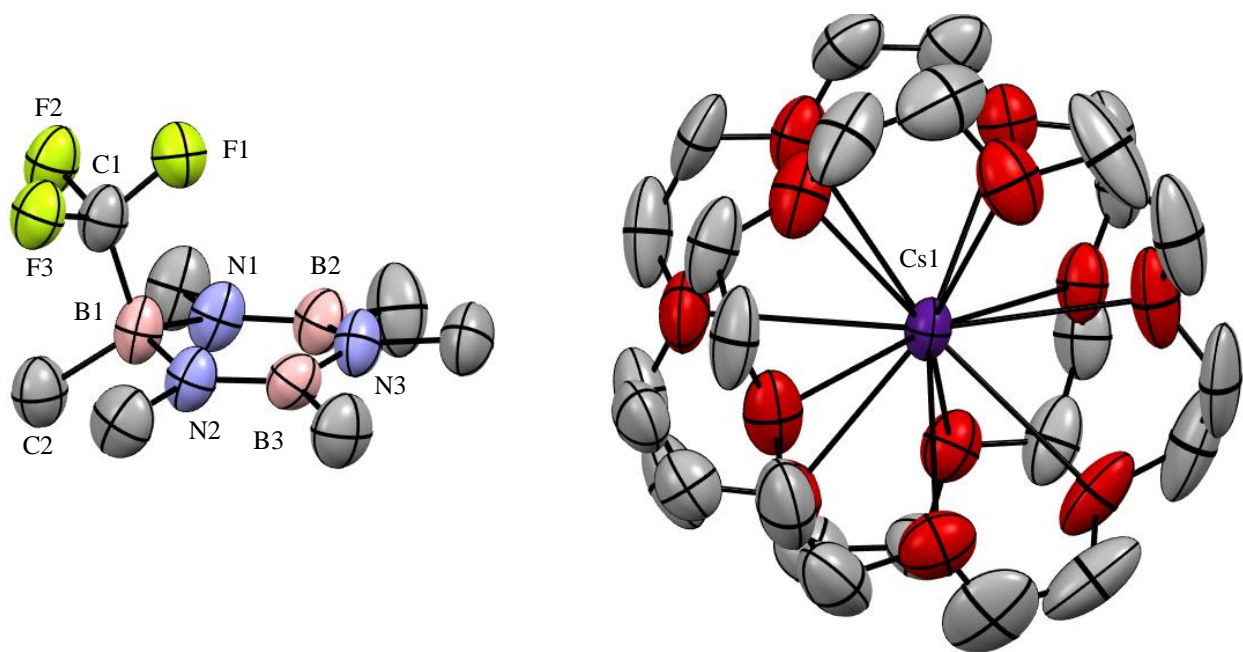
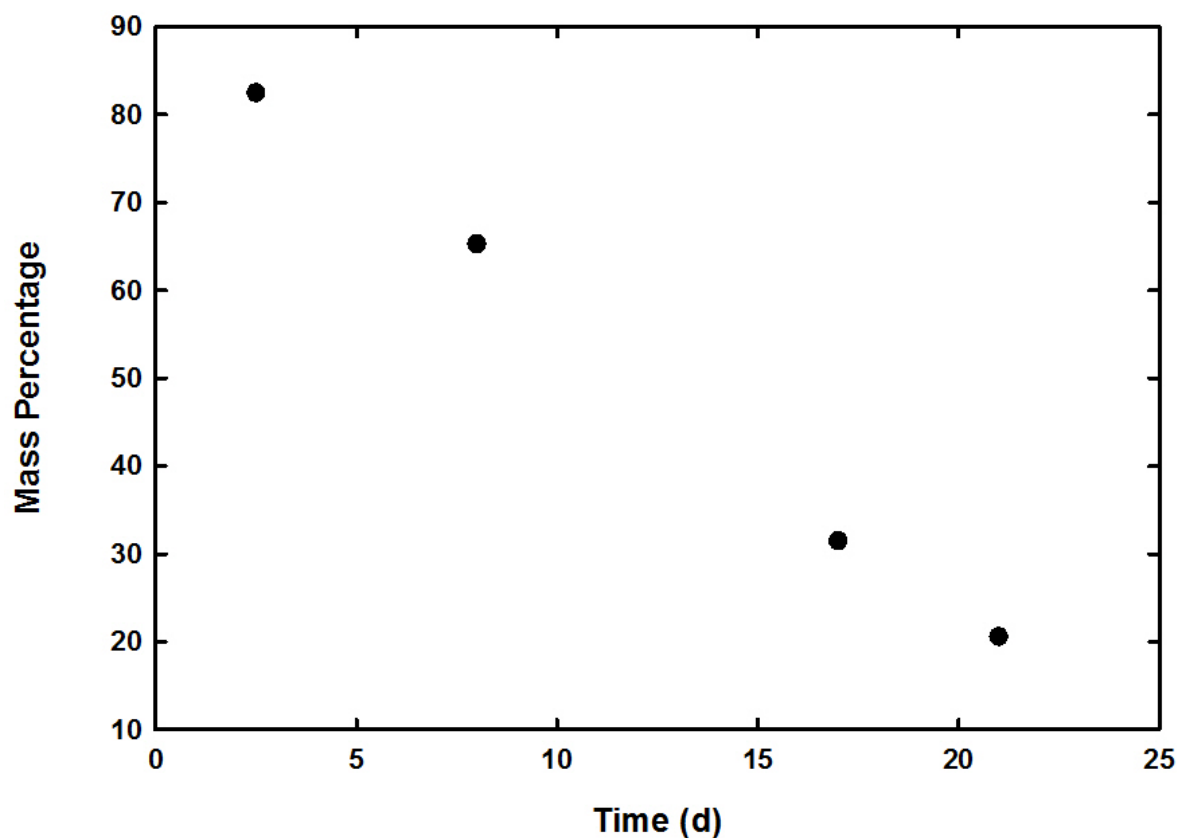


Fig. S4. X-Ray Crystal Structure:



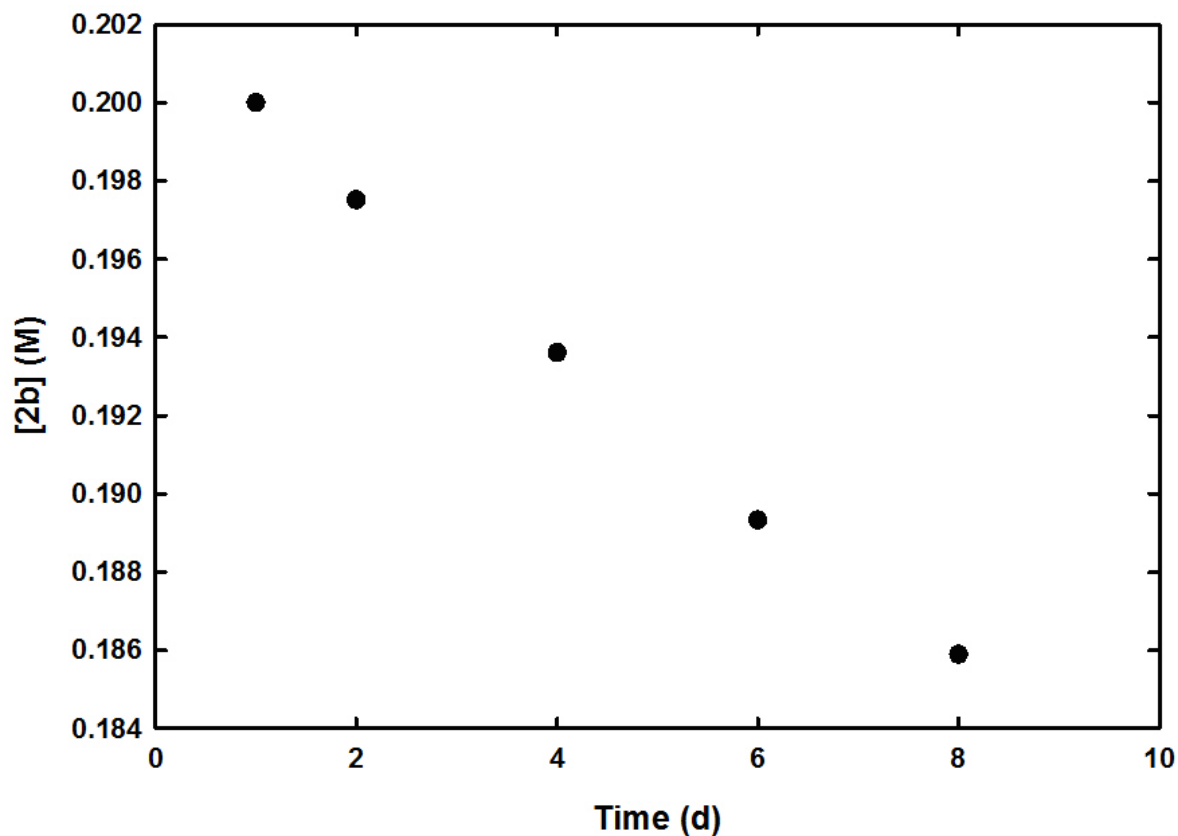
Selected bond distances: B1-C1: 1.630 Å, B1-C2: 1.644 Å, B1-N1: 1.553 Å, B1-N2: 1.546 Å, N1-B2: 1.401 Å, N2-B3: 1.389 Å, N3-B2: 1.436 Å, N3-B3: 1.446 Å, C1-F1: 1.367 Å, C1-F2: 1.382 Å, C1-F3: 1.393 Å

### Stability of **2b** at 25 °C in Solid State



**2b** decomposes at a rate of 3.4% per day ( $R^2 = 0.998$ ). Samples of pure solid (10-15 mg) were weighed into sealed vials and allowed to stand at 25°C for a desired amount of time. Mass percentage was determined by comparing the original mass of the sample to the number of moles of **2b** determined by dissolving the sample and integrating its resonance in the  $^{19}\text{F}$  NMR spectrum against 10.0  $\mu\text{L}$  added fluorobenzene standard.

### Stability of **2b** at 25 °C in Solution



A 0.2 M sample of **2b** was prepared in an NMR tube and periodically monitored by  $^{19}\text{F}$  NMR spectroscopy at room temperature. Rate of decomposition: 0.00201 M/d  $R^2 = 0.998$

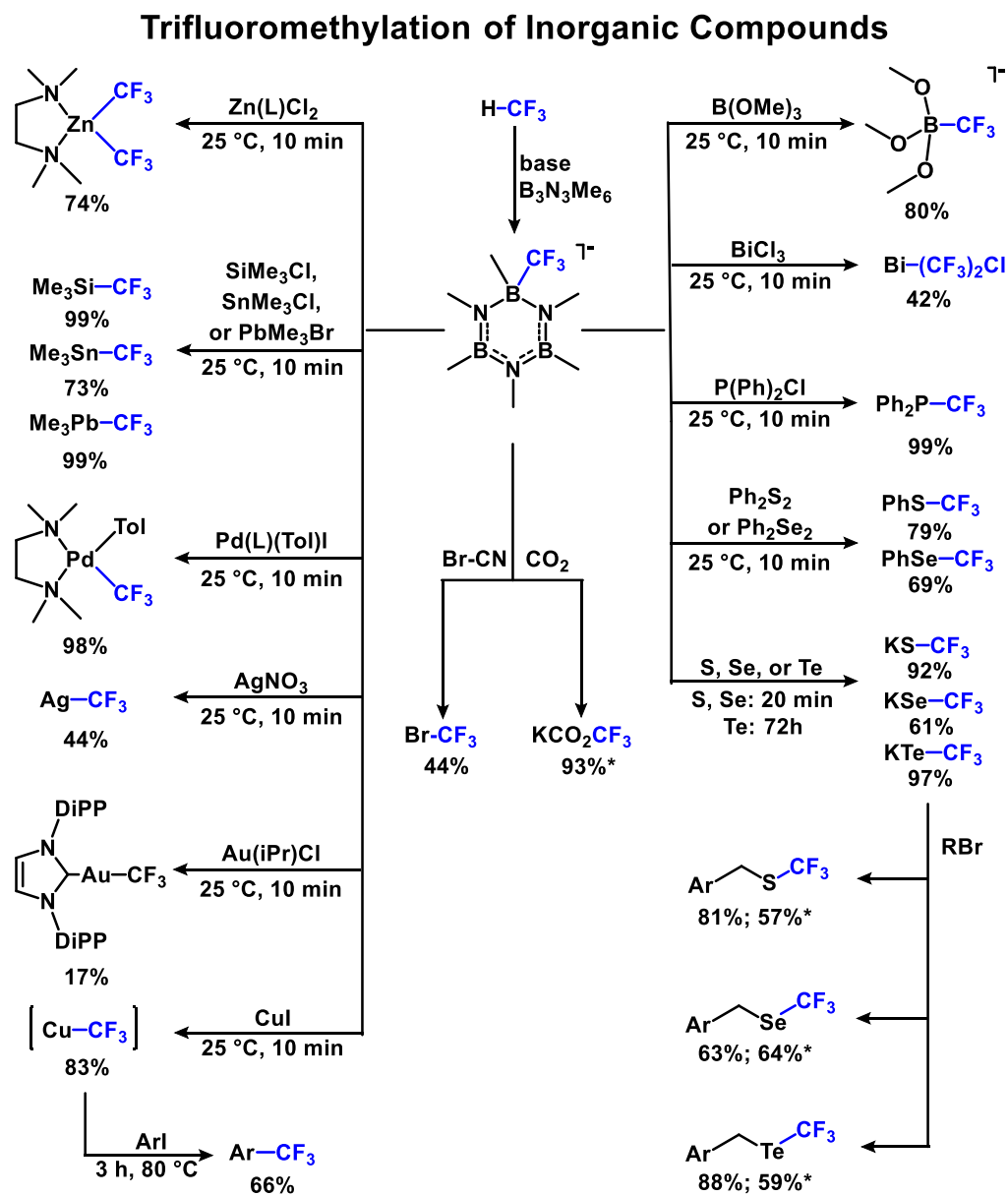
### Reactions with Inorganic Electrophiles

#### General Protocol:

To 0.100 mmol of substrate dissolved in 0.50 mL DMSO or THF was added 0.100 mmol K(18-crown-6)( $\text{B}_3\text{N}_3\text{Me}_6$ ) $\text{CF}_3$  as a solution in matching solvent. Characterization of  $\text{B}(\text{OMe})_3\text{CF}_3^-$  is provided for in our previous manuscript.<sup>[11]</sup>



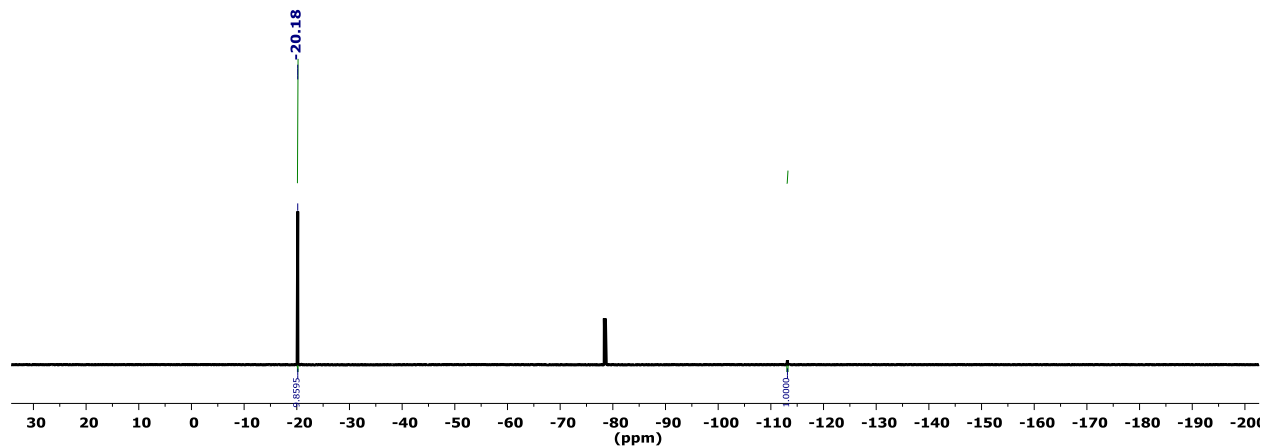
Fig. S5. Trifluoromethylation of Inorganic Compounds



### Pd(TMEDA)(Tol)CF<sub>3</sub>

Experimental: Pd(TMEDA)(Tol)I (Tol=C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) (22.0 mg, 0.0500 mmol) was placed in an NMR tube and dissolved in 1.5 mL THF. K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF) (0.250 mL 0.20 M stock in THF, 0.0500 mmol) was then added and the NMR tube and vigorously shaken. <sup>19</sup>F NMR spectra were recorded 10 minutes after CF<sub>3</sub><sup>-</sup> addition and the product peak integrated against 0.030 mmol fluorobenzene internal standard. The product conformed to literature spectra of Pd(TMEDA)(Ph). <sup>19</sup>F NMR (literature (in CDCl<sub>3</sub>): -21.14).<sup>[9]</sup> -20.18 (3F, s). Yield: 98%.

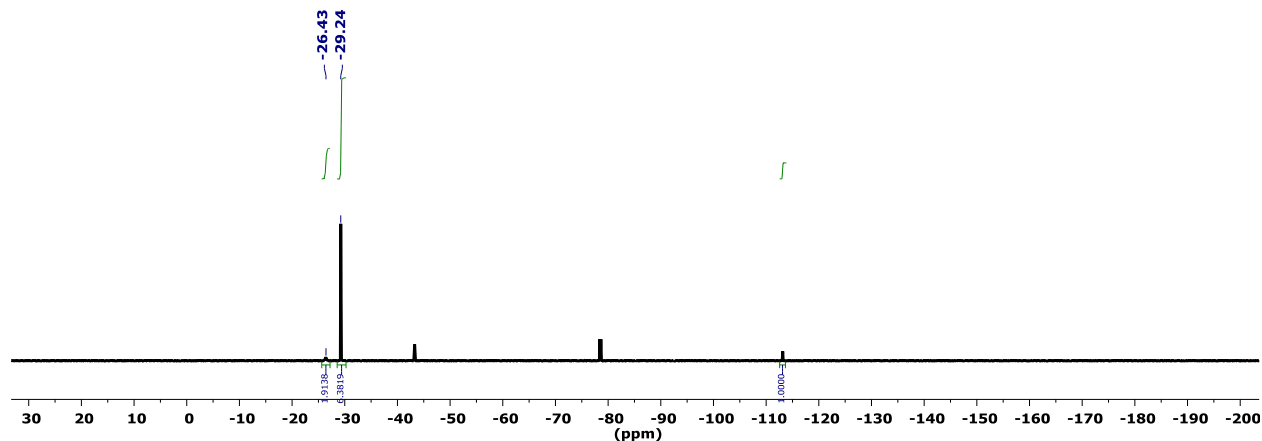
**Fig. S6. *In-Situ* <sup>19</sup>F NMR Spectrum:**



### CuCF<sub>3</sub>

Experimental: CuI (19.0 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL DMSO. K(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>) (0.50 mL 0.20 M stock in DMSO, 0.100 mmol) was then added and the NMR tube vigorously shaken. <sup>19</sup>F NMR spectra were recorded 10 minutes after CF<sub>3</sub><sup>-</sup> addition and the product peak integrated against 0.030 mmol fluorobenzene internal standard. The product conformed to literature spectra of CuCF<sub>3</sub>, in which a Schlenk equilibrium is observed. <sup>19</sup>F NMR (literature (in DMF): -28.8).<sup>[14]</sup> -29.24 (63%, s), -26.43 (19%, s). Yield: 83%.

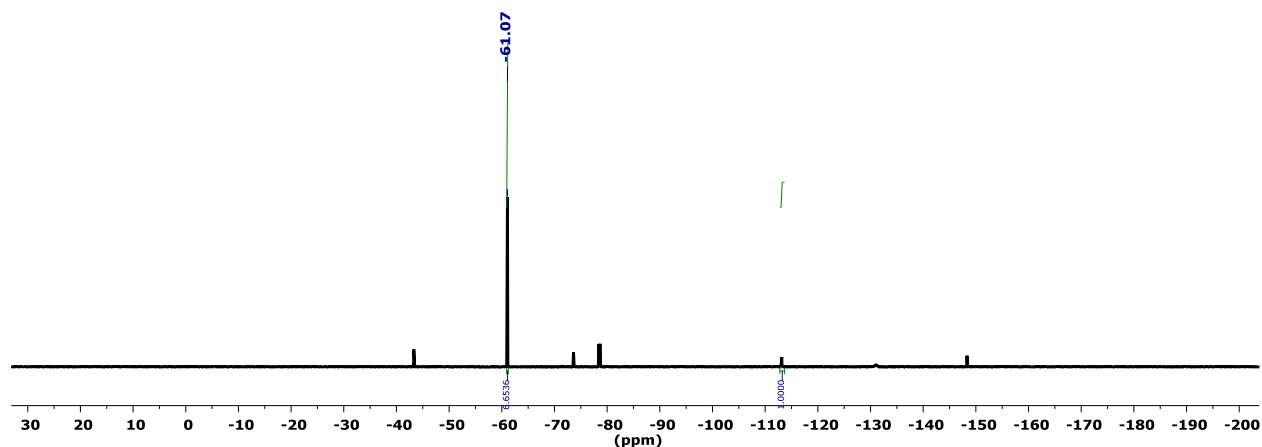
**Fig. S7. *In-Situ* <sup>19</sup>F NMR Spectrum:**



## Trifluoromethylbiphenyl

Experimental: Biphenyl iodide (28.0 mg, 0.100 mmol) was added to the solution of  $\text{CuCF}_3$  prepared and the NMR tube vigorously shaken. The mixture was heated to 80 °C for 12h.  $^{19}\text{F}$  NMR spectra were recorded and the product peak integrated against 0.030 mmol fluorobenzene internal standard. The product conformed to literature spectra of trifluoromethylbiphenyl.  $^{19}\text{F}$  NMR (literature ( $\text{CDCl}_3$ ): -62.4):<sup>[15]</sup> -61.07 (3F, s). Yield: 66%. HRMS (EI+): 222.0659 ( $\text{M}^+$ : 222.0656)

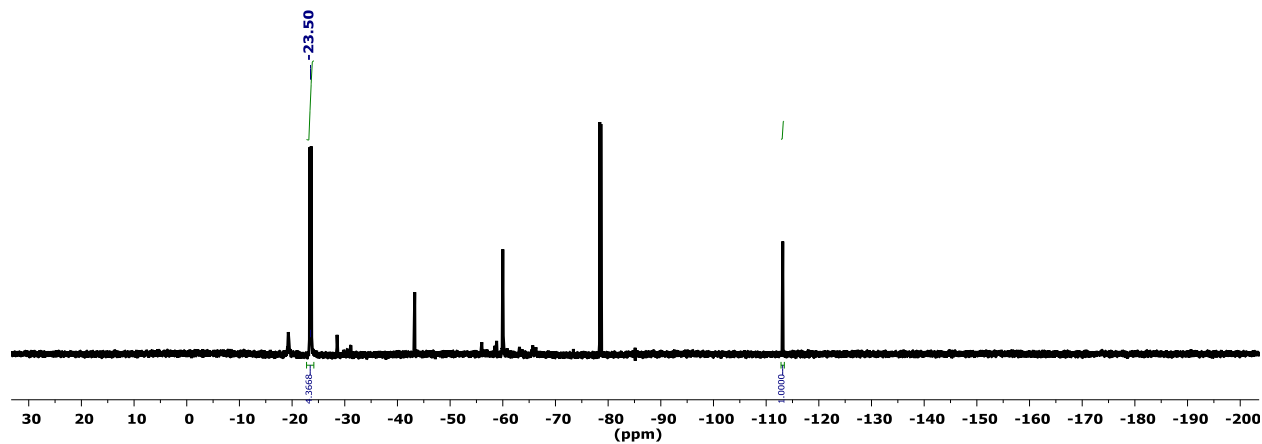
**Fig. S8. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



## $\text{AgCF}_3$

Experimental:  $\text{AgNO}_3$  (16.9 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL DMSO.  $\text{K}(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)$  (0.50 mL 0.20 M stock in DMSO, 0.10 mmol) was then added and the NMR tube vigorously shaken.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak was integrated against 0.030 mmol fluorobenzene internal standard. The product conformed to literature spectra of  $\text{AgCF}_3$ . In literature reports of  $\text{AgCF}_3$  compounds, the NMR shift varies between -20 and -30 and the coupling constant varies between 70 and 150 Hz depending on solvent and ancillary ligands.<sup>[16]</sup>  $^{19}\text{F}$  NMR (literature in DMF): -23-26,  $J_{109\text{Ag}-19\text{F}} = 100\text{-}125$ ):<sup>[17]</sup> -23.50 (3F, (d,  $J_{109\text{Ag}-19\text{F}} = 91.7$ ). Yield: 44%.

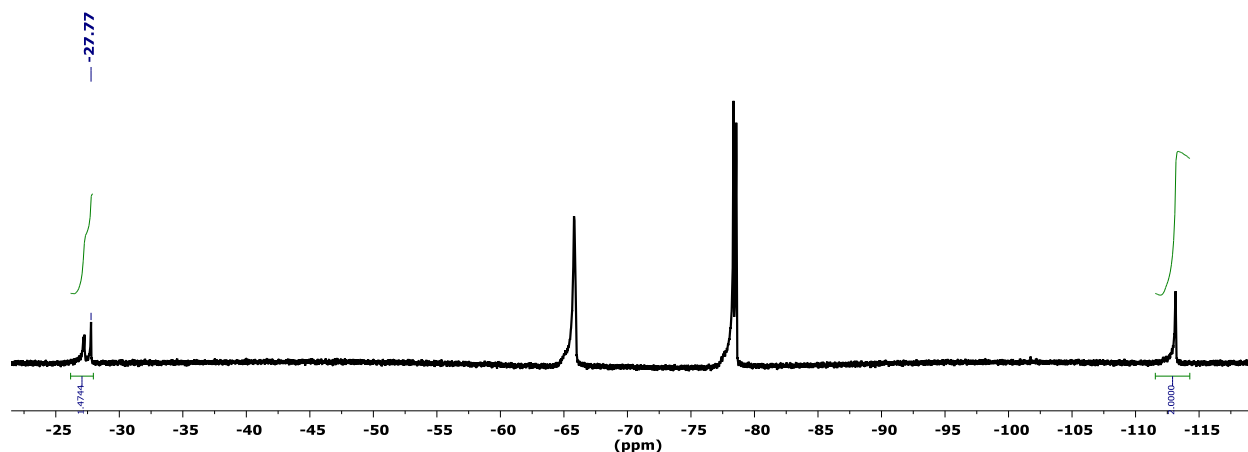
**Fig. S9. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



### Au(iPr)CF<sub>3</sub>

Experimental: Au(iPr)Cl (iPr=1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (31 mg, 0.050 mmol) was placed in an NMR tube and dissolved in 0.25 mL THF. K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF) (0.250 mL 0.20 M stock in THF, 0.0500 mmol) was then added and the NMR tube and vigorously shaken. <sup>19</sup>F NMR spectra were recorded 10 minutes after CF<sub>3</sub><sup>-</sup> addition and the product peak integrated against 0.030 mmol fluorobenzene internal standard. The product conformed to literature spectra of Au(iPr)CF<sub>3</sub>. <sup>19</sup>F NMR (literature (in CD<sub>2</sub>Cl<sub>2</sub>): -28.4):<sup>[18]</sup> -27.77 (3F, s). Yield: 15%.

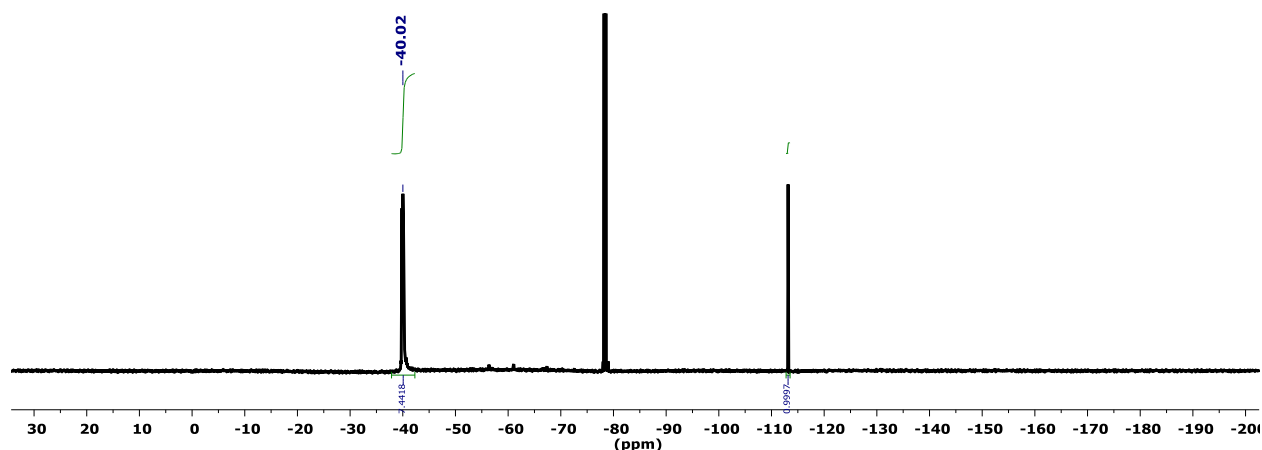
**Fig. S10. *In-Situ* <sup>19</sup>F NMR Spectrum:**



### Zn(TMEDA)(CF<sub>3</sub>)<sub>2</sub>

Experimental: ZnCl<sub>2</sub> (6.8 mg, 0.050 mmol) was placed in an NMR tube and dissolved in 0.5 mL THF. Tetramethylethylenediamine (TMEDA, 7.5 μL, 0.050 mmol) was then added and the homogeneous solution was allowed to stand for 10 minutes. K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF) (0.50 mL 0.20 M stock in THF, 0.10 mmol) was then added and the NMR tube vigorously shaken. <sup>19</sup>F NMR spectra were recorded 10 minutes after CF<sub>3</sub><sup>-</sup> addition and the product peak integrated against 0.030 mmol fluorobenzene internal standard. The product conformed to literature spectra of Zn(TMEDA)(CF<sub>3</sub>)<sub>2</sub>. <sup>19</sup>F NMR (literature (in CDCl<sub>3</sub>): -40.5):<sup>[19]</sup> -40.0 (6F, s). Yield: 74%.

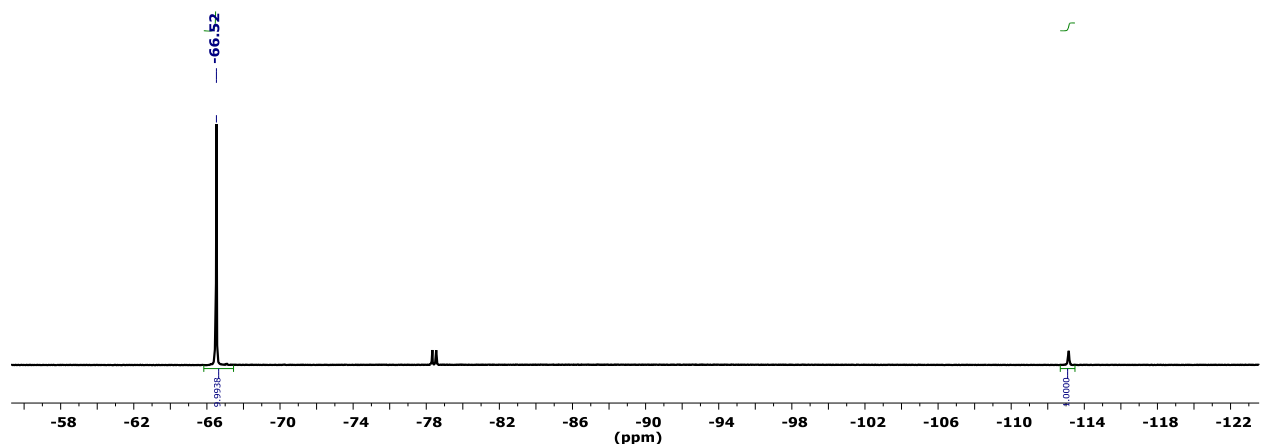
**Fig. S11. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



### **$\text{SiMe}_3\text{CF}_3$**

Experimental: Trimethylsilyl chloride (10.8 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL THF.  $\text{K}(18\text{-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (0.50 mL 0.20 M stock in THF, 0.10 mmol) was then added and the NMR tube vigorously shaken.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak integrated against 0.30 mmol fluorobenzene internal standard. The product conformed to literature spectra of  $\text{SiMe}_3\text{CF}_3$ .  $^{19}\text{F}$  NMR (literature ( $\text{CDCl}_3$ ): -66.81):<sup>[11]</sup> -66.52 (3F, s). Yield: 99%.

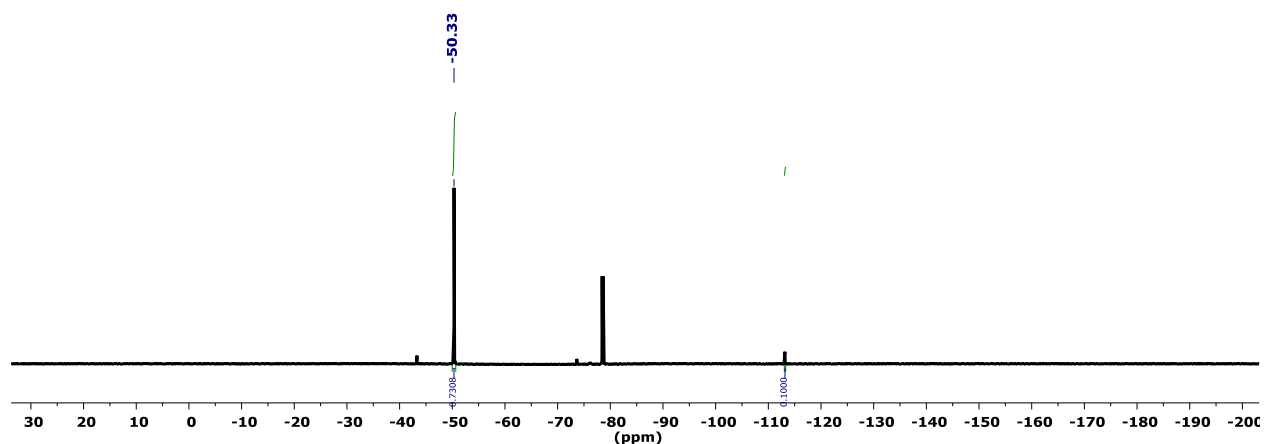
**Fig. S12. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



### **$\text{SnMe}_3\text{CF}_3$**

Experimental: Trimethyltin chloride (19.9 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL THF.  $\text{K}(18\text{-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (0.50 mL 0.20 M stock in THF, 0.10 mmol) was then added and the NMR tube vigorously shaken.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak integrated against 0.30 mmol fluorobenzene internal standard. The product conformed to literature spectra of  $\text{SnMe}_3\text{CF}_3$ .  $^{19}\text{F}$  NMR (literature (neat liquid): -49.1,  $J_{119\text{Sn}-19\text{F}}$ : 133):<sup>[20]</sup> -50.33 (3F, s, ( $^{119}\text{Sn}$  satellites:  $J_{119\text{Sn}-19\text{F}}$ : 136). Yield: 73%.

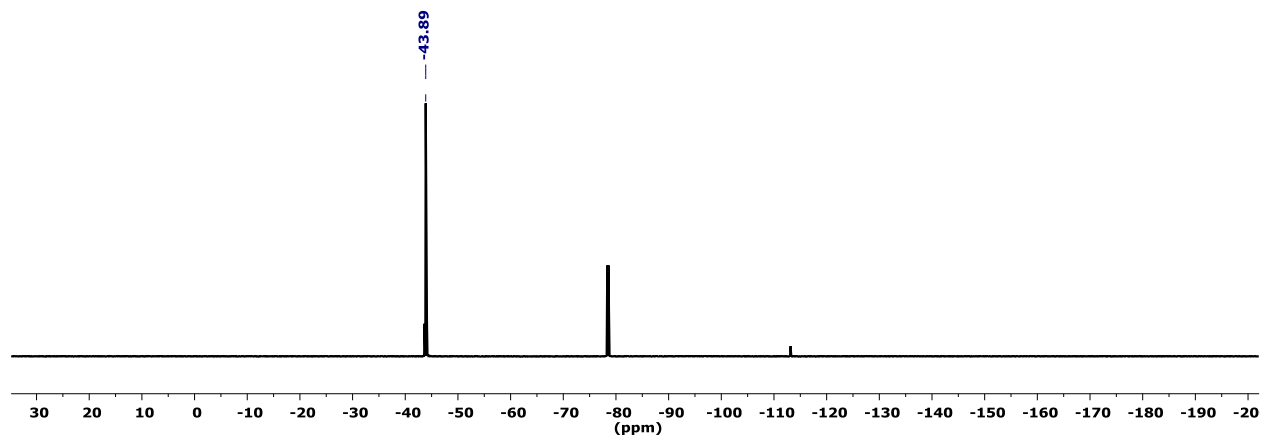
**Fig. S13. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



### **$\text{PbMe}_3\text{CF}_3$**

Experimental: Trimethyllead bromide (33.0 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL THF.  $\text{K}(18\text{-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (0.50 mL 0.20 M stock in THF, 0.10 mmol) was then added and the NMR tube vigorously shaken.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak integrated against 0.30 mmol fluorobenzene internal standard. The product conformed to literature spectra of  $\text{PbMe}_3\text{CF}_3$ .  $^{19}\text{F}$  NMR (literature (neat liquid): -43.9):<sup>[21]</sup>-43.8 (3F, s). Yield: 99%.

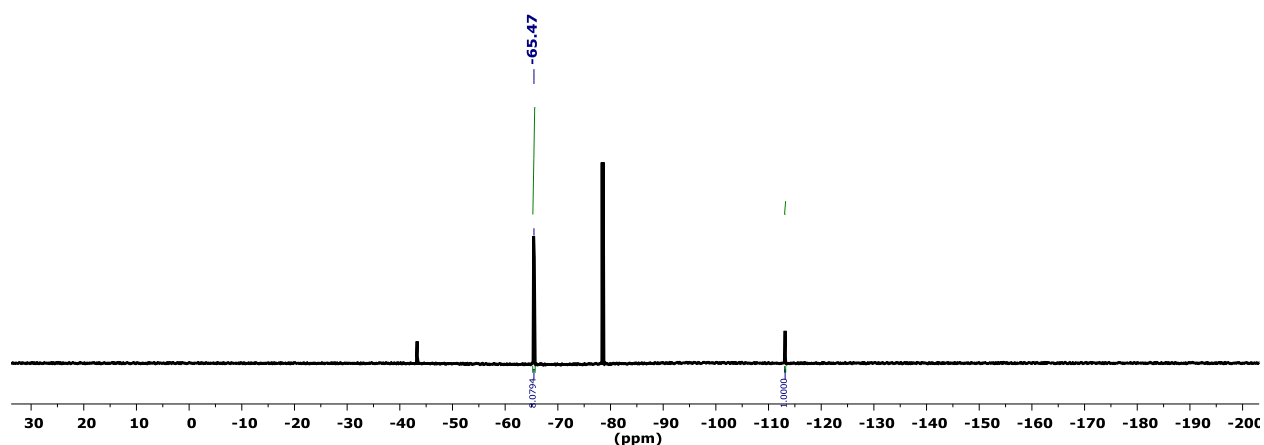
**Fig. S14. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



### **$\text{KB}(\text{OMe})_3\text{CF}_3$**

Experimental: Trimethyl borate (11.2  $\mu\text{L}$ , 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL DMSO.  $\text{K}(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)$  (0.50 mL 0.20 M stock in DMSO, 0.10 mmol) was then added and the NMR tube was vigorously shaken.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak integrated against 0.3 mmol fluorobenzene internal standard. The product was confirmed by comparison with an authentic sample prepared according to literature methods<sup>[22]</sup> dissolved in  $\text{DMSO-d}_6$  ( $^{19}\text{F}$ -NMR: -65.41 (3F, dd,  $J_{11\text{B}-19\text{F}}$ : 49, 24)): -65.47 (3F, dd,  $J_{11\text{B}-19\text{F}}$ : 49, 24). Yield: 80%.

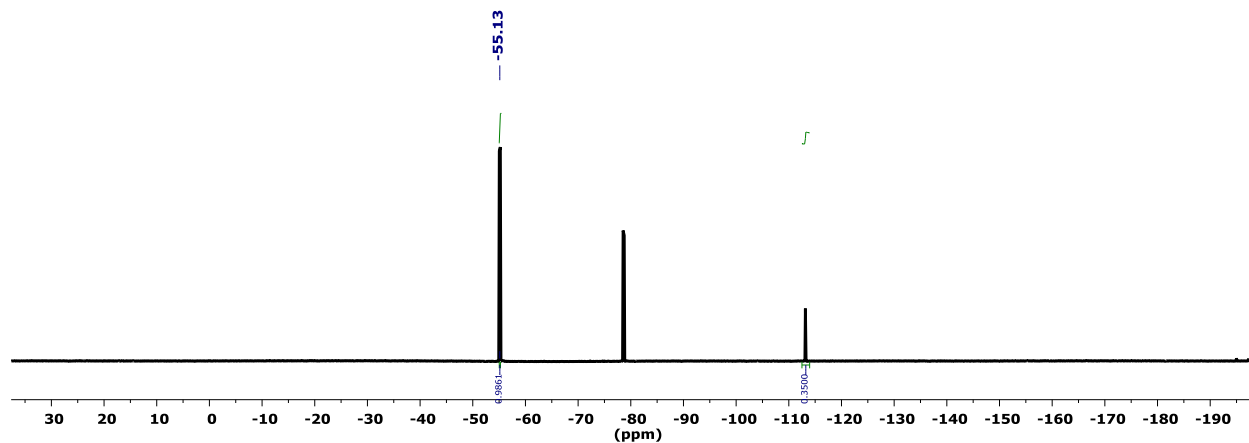
**Fig. S15. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



### **$\text{PPh}_2\text{CF}_3$**

Experimental: Diphenylphosphine chloride (22.0 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL THF.  $\text{K}(18\text{-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (0.50 mL 0.20 M stock in THF, 0.10 mmol) was then added and the NMR tube vigorously shaken. After five minutes, colorless crystals had formed and the solution became yellow.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak integrated against 0.11 mmol fluorobenzene internal standard. The product conformed to literature spectra of  $\text{PPh}_2\text{CF}_3$ .  $^{19}\text{F}$  NMR (literature (in  $\text{CDCl}_3$ ): -55.3,  $J_{31\text{P}-19\text{F}}$ : 73): $^{[23]}$  -55.13 (3F, (d,  $J_{31\text{P}-19\text{F}}$ : 73.2). Yield: 99%.

**Fig. S16. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**

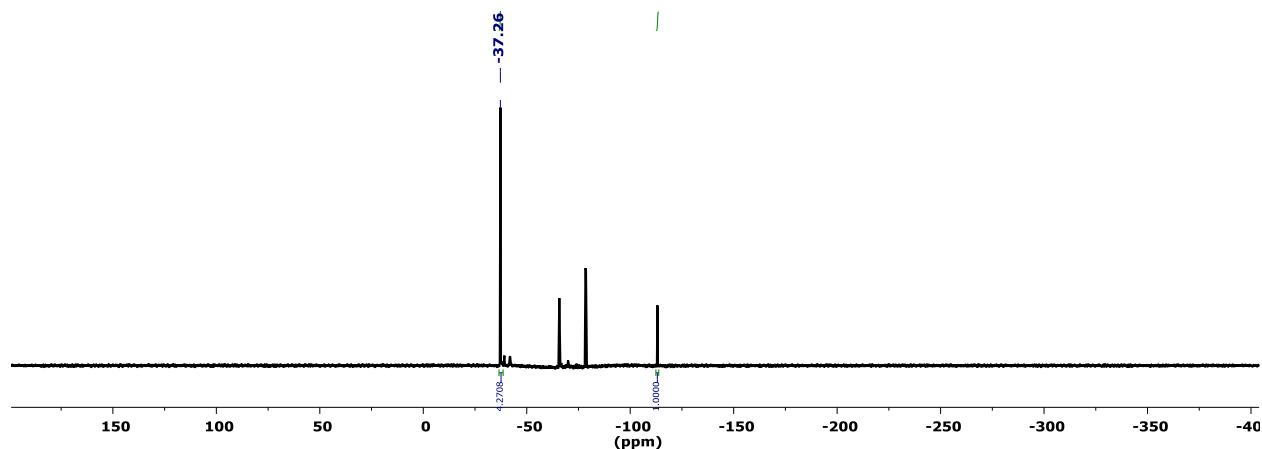


### **$\text{Bi}(\text{CF}_3)_2\text{Cl}$**

Experimental: Bismuth trichloride (10.5 mg, 0.033 mmol) was placed in an NMR tube and combined with 0.50 mL THF.  $\text{K}(18\text{-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (0.50 mL 0.20 M stock in THF, 0.10 mmol) was then added and the NMR tube vigorously shaken. After five minutes, colorless crystals had formed along with a black precipitate.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak integrated against 0.03 mmol fluorobenzene internal

standard. The product conformed to literature spectra of  $\text{Bi}(\text{CF}_3)_2\text{Cl}$ .  $^{19}\text{F}$  NMR (literature (in MeCN): -37.8):<sup>[24]</sup> -37.26. Yield: 42%.

**Fig. S17. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**

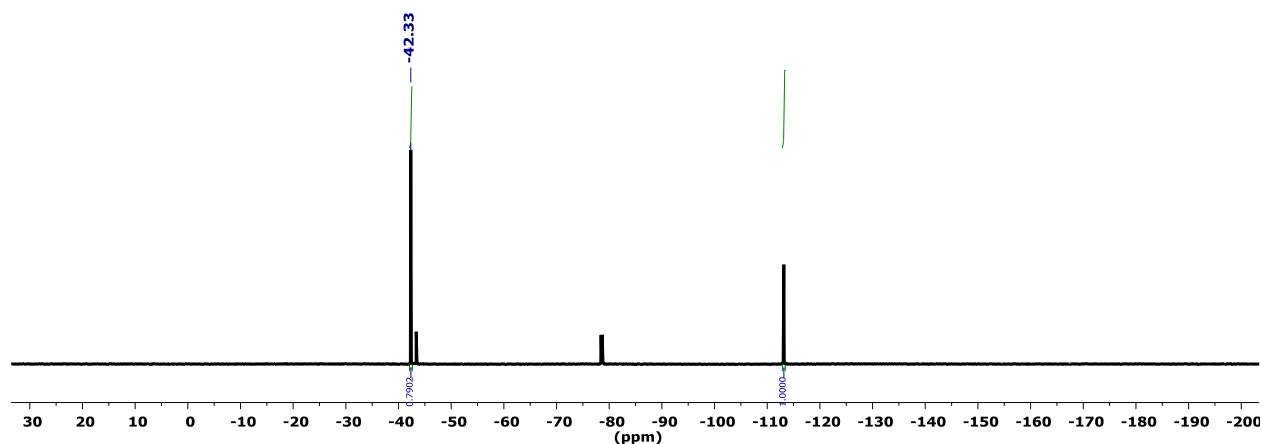


## Reactions with Organic and Inorganic Chalcogens

### PhSCF<sub>3</sub>

Experimental: Diphenyldisulfide (21.8 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL DMSO.  $\text{K}(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)$  (0.50 mL 0.20 M stock in DMSO, 0.10 mmol) was then added and the NMR tube vigorously shaken.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after  $\text{CF}_3^-$  addition and the product peak integrated against 0.3 mmol fluorobenzene internal standard. The product conformed to literature spectra of PhSCF<sub>3</sub>.  $^{19}\text{F}$  NMR (literature (in  $\text{CDCl}_3$ ): -42.7):<sup>[25]</sup> -42.33. Yield: 79%.

**Fig. S18. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**



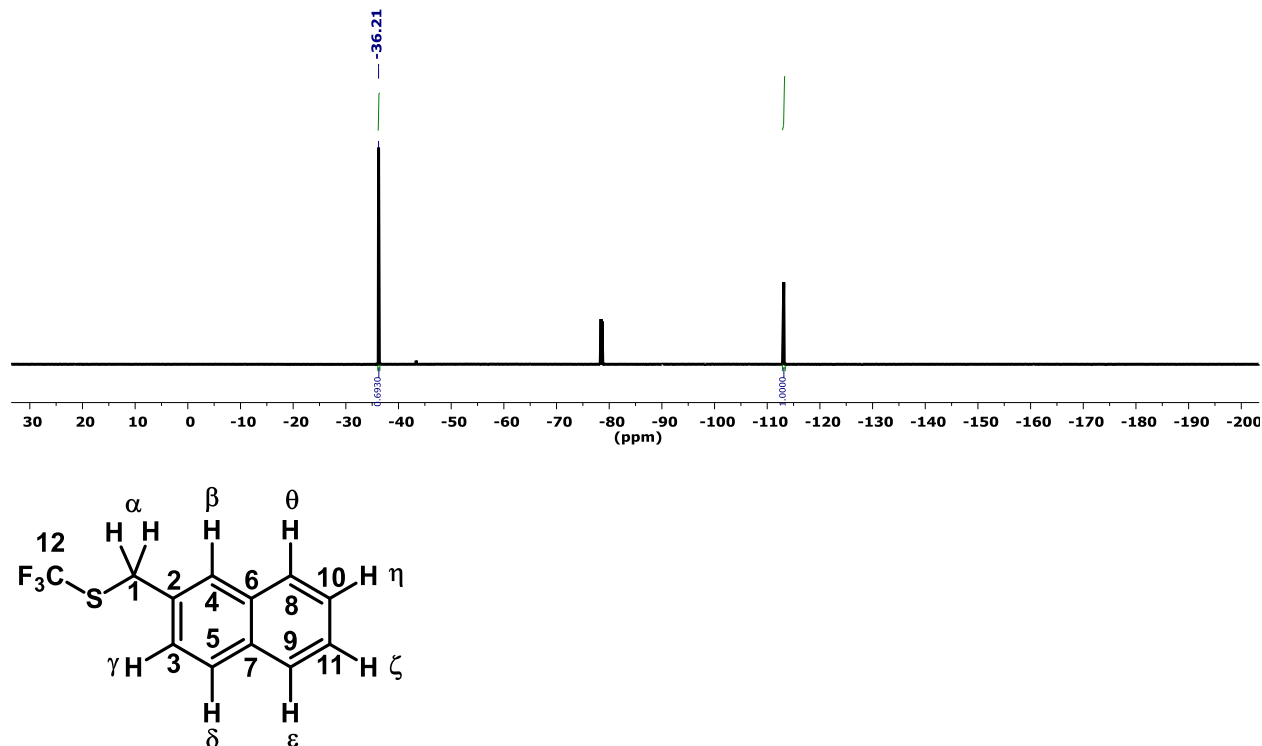
### PhSeCF<sub>3</sub>

Experimental: Diphenyldiselenide (31.2 mg, 0.100 mmol) was placed in an NMR tube and dissolved in 0.50 mL DMSO.  $\text{K}(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)$  (0.50 mL 0.20 M stock in DMSO, 0.10 mmol) was then added and the NMR tube vigorously shaken.  $^{19}\text{F}$  NMR spectra were recorded 10 minutes after



$\text{CF}_3^-$  addition and the product peak integrated against 0.30 mmol fluorobenzene internal standard. The product conformed to literature spectra of  $\text{PhSeCF}_3$ .  $^{19}\text{F}$  NMR (literature (in  $\text{CDCl}_3$ ): -36.6):<sup>[26]</sup> -36.21 (3F, s). Yield: 69%.

**Fig. S19. *In-Situ*  $^{19}\text{F}$  NMR Spectrum:**

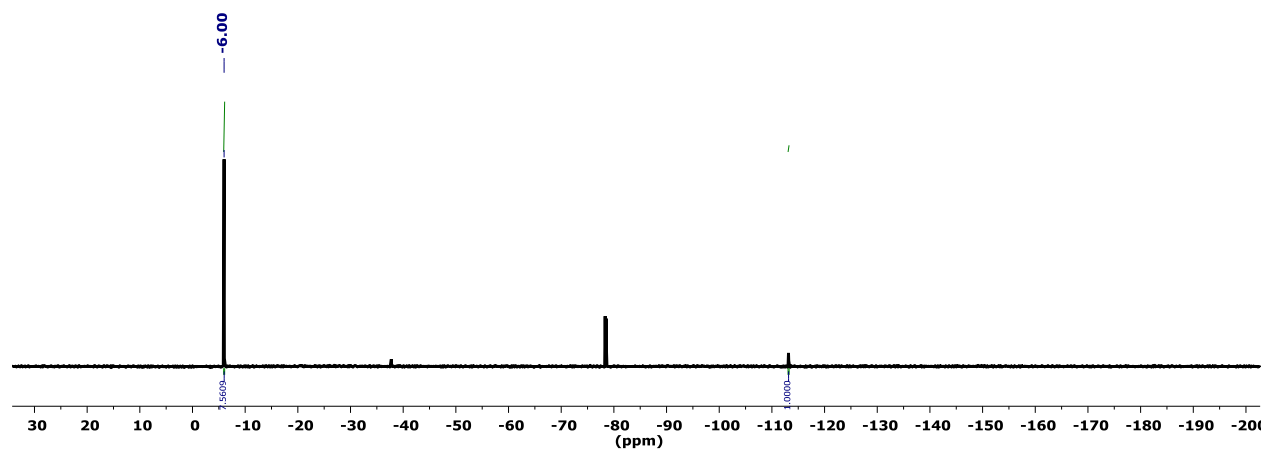


## 2-Naphthylmethyl trifluoromethyl sulfide:

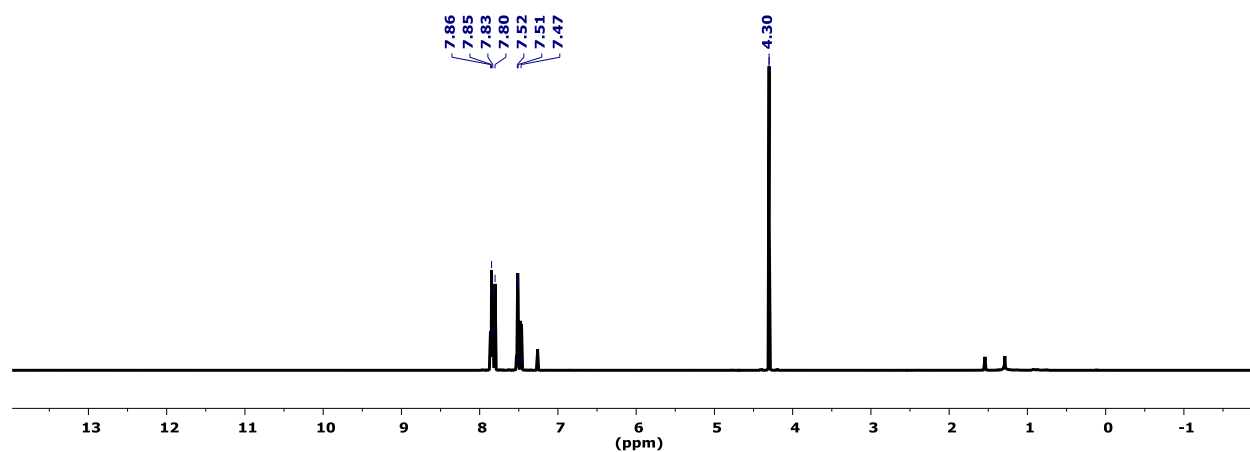
Experimental: Finely powdered elemental sulfur (12.8 mg, 0.400 mmol) was stirred in 10 mL THF for one minute to give a light yellow suspension. With vigorous stirring,  $\text{K}(18\text{-crown-}6)(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (2.00 mL, 0.2 M in THF, 0.400 mmol) was added. The color immediately changed to light green, then after 30 seconds to a deep blue. After 20 minutes, the color disappeared to afford a homogeneous solution of  $\text{K}(18\text{-crown-}6)\text{SCF}_3$ , from which a 30  $\mu\text{L}$  sample was removed for analysis by  $^{19}\text{F}$  NMR spectroscopy (92%  $\text{K}(18\text{-crown-}6)\text{SCF}_3$  *in-situ*). Bromomethyl naphthalene (0.400 mmol, 88.4 mg) was then added to the stirred solution. The solution was stirred for 30 minutes, and again sampled and analyzed by  $^{19}\text{F}$  NMR spectroscopy (81% 2-Naphthylmethyl trifluoromethyl sulfide *in-situ*). The THF solvent was removed by rotary evaporation, and the reaction was quenched with 10 mL water and extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL), the  $\text{CH}_2\text{Cl}_2$  extract was evaporated, and the crude solid was purified by flash silica chromatography. Chromatography conditions: 100% Hexane, 8 column volumes, 25 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 54.9 mg white solid (57% isolated).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 7.86 ( $\delta$ , 1H, (m,  $J_{\text{H-H}}=7.1, 2$ )), 7.85 ( $\epsilon$ , 1H, m (overlap)), 7.83 ( $\theta$ , 1H, m (overlap)), 7.80 ( $\beta$ , 1H, s), 7.52 ( $\eta$ , 1H, (m,  $J_{\text{H-H}}=7.1, 2$ )), 7.51 ( $\zeta$ , 1H, (m,  $J_{\text{H-H}}=7.1, 2$ )), 7.47 ( $\gamma$ , 1H, (dd,  $J_{\text{H-H}}=8.4, 1.6$ )), 4.30 ( $\alpha$ , 2H, s).  $^{13}\text{C}$ -NMR: 133.28 (6), 132.85 (7), 132.34 (2), 130.64 (12, q,  $J_{13\text{C}-19\text{F}}=307$ ), 128.79 (5), 127.92 (4), 127.77 (8), 127.74 (9), 126.51 (10), 126.49 (3), 126.37 (11), 34.58 (1, q,  $J_{13\text{C}-19\text{F}}=2.3$ ).  $^{19}\text{F}$ -NMR: -45.19 (s). HRMS (EI+): 242.0380 ( $\text{M}^+$ : 242.0377). Note: Use of superstoichiometric

sulfur severely reduces the yield of the reaction. The solubility of K(18-crown-6)SCF<sub>3</sub> appears to be between 0.04 and 0.06 moles/L in 25 °C THF.

**Fig. S20. *In-Situ* <sup>19</sup>F NMR Spectrum of K(18-crown-6)SCF<sub>3</sub>:**



**Fig. S21. <sup>1</sup>H NMR Spectrum:**



**Fig. S22. <sup>13</sup>C NMR Spectrum:**

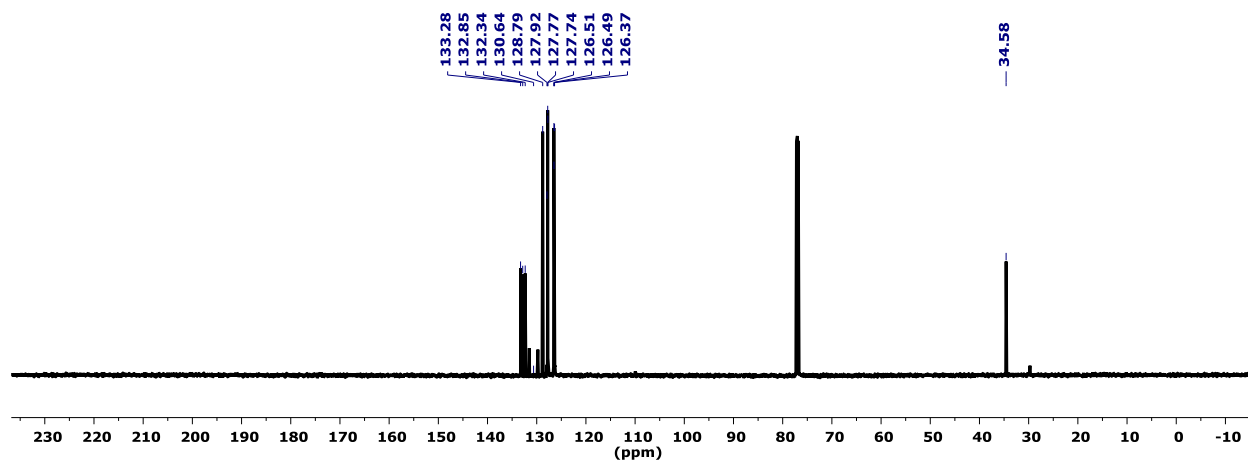


Fig. S23.  $^{19}\text{F}$  NMR Spectrum:

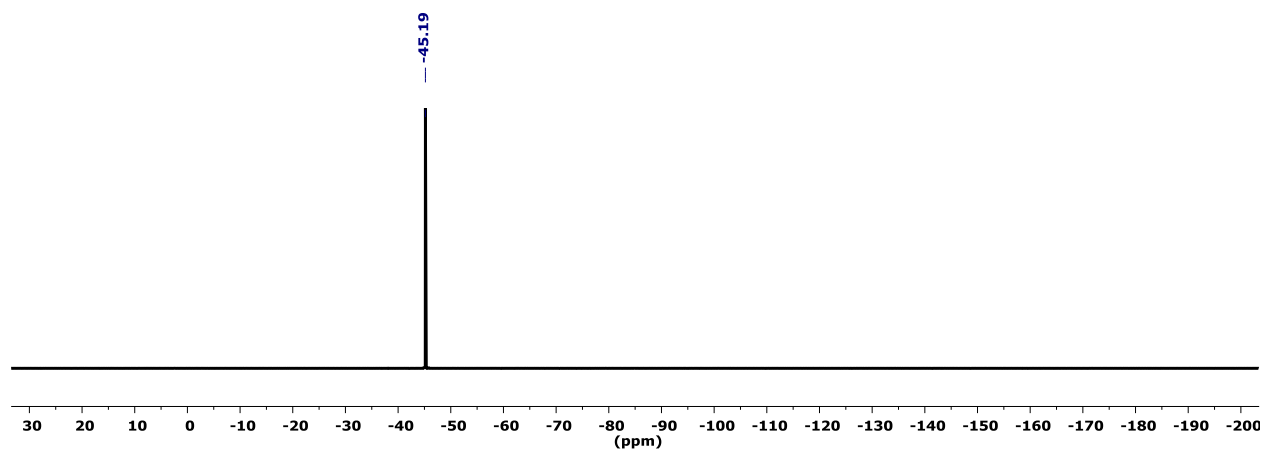
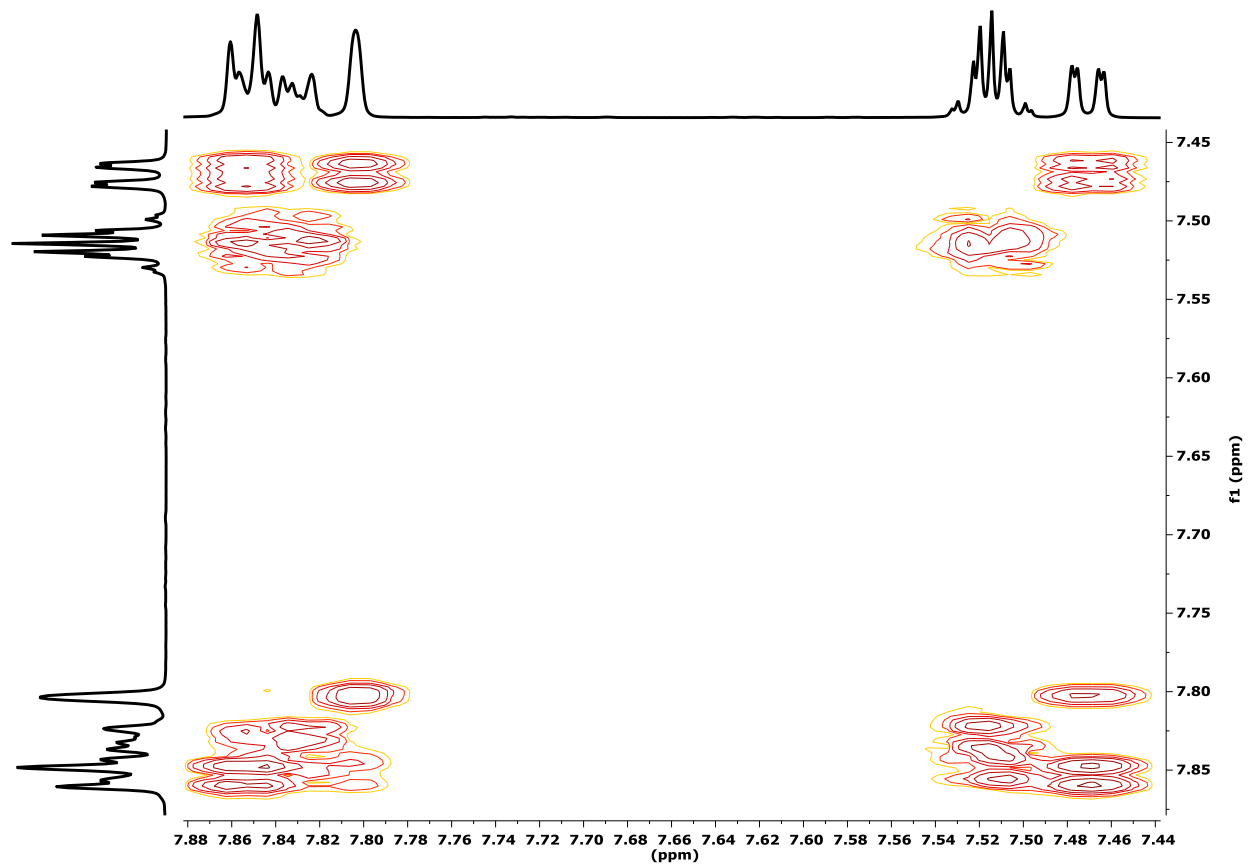
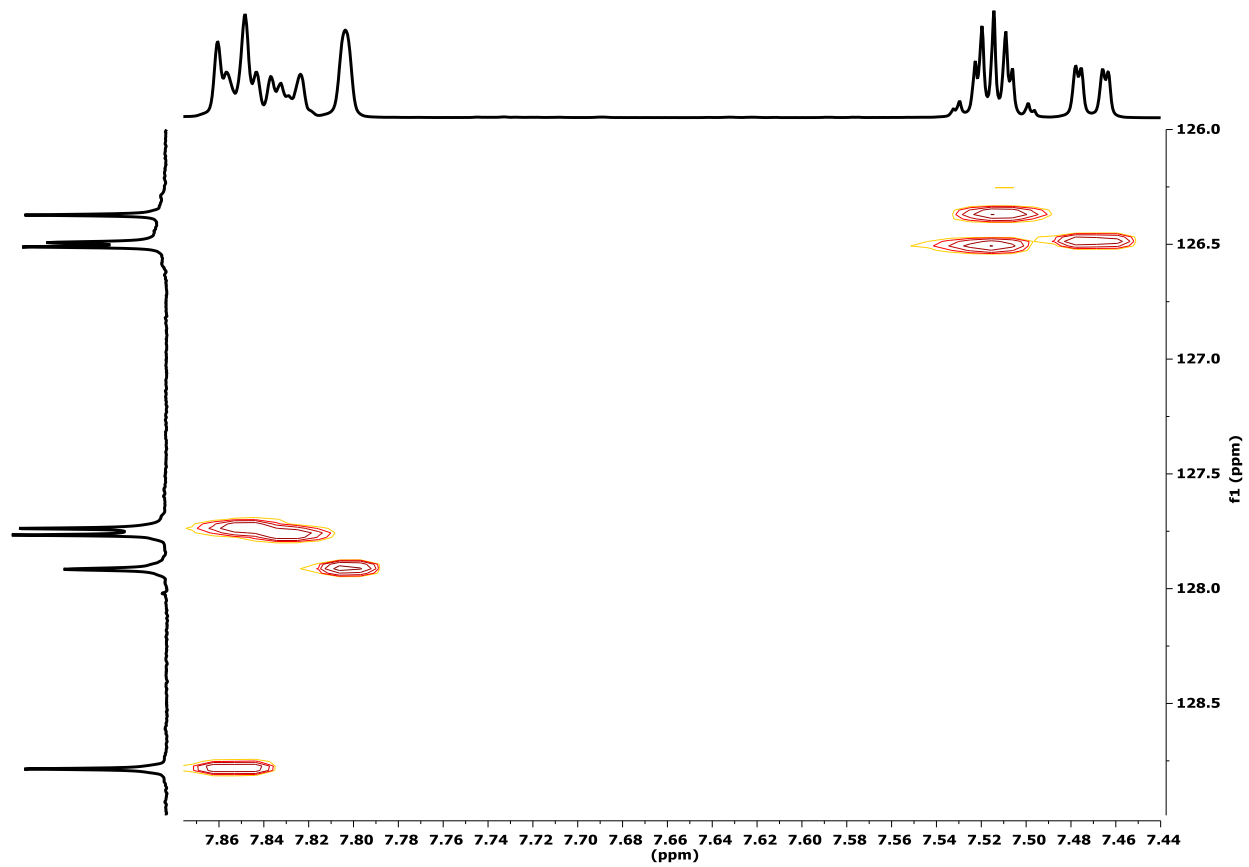


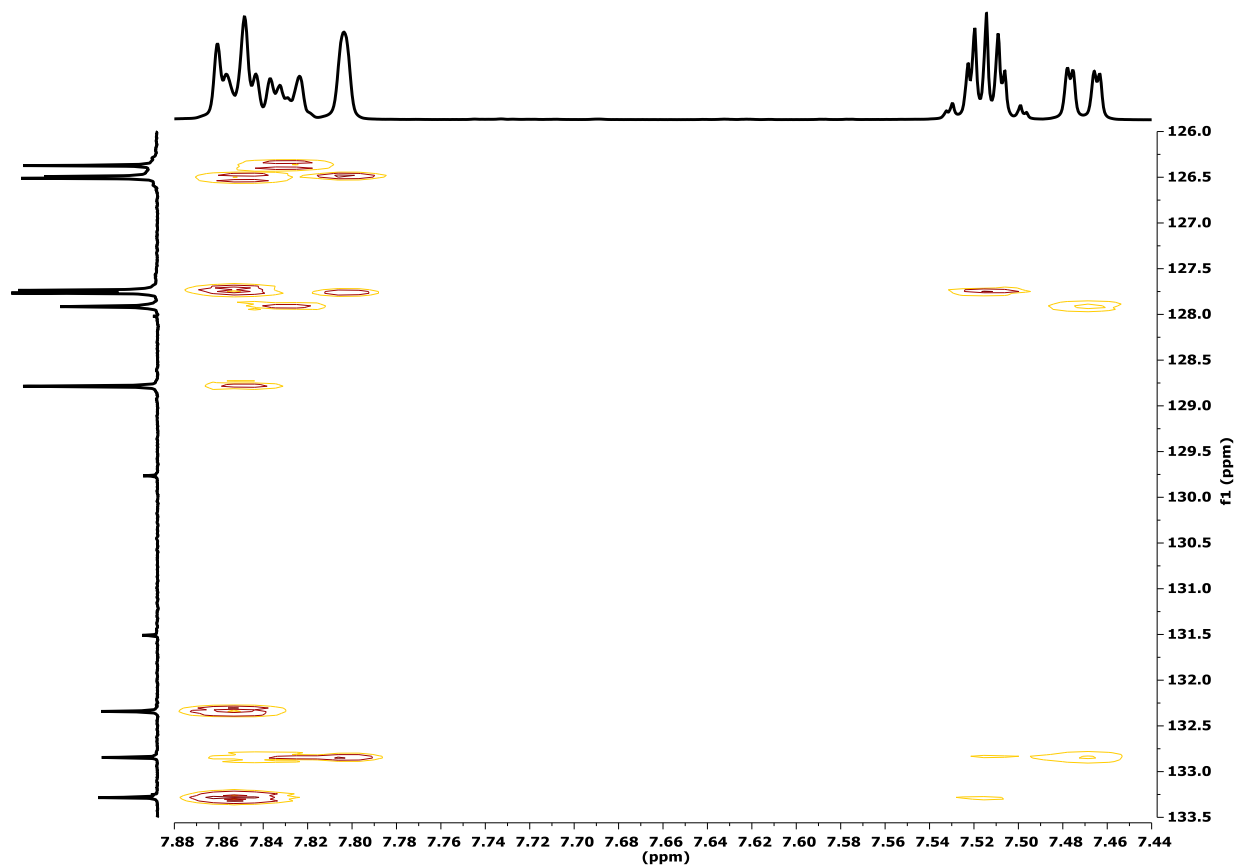
Fig. S24.  $^1\text{H}$ -gCOSY Spectrum:



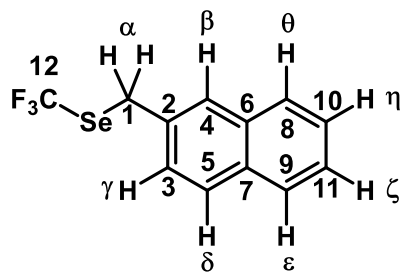
**Fig. S25.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:**



**Fig. S26.**  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:



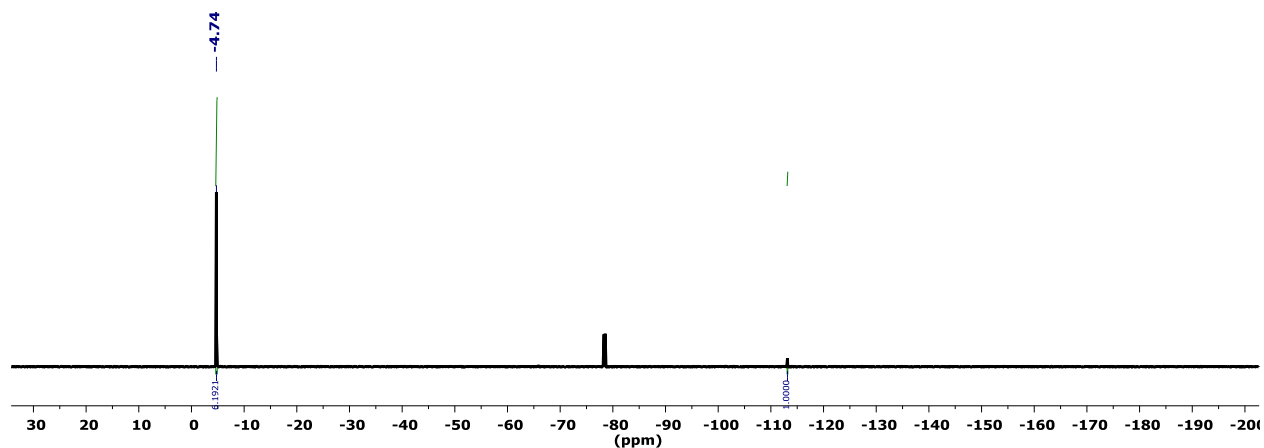
### 2-Naphthylmethyl trifluoromethyl selenide:



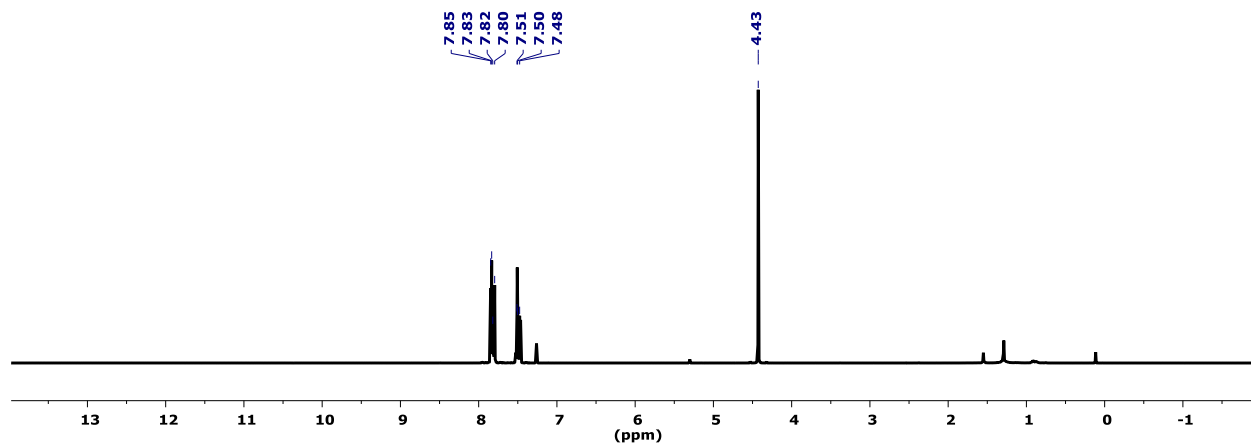
Experimental: 100 mesh grey elemental selenium (31.2 mg, 0.400 mmol) was stirred in 10 mL THF for one minute to give a light brown suspension. With vigorous stirring, K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF) (2.00 mL, 0.2 M in THF, 0.400 mmol) was added. The color immediately changed to a slightly darker brown. After 20 minutes, the reaction was slightly turbid. The amount of K(18-crown-6)SeCF<sub>3</sub> in solution was assessed through removal of a 30  $\mu$ L sample, analyzed by <sup>19</sup>F NMR spectroscopy (61% K(18-crown-6)SeCF<sub>3</sub> *in-situ*). Bromomethyl naphthalene (88.4 mg, 0.400 mmol) was then added to the stirred solution. Within one minute a thick, white solid precipitated. The solution was stirred for 30 minutes, and again sampled and analyzed by <sup>19</sup>F NMR spectroscopy (63% 2-naphthylmethyl trifluoromethyl selenide *in-situ*). The THF solvent was then removed by rotary evaporation, and the reaction was quenched with 10 mL water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 x 2 mL), the CH<sub>2</sub>Cl<sub>2</sub> extract evaporated, and the crude solid was purified by flash silica chromatography. Chromatography conditions: 100% Hexane, 8 column volumes, 25 g SiO<sub>2</sub>,

flow rate 1 column volume per minute. 61.2 mg white solid (64% isolated).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.85 ( $\delta$ , 1H, (m, overlap)), 7.83 ( $\epsilon$ , 1H, m (overlap)), 7.82 ( $\theta$ , 1H, m (overlap)), 7.80 ( $\beta$ , 1H, s), 7.51 ( $\eta$ , 1H, (m, overlap)), 7.50 ( $\zeta$ , 1H, (m, overlap)), 7.47 ( $\gamma$ , 1H, (dd,  $J_{\text{H-H}}=8.4, 1.8$ )), 4.43 ( $\alpha$ , 2H, s).  $^{13}\text{C-NMR}$ : 133.39 (6), 132.32 (7), 132.71 (2), 128.81 (5), 127.83 (4), 127.73 (8), 127.72 (9), 126.76 (10), 126.50 (3), 126.31 (11), 122.87 (12, q,  $J_{^{13}\text{C}-^{19}\text{F}}=331$ ), 29.54 (1, q,  $J_{^{13}\text{C}-^{19}\text{F}}=1.6$ ).  $^{19}\text{F-NMR}$ : -34.35 (s).  $^{77}\text{Se-NMR}$ : 505.92 (q,  $J_{^{77}\text{Se}-^{19}\text{F}}=13.5$ ). HRMS (EI+): 289.9821 ( $\text{M}^+$ : 289.9822). Notes: Use of superstoichiometric selenium severely reduces the yield of the reaction.

**Fig. S27. *In-Situ*  $^{19}\text{F}$  NMR Spectrum of  $\text{K}(\text{18-crown-6})\text{SeCF}_3$ :**



**Fig. S28.  $^1\text{H}$  NMR Spectrum:**



**Fig. S29.  $^{13}\text{C}$  NMR Spectrum:**

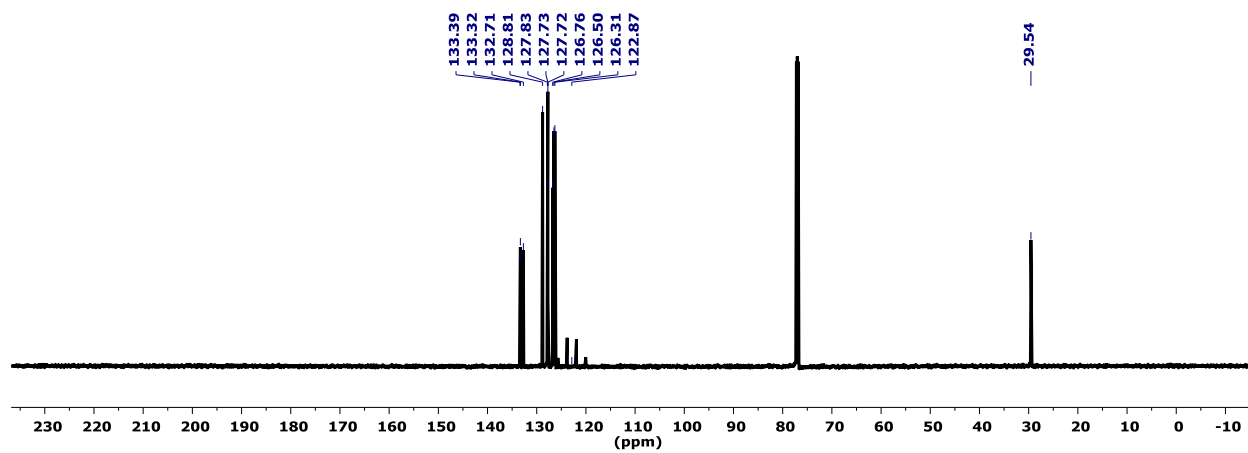


Fig. S30.  $^{19}\text{F}$  NMR Spectrum:

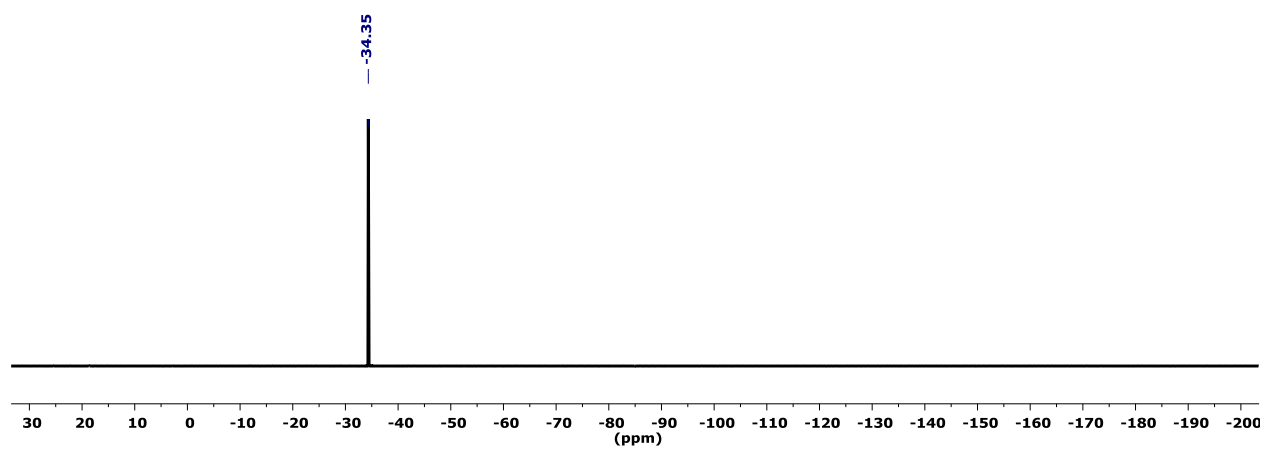


Fig. S31.  $^{77}\text{Se}$  NMR Spectrum:

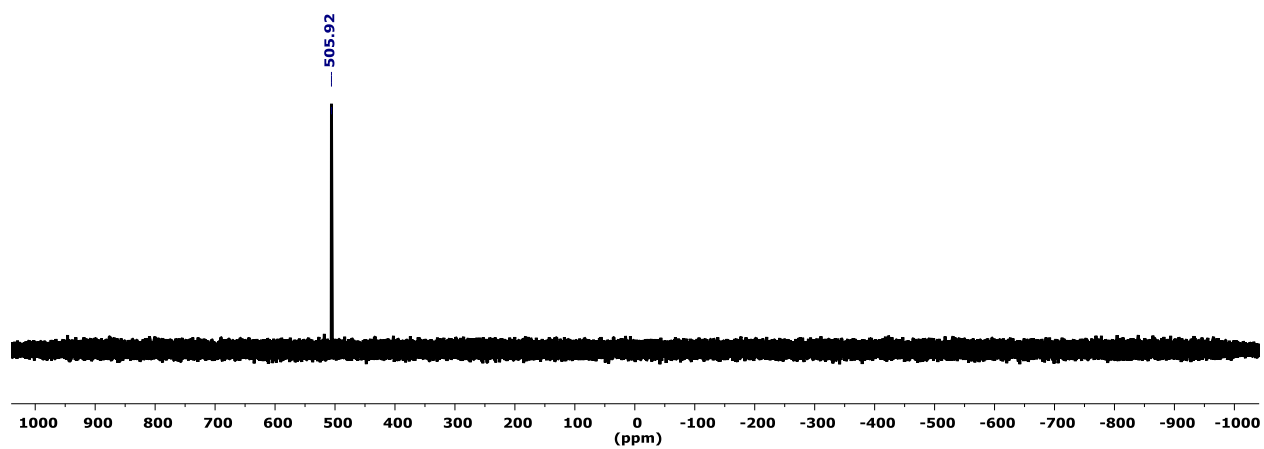
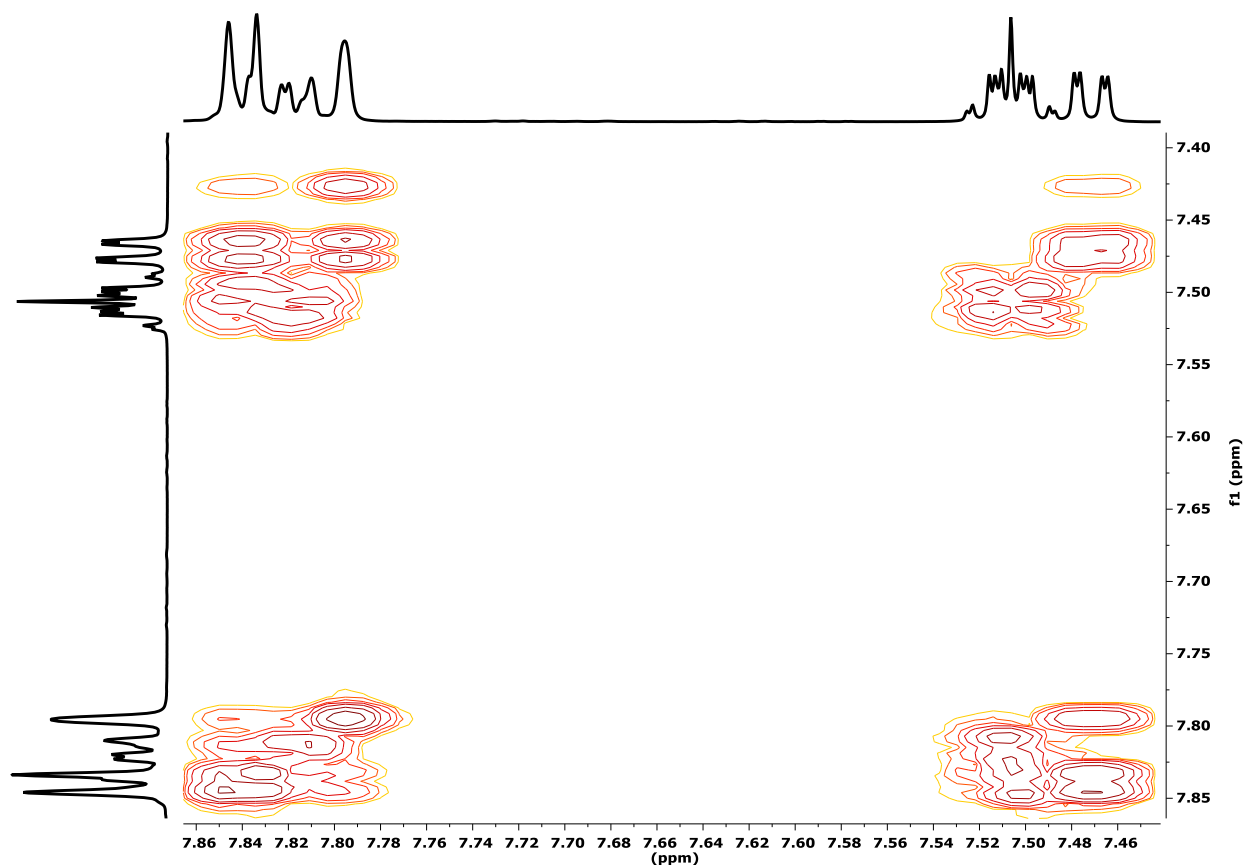
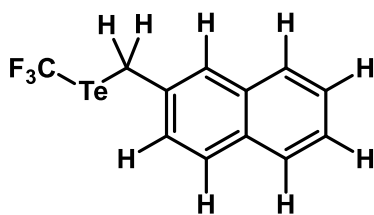




Fig. S32.  $^1\text{H}$ -gCOSY Spectrum:



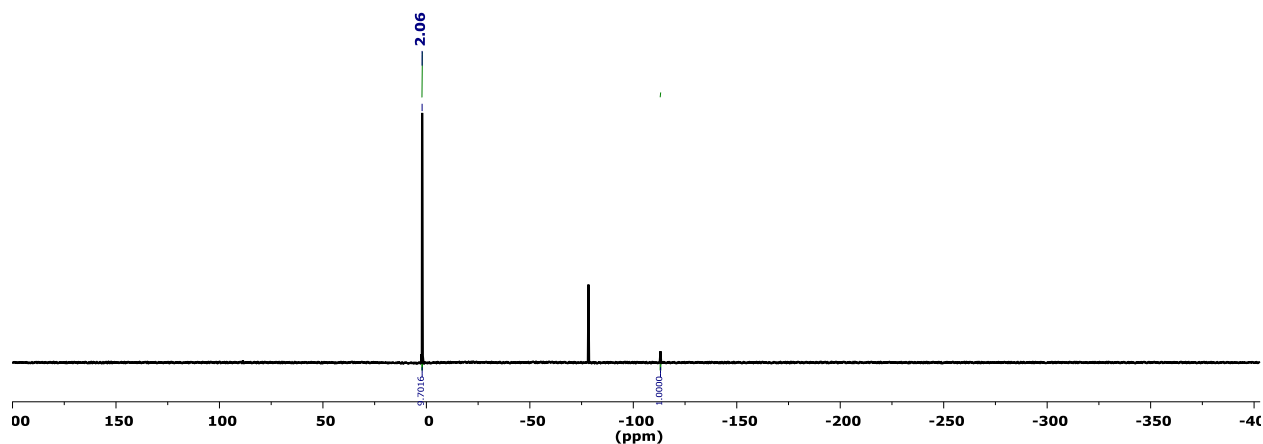
**2-Naphthylmethyl trifluoromethyl telluride:**



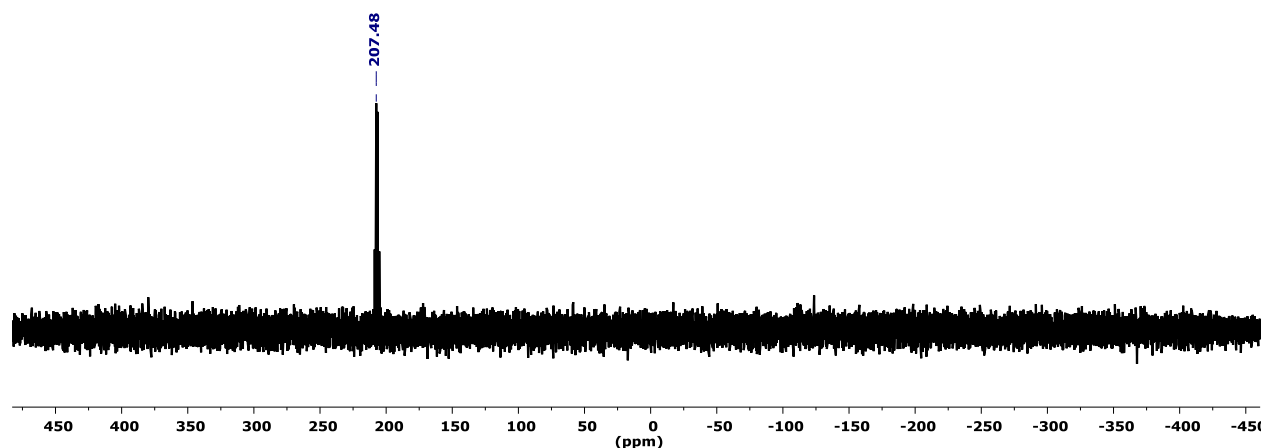
Experimental: Elemental tellurium (51.0 mg, 0.400 mmol) was stirred in 10 mL THF for 10 minutes to give a suspension. With vigorous stirring,  $\text{K}(18\text{-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (2.00 mL, 0.2 M in THF, 0.400 mmol) was added. The color immediately changed to a light purple. After 72 hours, the reaction was slightly turbid and deep purple in color. The amount of  $\text{K}(18\text{-crown-6})\text{TeCF}_3$  in solution was assessed through removal of a 30  $\mu\text{L}$  sample, analyzed by  $^{19}\text{F}$  NMR spectroscopy (97%  $\text{K}(18\text{-crown-6})\text{TeCF}_3$  *in-situ*;  $^{19}\text{F}$  NMR: 2.06;  $^{125}\text{Te}$  NMR: 207.48 ( $J_{125\text{Te}-19\text{F}}=251.8$ ). Bromomethyl naphthalene (88.4 mg, 0.400 mmol) was then added to the stirred solution. Within one minute a thick, white solid precipitated. The solution was stirred for 30 minutes, and again sampled and analyzed by  $^{19}\text{F}$  NMR spectroscopy (88% 2-naphthylmethyl trifluoromethyl selenide *in-situ*). The THF solvent was then removed by rotary evaporation, and the reaction was quenched with 10 mL water and extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL), the  $\text{CH}_2\text{Cl}_2$  extract evaporated, and the crude solid was purified by flash silica chromatography.

Chromatography conditions: 100% Hexane, 8 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 80.1 mg white solid (59% isolated). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.75 (4H, (m, overlap)), 7.45 (3H, m (overlap)), 4.69 (2H, s). <sup>19</sup>F-NMR: -27.28 (s). MS (EI+): 340.1 (M<sup>+</sup>: 339.9719)

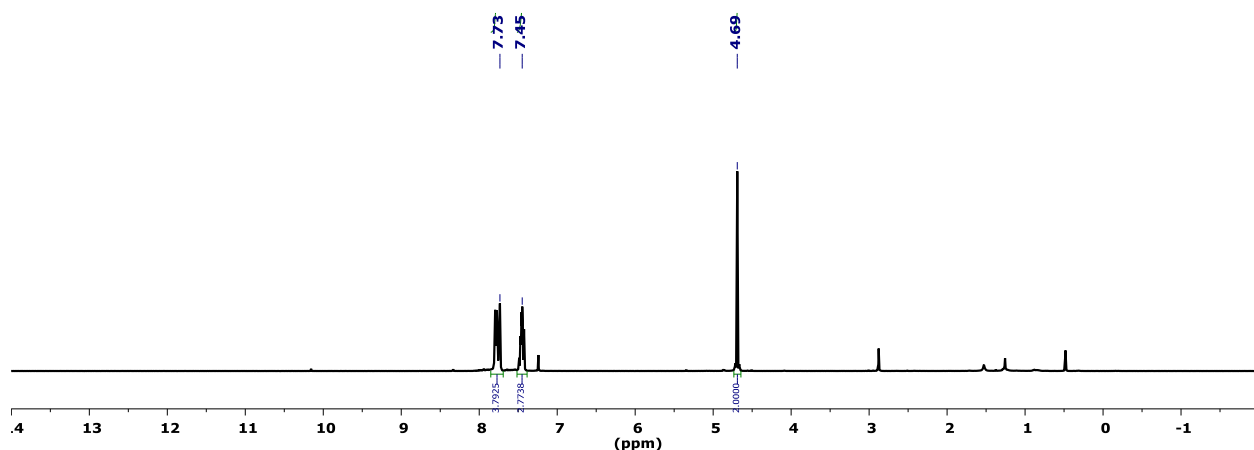
**Fig. S33. *In-Situ* <sup>19</sup>F NMR Spectrum of K(18-crown-6)TeCF<sub>3</sub>:**



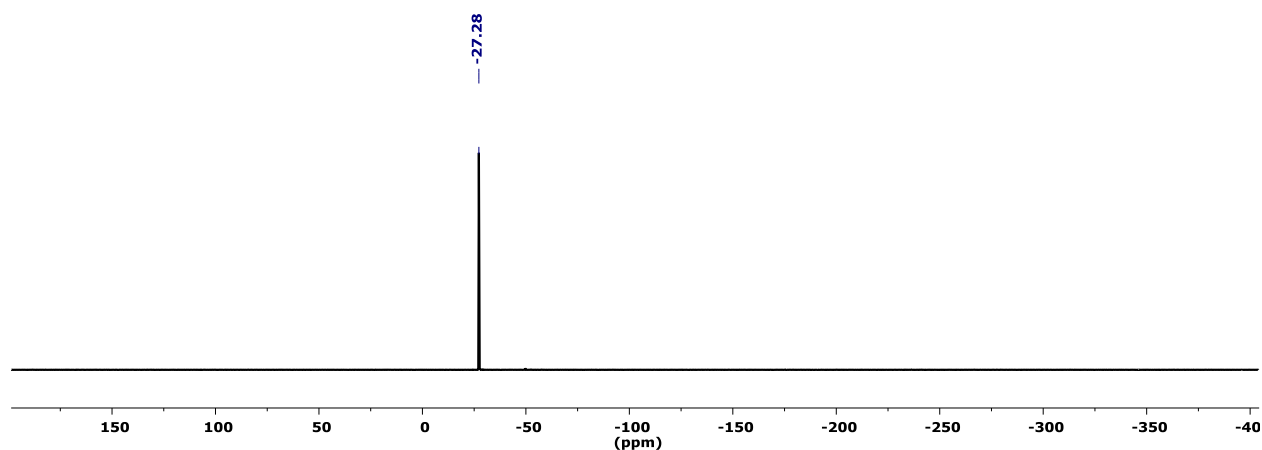
**Fig. S34. *In-Situ* <sup>125</sup>Te NMR Spectrum of K(18-crown-6)TeCF<sub>3</sub>:**



**Fig. S35.  $^1\text{H}$  NMR Spectrum:**



**Fig. S36.  $^{19}\text{F}$  NMR Spectrum:**



## **Nucleophilic Trifluoromethylation of Inorganic Compounds with LA- $\text{CF}_3$ : Comparison between 2 and previously reported $\text{CF}_3^-$ sources (1a-c)**

### **Protocol for reactions with $\text{KB}(\text{OMe})_3\text{CF}_3$ :**

To 0.100 mmol of substrate dissolved in 0.50 mL of THF was added 0.100 mmol  $\text{KB}(\text{OMe})_3\text{CF}_3$  as a solution in 0.50 mL THF. Yields were determined by  $^{19}\text{F}$  NMR integration against fluorobenzene internal standard after 10 minutes at room temperature.

### **Protocol for reactions with $\text{SiMe}_3\text{CF}_3/\text{KF}/18\text{-crown-6}$ :**

To 0.100 mmol of substrate dissolved in 0.50 mL of THF was added 0.100 mmol of a 1:1 mixture of  $\text{SiMe}_3\text{CF}_3/18\text{-crown-6}$  as a solution in 0.5 mL THF. 0.10 mmol KF was then added as a solid, and the mixture vigorously shaken for 10 minutes at room temperature. Yields were determined by  $^{19}\text{F}$  NMR integration against fluorobenzene internal standard.

### **Protocol for reactions with $\text{KDMF}\cdot\text{CF}_3$ :**

To 0.100 mmol of substrate dissolved in 0.50 mL DMF was added 0.100 mmol  $\text{KDMF}\cdot\text{CF}_3$  as a solution in 0.50 mL DMF. Both solutions were chilled to  $-40\text{ }^\circ\text{C}$  prior to combination, and the reaction mixtures were then rapidly warmed to room temperature ( $<1$  minute) and allowed to react for 10 minutes. Yields were determined by  $^{19}\text{F}$  NMR integration against fluorobenzene internal standard.

Fig. S37. Comparison between 2 and previously reported CF<sub>3</sub><sup>-</sup> sources

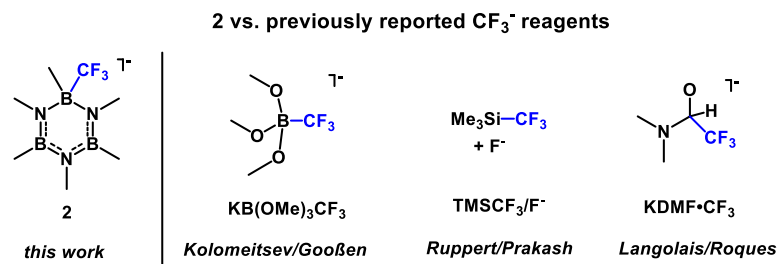
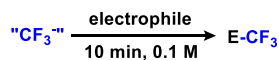
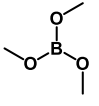
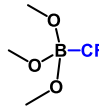
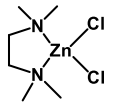
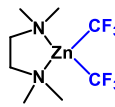
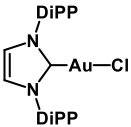
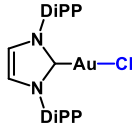
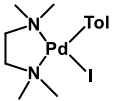
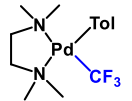


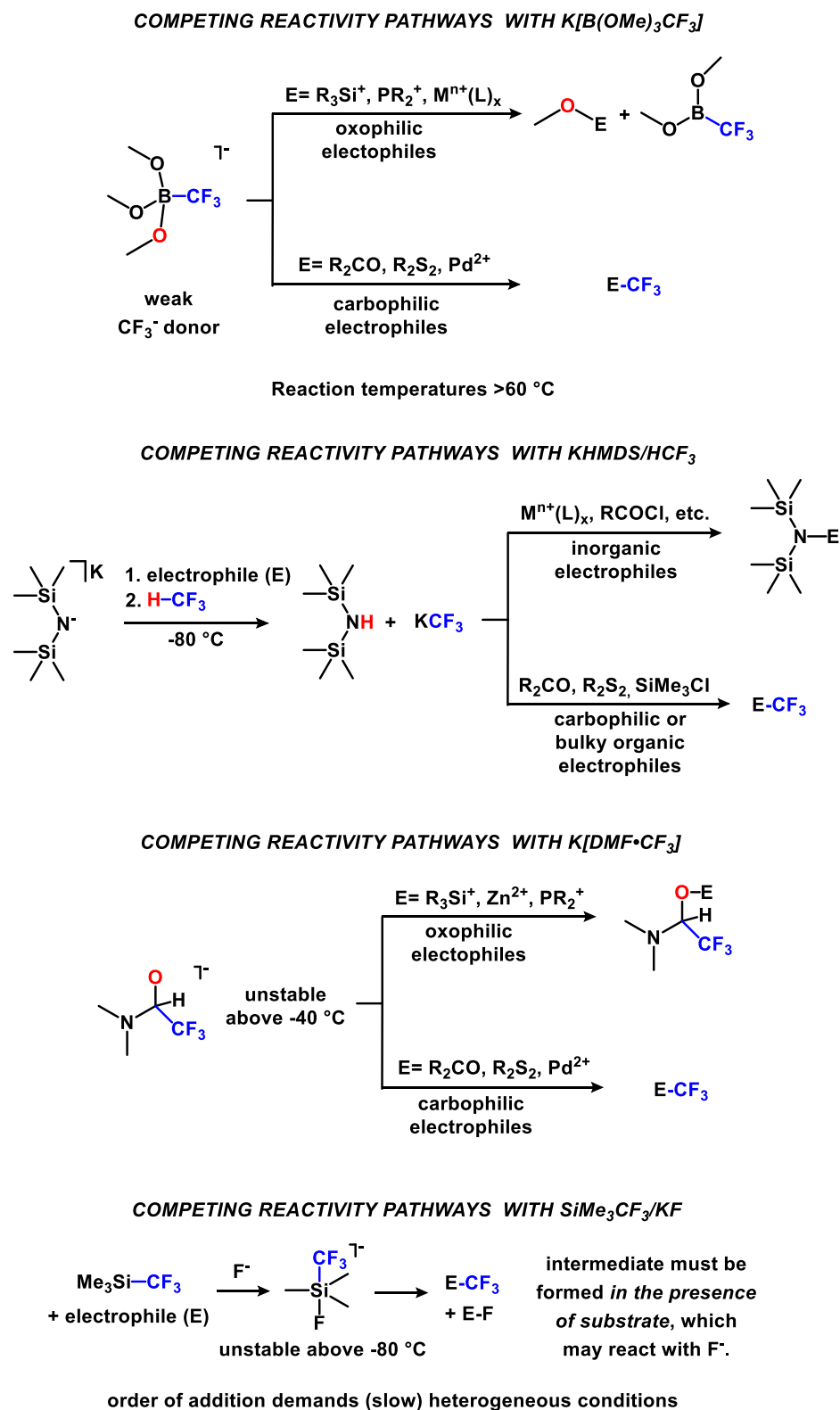
Table: Reactivity of CF<sub>3</sub><sup>-</sup> Sources with Inorganic Electrophiles



Electrophile	Product	CF <sub>3</sub> <sup>-</sup> Reagents			
		1	KB(OMe) <sub>3</sub> CF <sub>3</sub>	TMSCF <sub>3</sub> /F <sup>-</sup>	KDMF-CF <sub>3</sub>
S	KS-CF <sub>3</sub>	92%	0.0%	0.0%	5.2%
Se	KSe-CF <sub>3</sub>	61%	0.0%	0.3%	86%
NCBr	Br-CF <sub>3</sub>	44%	0.3%	2.2%	0.3%
PPh <sub>2</sub> Cl	PPh <sub>2</sub> -CF <sub>3</sub>	99%	0.0%	0.0%	6.8%
BiCl <sub>3</sub>	Bi-(CF <sub>3</sub> ) <sub>2</sub> Cl	42%	0.0%	0.0%	0.0%
		80%	--	0.0%	0.0%
Me <sub>3</sub> SiCl	Me <sub>3</sub> Si-CF <sub>3</sub>	96%	0.2%	--	0%
Me <sub>3</sub> SnCl	Me <sub>3</sub> Sn-CF <sub>3</sub>	73%	0.2%	47%	0%
Me <sub>3</sub> PbBr	Me <sub>3</sub> Pb-CF <sub>3</sub>	99%	0.2%	32%	0%
		74%	0.1%	0.0%	0.0%
CuI	Cu-CF <sub>3</sub>	83%	0.0%	0.0%	1.4%
AgNO <sub>3</sub>	Ag-CF <sub>3</sub>	44%	0.0%	7.8%	19%
		15%	0.0%	0.0%	56%
		98%	0.1%	2.1%	63%

\* Conditions: 1: 25 °C, THF; KB(OMe)<sub>3</sub>CF<sub>3</sub>: 25 °C, THF; KDMF-CF<sub>3</sub>: -40 °C to 25 °C, DMF

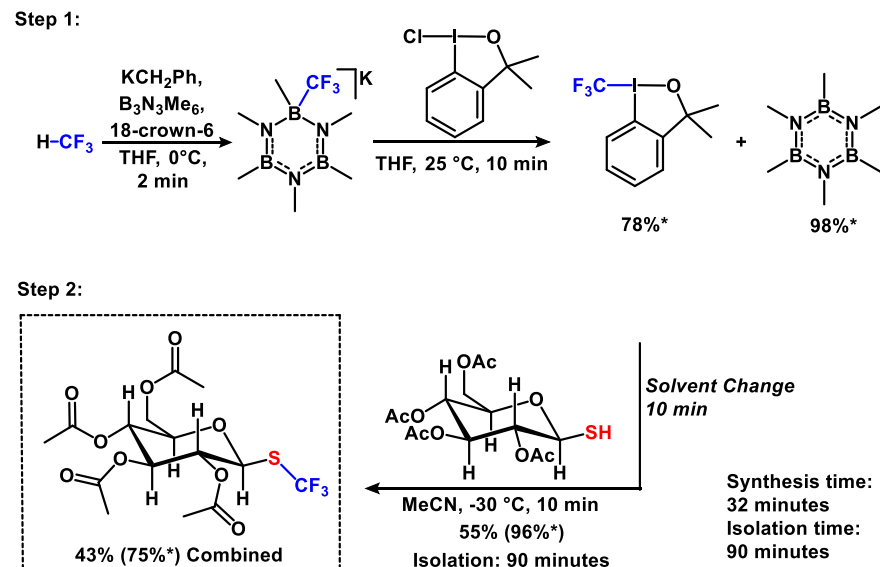
**Fig. S38. Disadvantages of previously reported  $\text{CF}_3^-$  sources**



## Rapid Electrophilic Trifluoromethylation of Thiols using **2**

### 1-Trifluoromethylthio- $\beta$ -D-glucose tetraacetate

Fig. S39. Reaction Scheme:

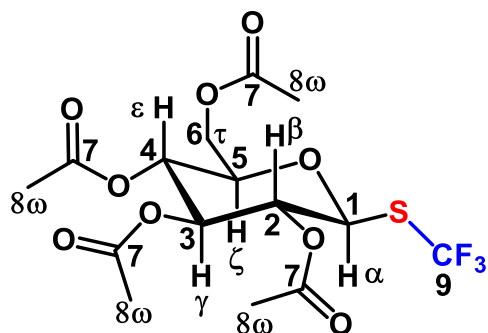


Step 1:

This procedure was reported in our manuscript describing the preparation of **2**.<sup>[11]</sup>

Hexamethylborazine (0.290 mmol, 47.7 mg) and 18-crown-6 (0.290 mmol, 76.6 mg) were dissolved in 1.5 mL THF in a 20 mL flask equipped with a Teflon-coated magnetic stirbar. The vessel was then allowed to cool to 0 °C in a glovebox cold-well for 30 minutes. Benzylpotassium (0.270 mmol, 35.2 mg) was then quickly added to this cold solution, and the initial deep red color of dissolved benzylpotassium quickly changed to a faint purple color. The homogeneous solution was stirred for 2 minutes, giving a homogeneous purple solution. The flask was then sealed with a tightly belt-clamped septum. Gaseous HCF<sub>3</sub> was added to the sealed vessel with a 30 mL syringe (0.32 mmol, 8.0 mL) and continuous efficient stirring. The colorless solution was stirred for 2 minutes, and brought to room temperature. 1 equivalent 1-chloro-3,3-dimethyl-1,3-dihydro-1λ-benzo[d][1,2]iodaoxole (0.27 mmol, 80 mg) was then added to the reaction mixture, and stirred at room temperature for 10 minutes; in this time, a white precipitate appeared. A 60 μL sample was removed for analysis by <sup>19</sup>F and <sup>1</sup>H NMR; conversion to 1-trifluoromethyl-3,3-dimethyl-1,3-dihydro-1λ-benzo[d][1,2]iodaoxole was 78%, while hexamethylborazine was regenerated (98%). The fluorine NMR spectra of the product matched literature spectra (<sup>19</sup>F-NMR (CDCl<sub>3</sub>): -40.1).<sup>[27]</sup> <sup>19</sup>F-NMR (THF): -41.32 (s).

Step 2:

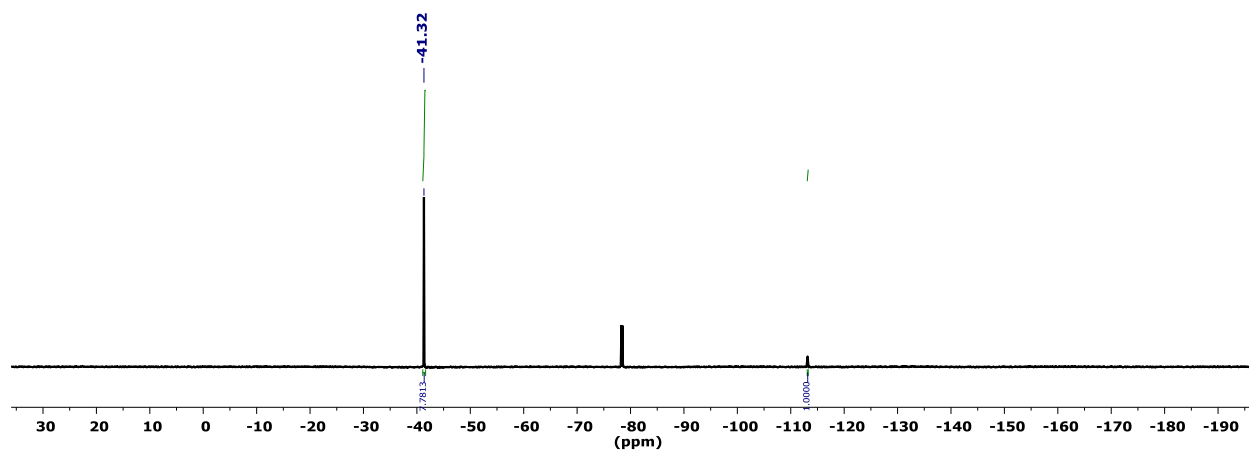


The solvent was removed under vacuum (5 minutes), reconstituted in 1.5 mL acetonitrile, cooled to -30 °C (5 minutes), and a -30 °C solution of 1-thio-β-D-glucose tetraacetate (0.270 mmol, 100 mg) in 1.5 mL acetonitrile quickly added. The reaction was then immediately allowed to warm to room temperature and vigorously stirred for 10 minutes (synthesis time: 32 minutes). A 30 μL sample was removed for analysis by <sup>19</sup>F NMR spectroscopy, the reaction was opened to air, and the solvent was removed by rotary evaporation. The white solid was then suspended in 10 mL water, and the organic components extracted into dichloromethane (4 x 2 mL). The dichloromethane extract was then dried with magnesium sulfate, filtered, concentrated to 2 mL, and purified by flash chromatography. Chromatography conditions: 50 g SiO<sub>2</sub>, 12%-100% ethyl acetate/hexanes over 10 column volumes, R<sub>f</sub>: 0.58. The product is not UV active, so it was detected during elution by means of an attached evaporative light scattering detector (Biotage ELSD-A120; settings: nebulizer temperature: 40 °C, evaporation temperature: 60 °C, flow: 2.5). The fractions containing 1-trifluoromethylthio-β-D-glucose tetraacetate were combined and evaporated by rotary evaporation, then dried under high vacuum (50.4 mg, 43% combined yield from benzylpotassium). Time required for isolation: 90 minutes. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 5.23 (1H, γ, (t, J<sub>1H-1H</sub>=9.3)), 5.07 (1H, ε, (t, J<sub>1H-1H</sub>=9.8)), 5.01 (1H, β, (t, J<sub>1H-1H</sub>=9.7)), 4.96 (1H, α, (d, J<sub>1H-1H</sub>=10.3)), 4.26 (1H, τ, (dd, J<sub>1H-1H</sub>=12.5, 5.3)), 4.10 (1H, τ, (dd, J<sub>1H-1H</sub>=12.4, 2.2)), 3.77 (1H, ζ, (ddd, J<sub>1H-1H</sub>=10.1, 5.3, 2.3)). <sup>13</sup>C-NMR: 170.49 (7), 169.90 (7), 169.25 (7), 129.33 (9, q, J<sub>13C-19F</sub>=308), 81.43 (1, q, J<sub>13C-19F</sub>=2.8), 76.24 (5), 73.32 (3), 69.22 (2), 67.76 (4), 61.67 (6), 20.56 (8), 20.47 (8), 20.44 (8). <sup>19</sup>F-NMR: -40.08 (s). HRMS (ESI<sup>+</sup>): 450.1045 (M+NH<sub>4</sub><sup>+</sup>: 450.1040).

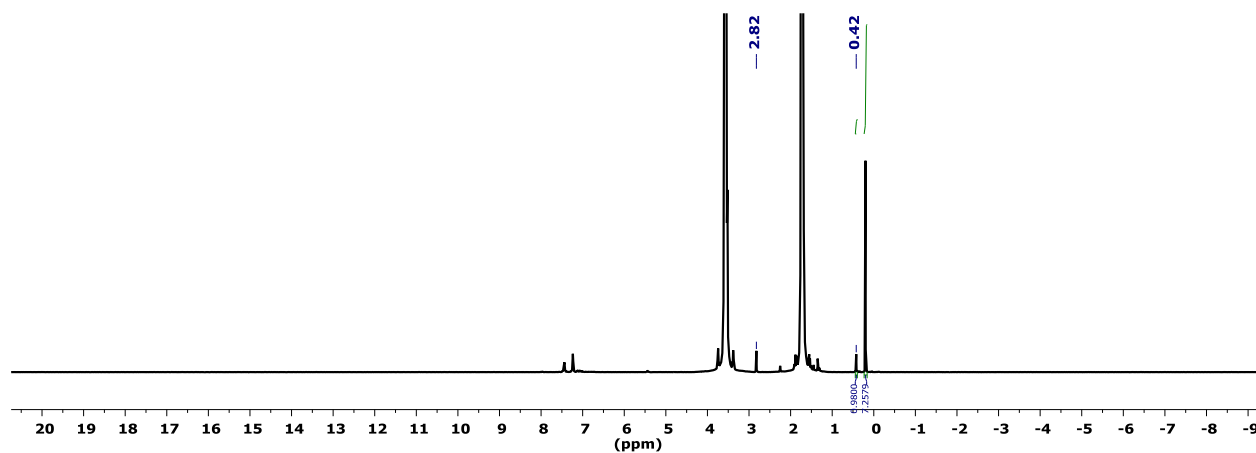


***In-Situ* Characterization:**

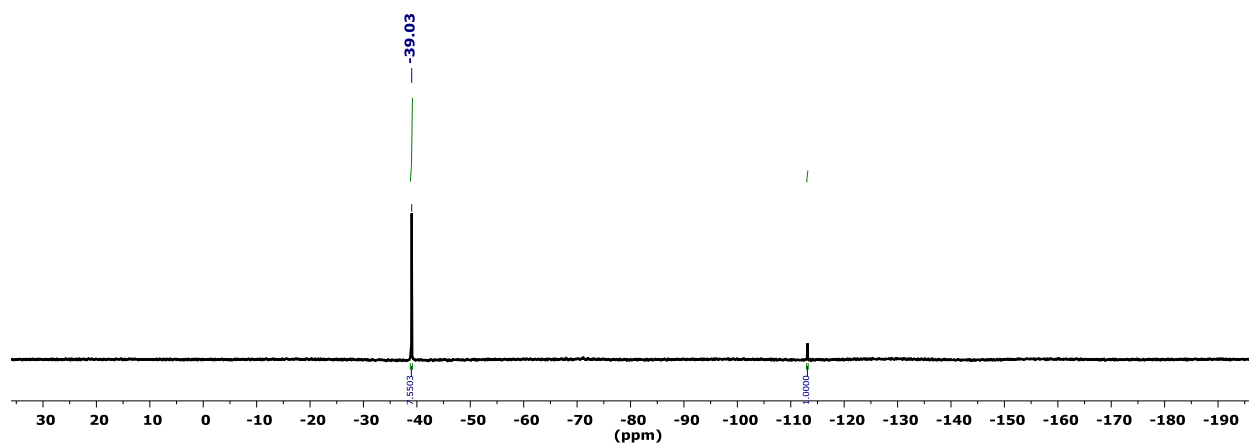
**Fig. S40. *In-situ*  $^{19}\text{F}$  NMR spectrum of 1-trifluoromethyl-3,3-dimethyl-1,3-dihydro-1 $\lambda$ -benzo[d][1,2]iodaoxole:**



**Fig. S41. *In-situ*  $^1\text{H}$  NMR spectrum of Regenerated Hexamethylborazine:**



**Fig. S42. *In-situ*  $^{19}\text{F}$  NMR spectrum of 1-Trifluoromethylthio- $\beta$ -D-glucose tetraacetate:**



Characterization of isolated 1-trifluoromethylthio- $\beta$ -D-glucose tetraacetate:

Fig. S43.  $^1\text{H}$  NMR Spectrum:

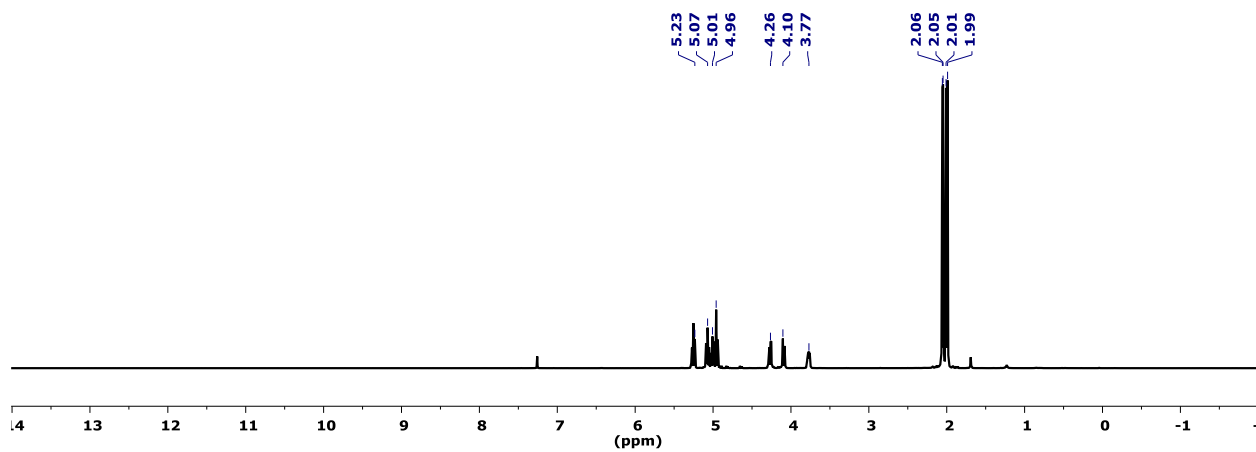


Fig. S44.  $^{13}\text{C}$  NMR Spectrum:

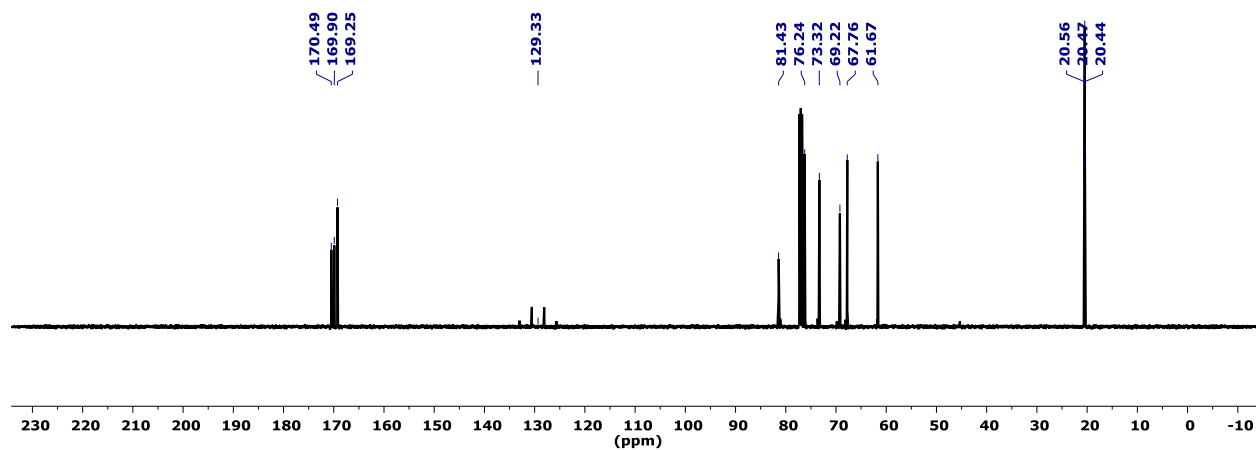


Fig. S45.  $^{19}\text{F}$  NMR Spectrum:

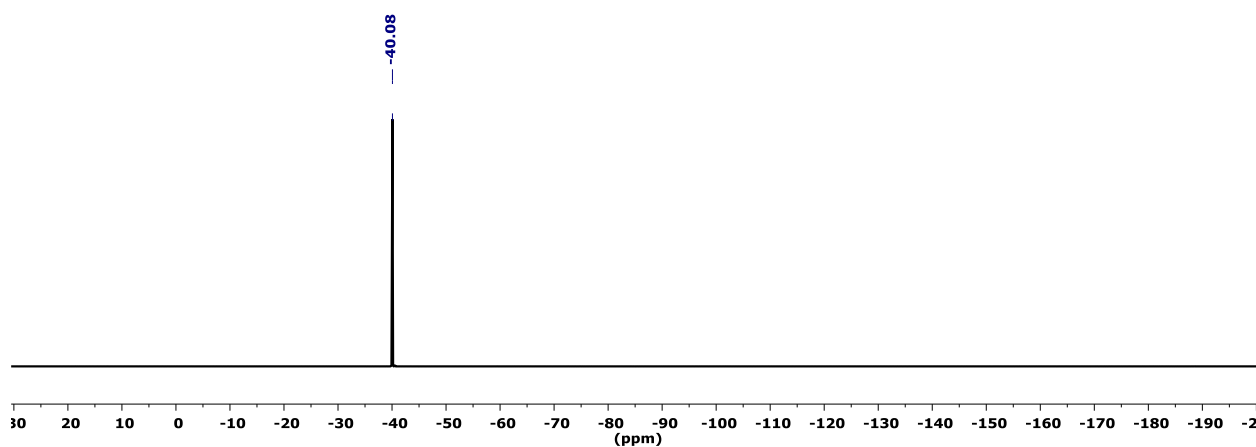


Fig. S46.  $^1\text{H}$ - $^1\text{H}$  gCOSY NMR Spectrum:

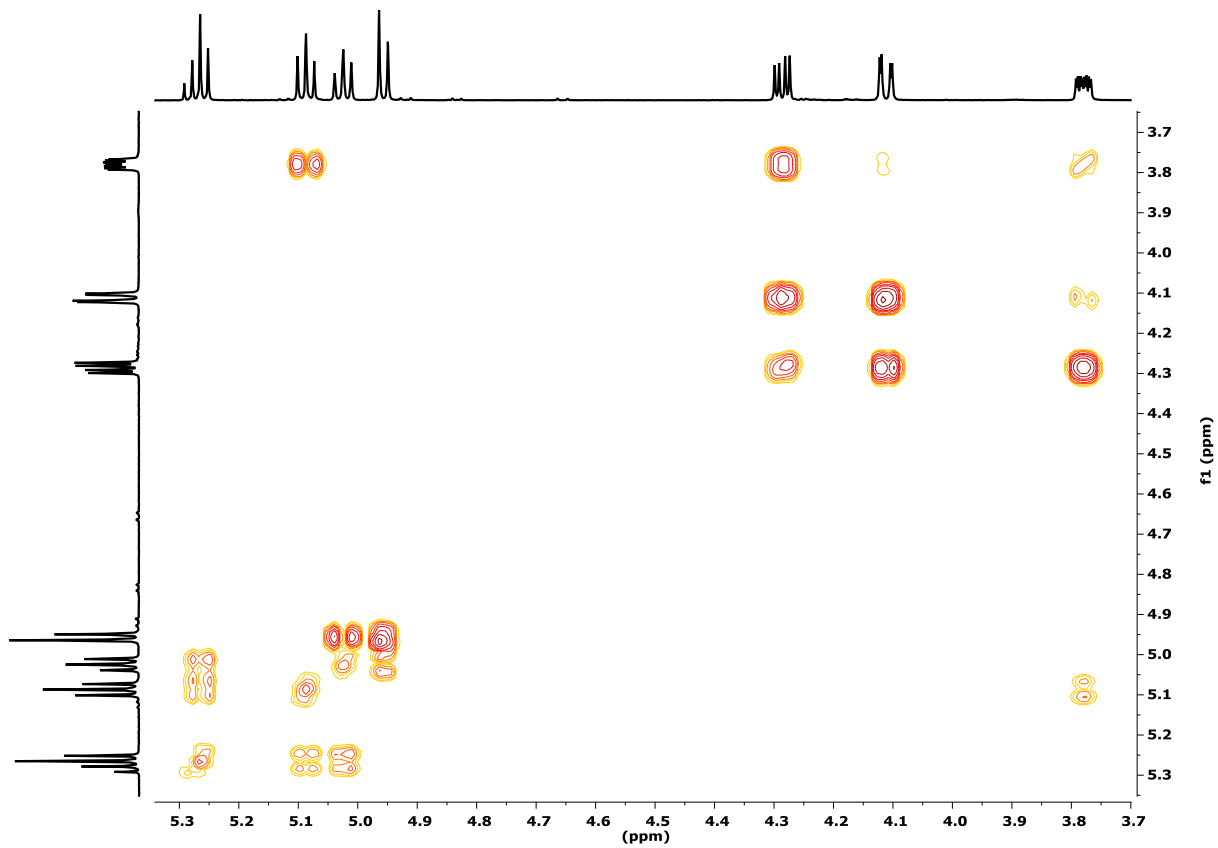
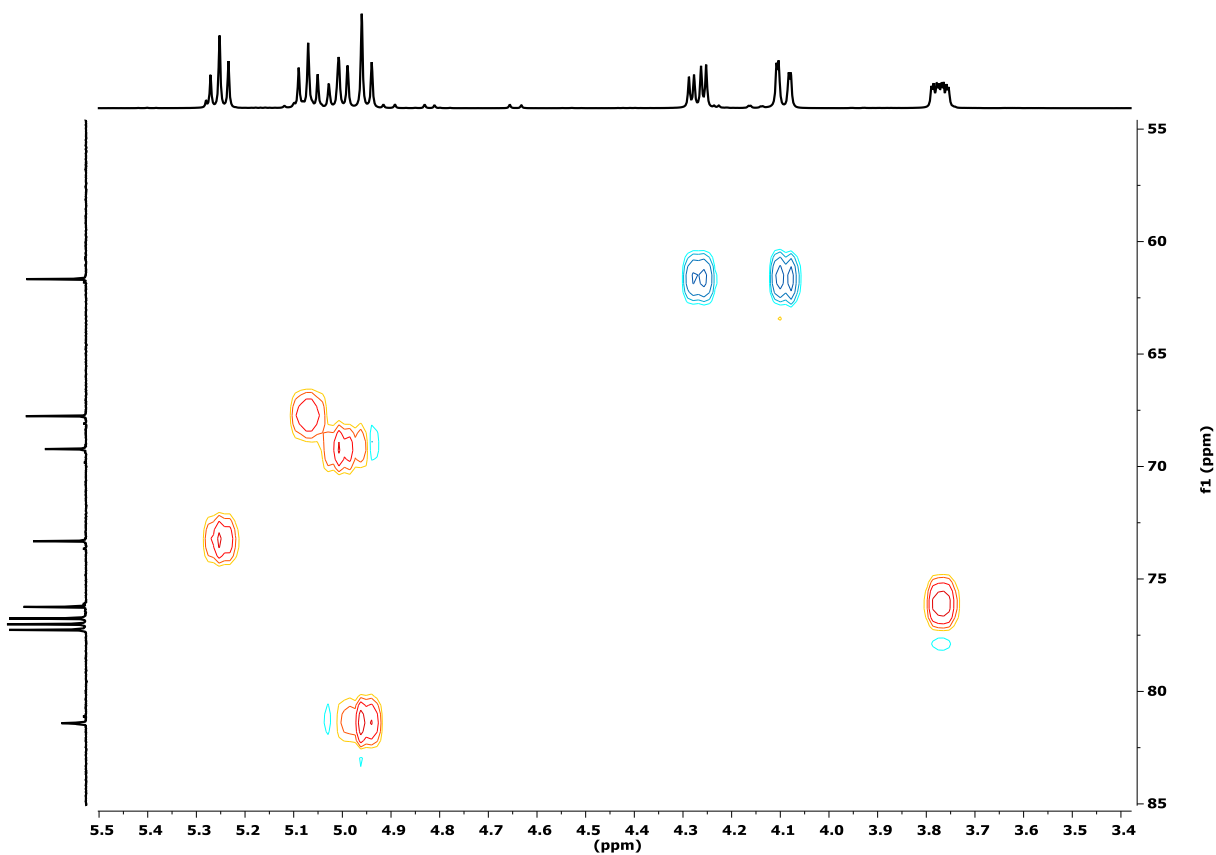


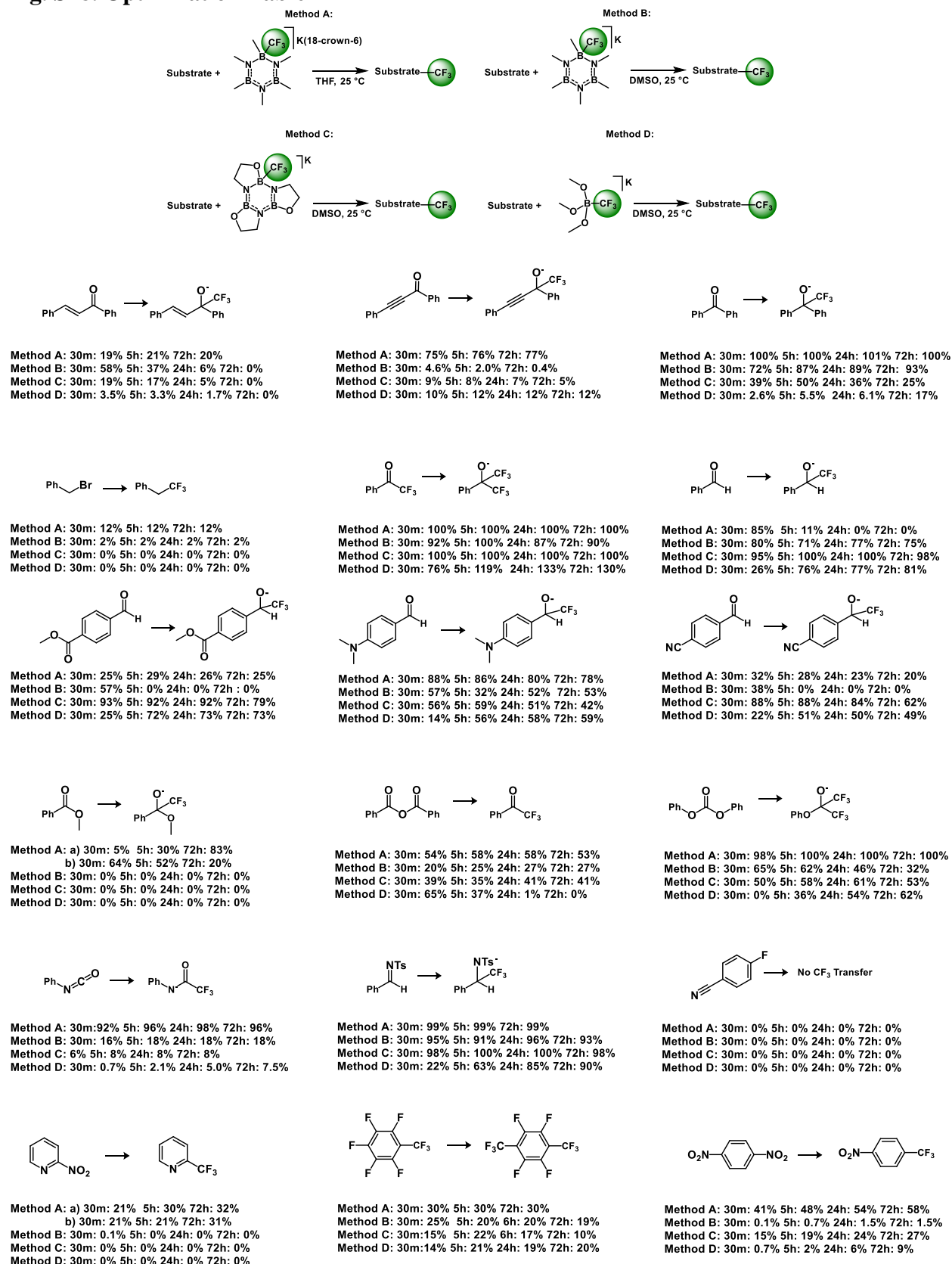
Fig. S47.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD NMR Spectrum:



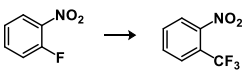
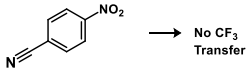
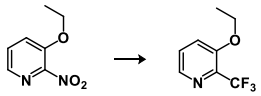
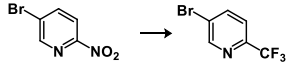
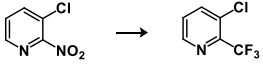

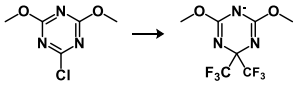
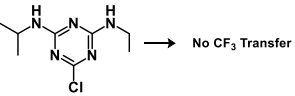
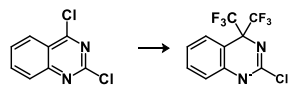
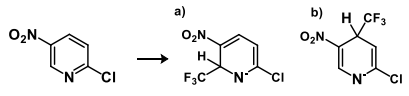
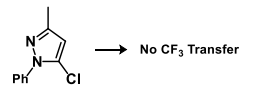
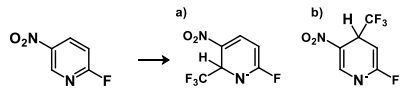
### Nucleophilic Trifluoromethylation of Organic Compounds with LA- $\text{CF}_3$ : Initial Condition Screening

To 0.1 mmol of substrate dissolved in 0.50 mL DMSO or THF was added one of the above stock solutions of the  $\text{HCF}_3$  derived  $\text{CF}_3^-$  reagent. NMR spectra were recorded at 30 minute, 1 hour, 5 hour, and 24 hour time points to monitor conversion to trifluoromethylated product through integration against a 0.030 mmol fluorobenzene internal standard. In cases where anionic addition products were observed, confirmation of product identity was made through GCMS.

**Fig. S48. Optimization Table**



**Fig. S49. Optimization Table Cont.**

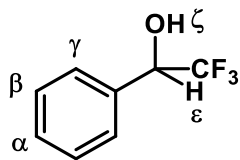
 <p>Method A: 30m: 3.2% 5h: 10% 24h: 9%            Method B: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method C: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method D: 30m: 0% 5h: 0% 24h: 0% 72h: 0%</p>	 <p>No CF<sub>3</sub> Transfer</p> <p>Method A: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method B: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method C: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method D: 30m: 0% 5h: 0% 24h: 0% 72h: 0%</p>	 <p>Method A: 30m: 3% 5h: 4% 24h: 7% 72h: 10%            Method B: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method C: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method D: 30m: 0% 5h: 0% 24h: 0% 72h: 0%</p>
 <p>Method A: 30m: 8.6% 5h: 8.6% 24h: 8.6% 72h: 7.6%            Method B: 30m: 0% 5h: 0.1% 24h: 0.1% 72h: 0.2%            Method C: 30m: 3.6% 5h: 5.9% 24h: 6.4% 72h: 6.4%            Method D: 30m: 0.3% 5h: 0.8% 24h: 1.8% 72h: 2.8%</p>	 <p>Method A: 30m: 3.7% 5h: 3.7% 24h: 3.7% 72h: 3.7%            Method B: 30m: 0% 5h: 0.5% 24h: 0.6% 72h: 0.6%            Method C: 30m: 3.0% 5h: 5.1% 24h: 5.2% 72h: 5.4%            Method D: 30m: 0.3% 5h: 0.6% 24h: 1.4% 72h: 2.1%</p>	 <p>Method A: 30m: 22% 5h: 0% 24h: 0% 72h: 0%            Method B: 30m: 69% 5h: 69% 24h: 31% 72h: 0%            Method C: 30m: 58% 5h: 79% 24h: 78% 72h: 56%            Method D: 30m: 5% 5h: 13% 24h: 26% 72h: 36%</p>
 <p>Method A: 30m: 87% 5h: 91% 24h: 79% 72h: 41%            Method B: 30m: 61% 5h: 39% 24h: 0% 72h: 0%            Method C: 30m: 44% 5h: 54% 24h: 0% 72h: 0%            Method D: 30m: 0% 5h: 2% 24h: 6% 72h: 6.2%</p>	 <p>No CF<sub>3</sub> Transfer</p> <p>Method A: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method B: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method C: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method D: 30m: 0% 5h: 0% 24h: 0% 72h: 0%</p>	 <p>Method A: 30m: 100% 5h: 98% 24h: 100% 72h: 95%            Method B: 30m: 75% 5h: 70% 24h: 70% 72h: 66%            Method C: 30m: 59% 5h: 63% 24h: 62% 72h: 61%            Method D: 30m: 16% 5h: 50% 24h: 56% 72h: 46%</p>
 <p>Method A: a) 30m: 24% 5h: 29% 24h: 3%            b) 30m: 18% 5h: 22% 24h: 15%            Method B: a) 30m: 22% 5h: 24% 24h: 24% 72h: 23%            b) 30m: 12% 5h: 13% 24h: 13% 72h: 13%            Method C: a) 30m: 41% 5h: 44% 24h: 45% 72h: 45%            b) 30m: 34% 5h: 36% 24h: 37% 72h: 37%            Method D: a) 30m: 5% 5h: 12% 24h: 18% 72h: 19%            b) 30m: 6% 5h: 15% 24h: 22% 72h: 24%</p>	 <p>No CF<sub>3</sub> Transfer</p> <p>Method A: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method B: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method C: 30m: 0% 5h: 0% 24h: 0% 72h: 0%            Method D: 30m: 0% 5h: 0% 24h: 0% 72h: 0%</p>	 <p>Method A: a) 30m: 50% 5h: 51% 24h: 47%            b) 30m: 36% 5h: 24% 24h: 10%            Method B: a) 30m: 61% 5h: 58% 24h: 58% 72h: 56%            b) 30m: 21% 5h: 17% 24h: 12% 72h: 12%            Method C: a) 30m: 47% 5h: 50% 24h: 50% 72h: 50%            b) 30m: 17% 5h: 17% 24h: 17% 72h: 17%            Method D: a) 30m: 6% 5h: 6% 24h: 5% 72h: 4%            b) 30m: 11% 5h: 20% 24h: 24% 72h: 25%</p>

## Nucleophilic Trifluoromethylation of Organic Compounds with LA-CF<sub>3</sub>: Isolated Compounds and Characterization

### General Protocol:

An appropriate quantity of a 0.2 M stock solution of K(LA-CF<sub>3</sub>) was added to a 0.2 M solution of substrate in a 20 mL scintillation vial. The mixture was then stirred for the specified time (*vide infra*) then quenched by adding 15 mL of 5% aqueous HCl or saturated aqueous ammonium chloride. The product was then extracted into CH<sub>2</sub>Cl<sub>2</sub> (5 x 3 mL CH<sub>2</sub>Cl<sub>2</sub>) and the organic phase dried with MgSO<sub>4</sub>. The dried organic phase was then filtered, concentrated to 1 mL, then purified by silica chromatography using a Biotage Isolera automated flash chromatography apparatus. The collected fractions were concentrated by rotary evaporation and further dried under high vacuum to afford the pure products.

## 1,2 Addition Reactions with C=O and C=N compounds



### 1-Phenyl-1-trifluoromethylmethanol:

Substrate: Benzaldehyde. Conditions: Solvent: DMSO. LA:  $\text{K}(\text{BOCH}_2\text{CH}_2\text{N})_3\text{CF}_3$ . 1.0 equivalents  $\text{K}(\text{LA}-\text{CF}_3)$  used. 0.40 mmol substrate. Reaction time: 1 hour. Quench: 5% HCl. Chromatography conditions: 100%  $\text{CH}_2\text{Cl}_2$ , 9 column volumes, 10g  $\text{SiO}_2$ , flow rate: 1 column volume per minute. 62 mg colorless oil, 88%. Due to the volatile nature of the product it could not be dried under high vacuum.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.46 ( $\beta$ , 2H, m), 7.41 ( $\alpha$ ,  $\gamma$ , 3H, m), 4.98 ( $\epsilon$ , 1H, (q,  $J_{\text{H}-^{19}\text{F}}=6.7$ )), 2.88 ( $\zeta$ , 1H, s).  $^{13}\text{C-NMR}$ : 133.92, 129.53, 128.60, 127.41, 124.22 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=282$ ), 72.79 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=32$ ).  $^{19}\text{F-NMR}$ : -78.36 (d,  $J_{^{19}\text{F}-^1\text{H}}=6.7$ ). HRMS (ESI<sup>-</sup>): 221.0435 ( $\text{M}+\text{HCO}_2$ : 221.0431).

Fig. S50.  $^1\text{H}$  NMR Spectrum:

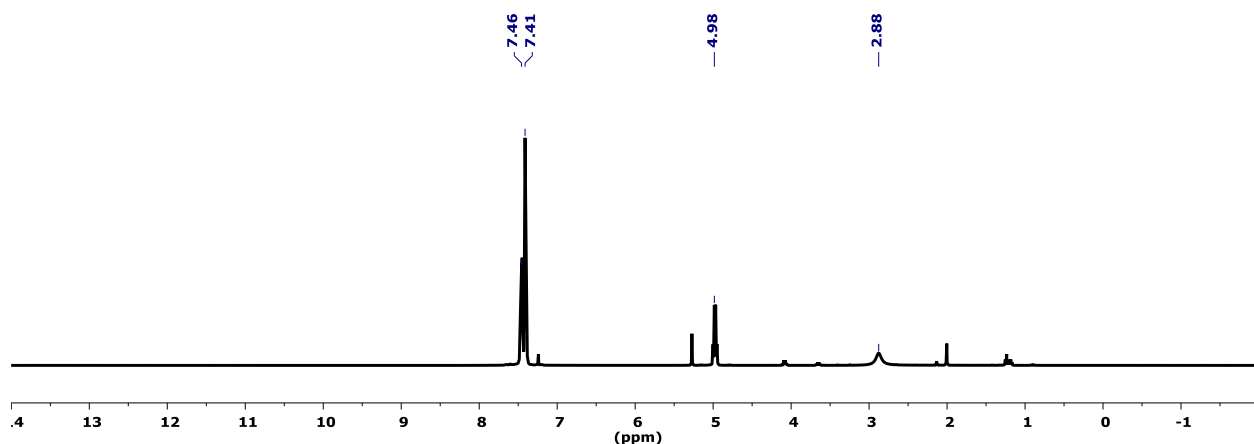


Fig. S51.  $^{13}\text{C}$  NMR Spectrum:

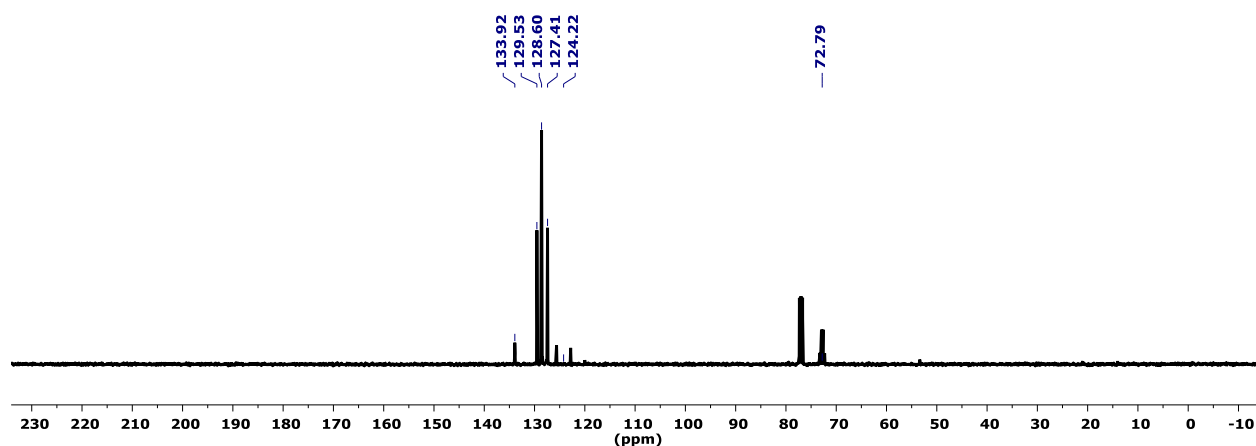
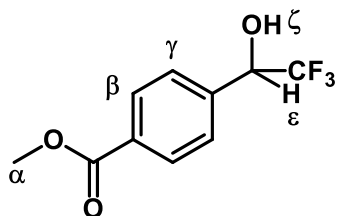
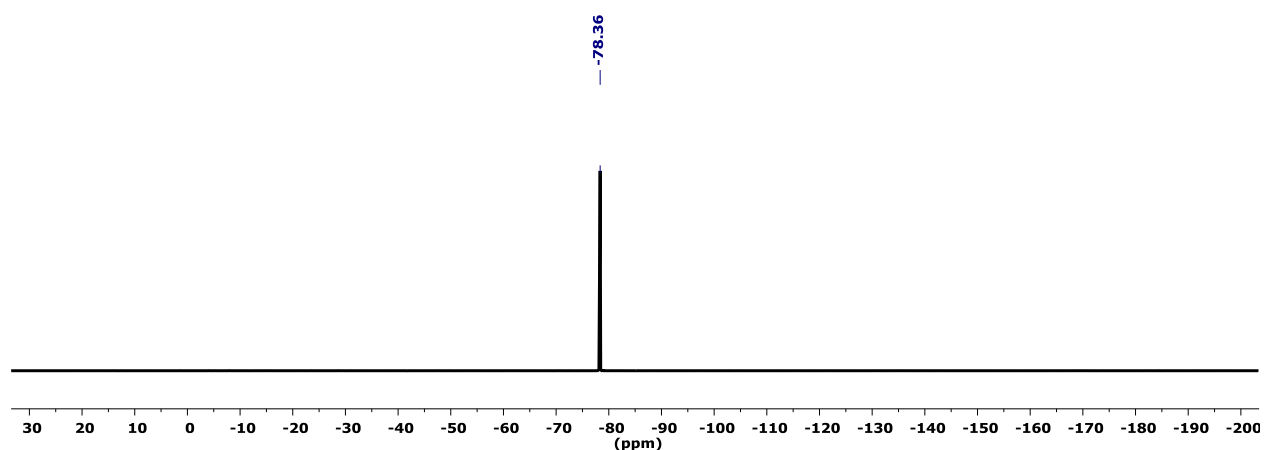


Fig. S52.  $^{19}\text{F}$  NMR Spectrum:



### Methyl 4-(trifluoro-1-ethanol)benzoate

Substrate: Methyl 4-formyl benzoate. Conditions: Solvent: DMSO. LA:  $\text{K}(\text{BOCH}_2\text{CH}_2\text{N})_3\text{CF}_3$ . 1.0 equivalents  $\text{K}(\text{LA}-\text{CF}_3)$  used. 0.40 mmol substrate. Reaction time: 1 hours. Quench: 5% HCl. Chromatography conditions: 0-100% hexane/ethyl acetate, 16 column volumes, 50 g  $\text{SiO}_2$ , flow rate 0.5 column volume per minute. 56 mg white solid, 60%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 8.00 ( $\beta$ , 2H, (d,  $J_{\text{H-H}}=8.1$ )), 7.54 ( $\gamma$ , 2H, (d,  $J_{\text{H-H}}=7.9$ )), 5.08 ( $\epsilon$ , 1H, (q,  $J_{\text{H-}^{19}\text{F}}=6.7$ )), 3.89 ( $\alpha$ , 3H, s), 3.72 ( $\zeta$ , 1H, s).  $^{13}\text{C}$ -NMR: 167.00, 139.02, 130.83, 129.69, 127.51, 124.02 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=282$ ), 72.25 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=32$ ), 52.39.  $^{19}\text{F}$ -NMR: -78.18 (d,  $J_{^{19}\text{F}-\text{H}}=6.7$ ). HRMS (ESI-): 235.0573 (M-H: 235.0577).



Fig. S53.  $^1\text{H}$  NMR Spectrum:

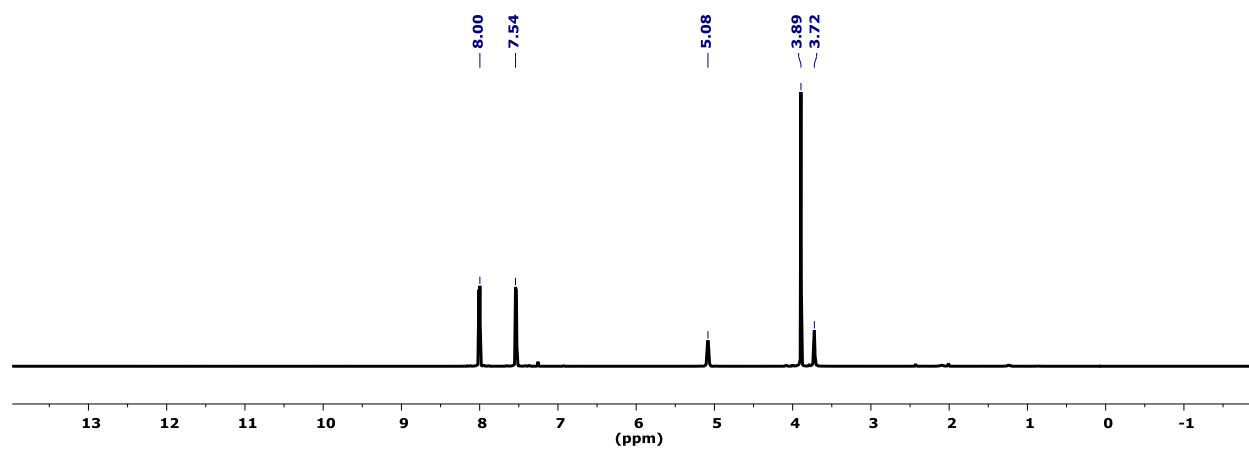


Fig. S54.  $^{13}\text{C}$  NMR Spectrum:

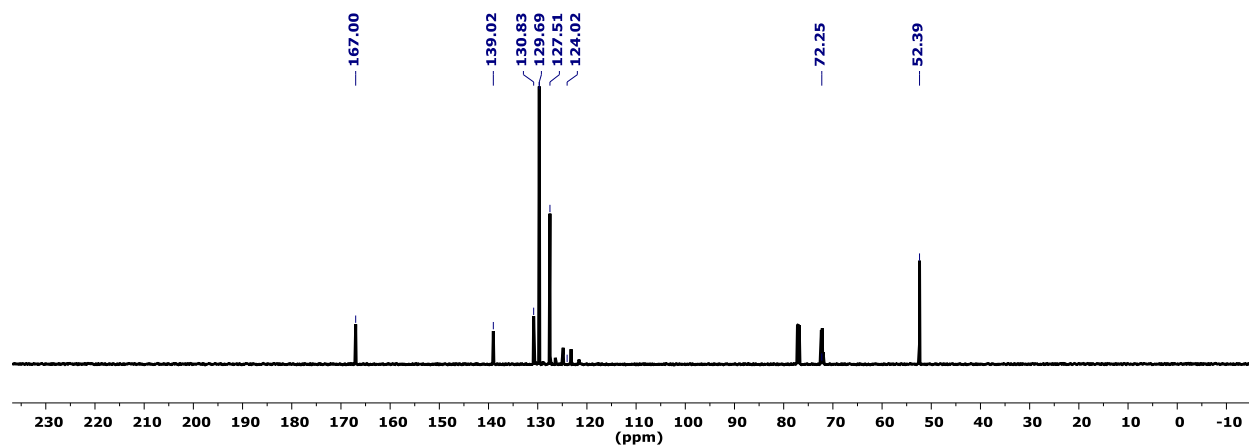
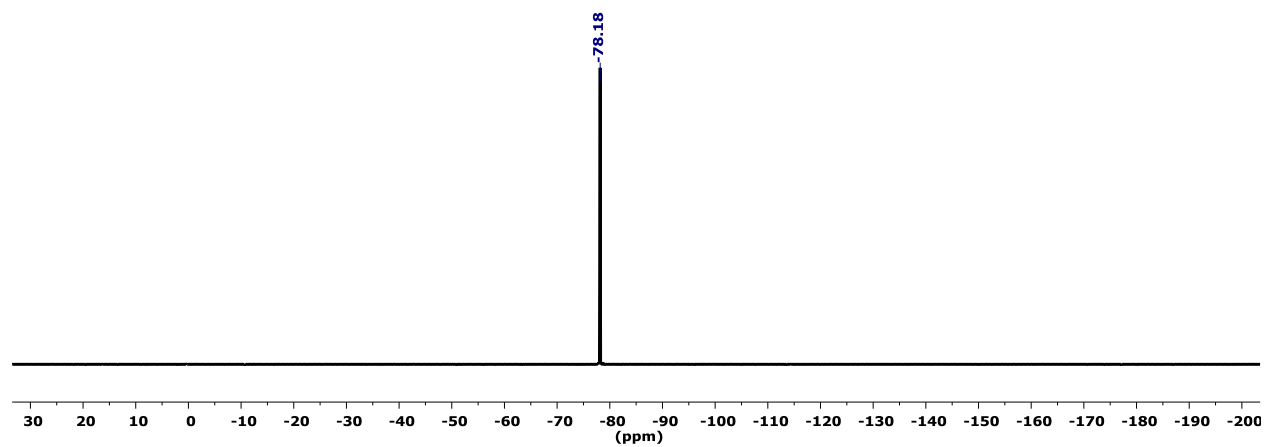
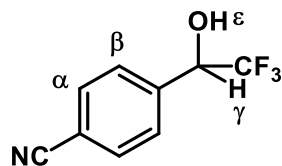


Fig. S55.  $^{19}\text{F}$  NMR Spectrum:





#### 4-(Trifluoro-1-ethanol)benzonitrile

Substrate: 4-formyl-benzonitrile. Conditions: Solvent: DMSO. LA:  $\text{K}(\text{BOCH}_2\text{CH}_2\text{N})_3\text{CF}_3$ . 1.0 equivalent  $\text{K}(\text{LA}-\text{CF}_3)$  used. 0.40 mmol substrate. Reaction time: 1 hours. Quench: 5% HCl. Chromatography conditions: 0-100%  $\text{CH}_2\text{Cl}_2$ /ethyl acetate, 8 column volumes, 10 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 39 mg white solid, 48%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 7.68 ( $\beta$ , 2H, (d,  $J_{\text{H-H}}=8.2$ )), 7.63 ( $\alpha$ , 2H, (d,  $J_{\text{H-H}}=8.1$ )), 5.11 ( $\gamma$ , 1H, (p,  $J_{\text{H-}^{19}\text{F}}=6.2$ )), 3.44 ( $\epsilon$ , 1H, (d,  $J_{\text{H-H}}=4.6$ )).  $^{13}\text{C-NMR}$ : 139.19, 132.28, 128.27, 123.78(q,  $J_{^{13}\text{C}-^{19}\text{F}}=282$ ), 118.27, 112.94, 72.25 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=32$ ).  $^{19}\text{F-NMR}$ : -78.18 (d,  $J_{^{19}\text{F}-\text{H}}=6.4$ ). HRMS (ESI-): 200.0322 (M-H: 200.0329).

Fig. S56.  $^1\text{H}$  NMR Spectrum:

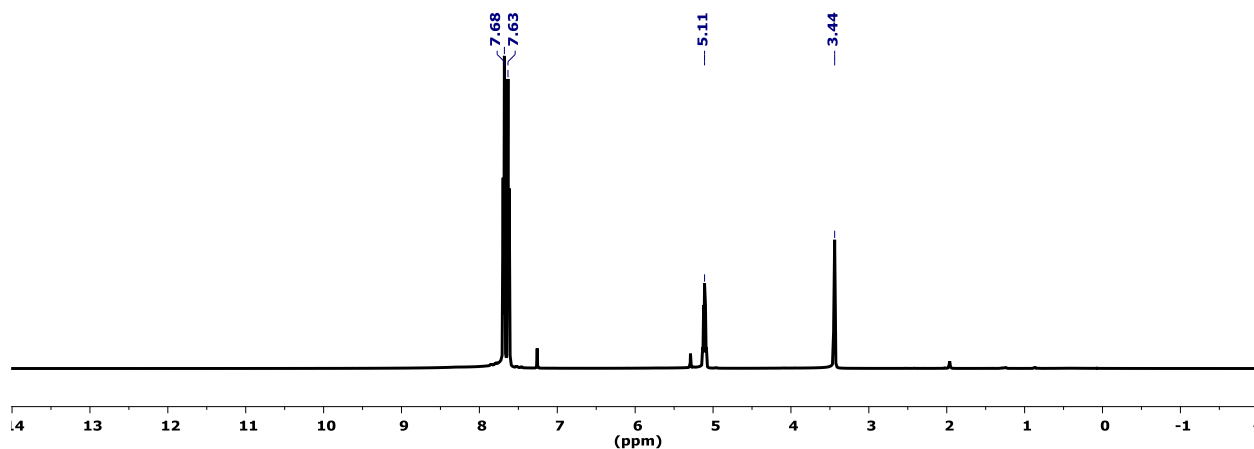


Fig. S57.  $^{13}\text{C}$  NMR Spectrum:

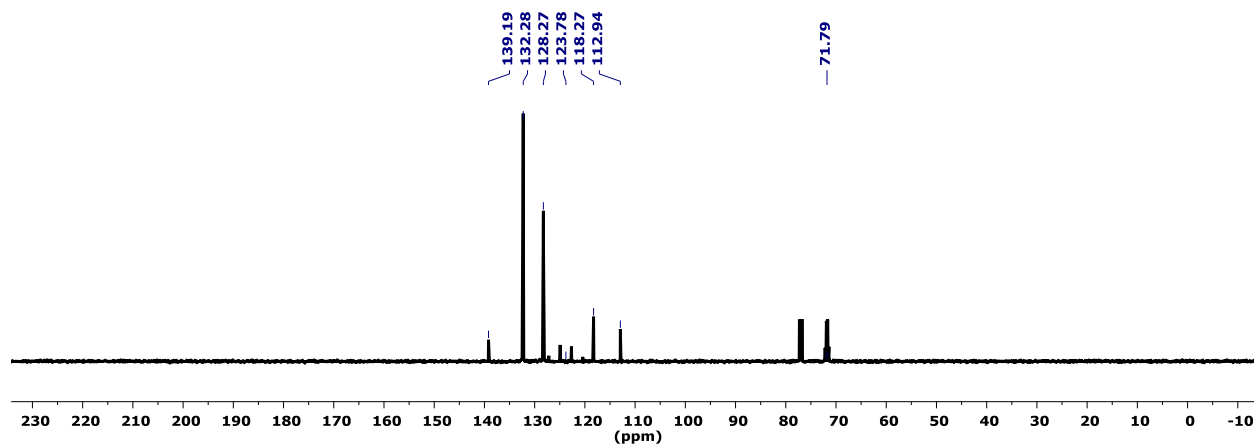
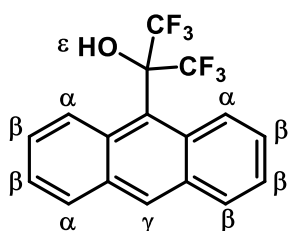
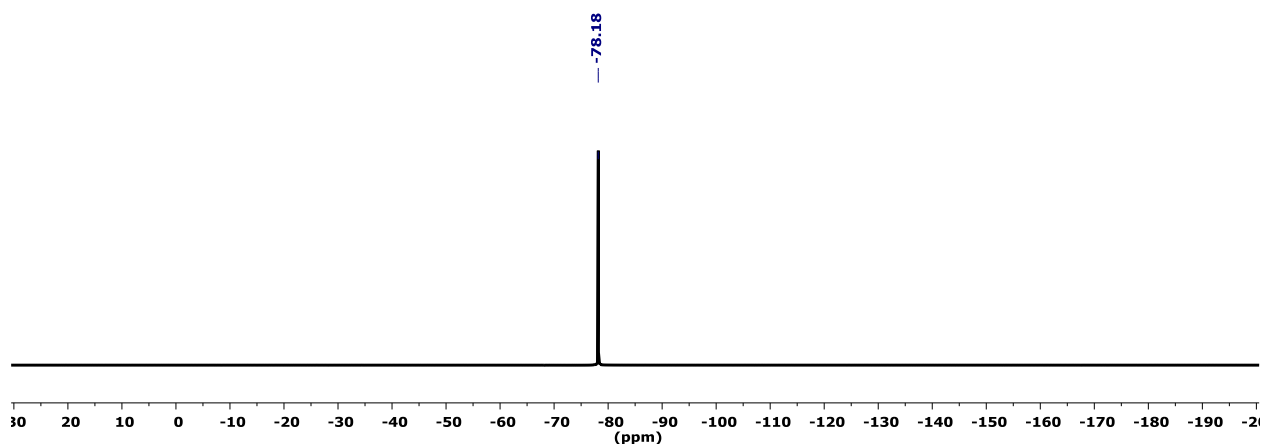


Fig. S58.  $^{19}\text{F}$  NMR Spectrum:



### 1-(Anthracen-9-yl)-1,1-bistrifluoromethylcarbinol

Substrate: Anthracen-9-yl trifluoromethyl ketone. Conditions: Solvent: THF. LA:  $\text{K}(\text{18-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$ . 2.0 equivalents  $\text{K}(\text{LA}-\text{CF}_3)$  used. 0.40 mmol substrate. Reaction time: 1 hour. Quench: 5% HCl. Chromatography conditions: 0-100% hexane ethyl acetate, 16 column volumes, 25 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 120 mg yellow crystals, 87%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 9.02 ( $\alpha$ , 1H, (d,  $J_{\text{H-H}}=9.3$ )), 8.55 ( $\alpha$ , 1H, (d,  $J_{\text{H-H}}=9.3$ )), 8.51 ( $\gamma$ , 1H, s), 7.99 ( $\beta$ , 2H, (t,  $J_{\text{H-H}}=9.5$ )), 7.59 ( $\beta$ , 1H, (t,  $J_{\text{H-H}}=8.3$ )), 7.49 ( $\alpha$ ,  $\beta$ , 3H, m), 3.98 ( $\epsilon$ , 1H, s).  $^{13}\text{C}$ -NMR: 134.06, 133.11, 132.46, 132.41, 131.38, 131.15, 129.39, 129.11, 127.34, 126.71, 125.98, 124.78, 124.61, 123.94(q,  $J_{13\text{C}-19\text{F}}=290$ ), 121.94, 83.46(p,  $J_{13\text{C}-19\text{F}}=31$ ).  $^{19}\text{F}$ -NMR: -69.31 (s). HRMS (ES $^+$ ): 344.0630 ( $\text{M}^+$ : 344.0636).

Fig. S59.  $^1\text{H}$  NMR Spectrum:

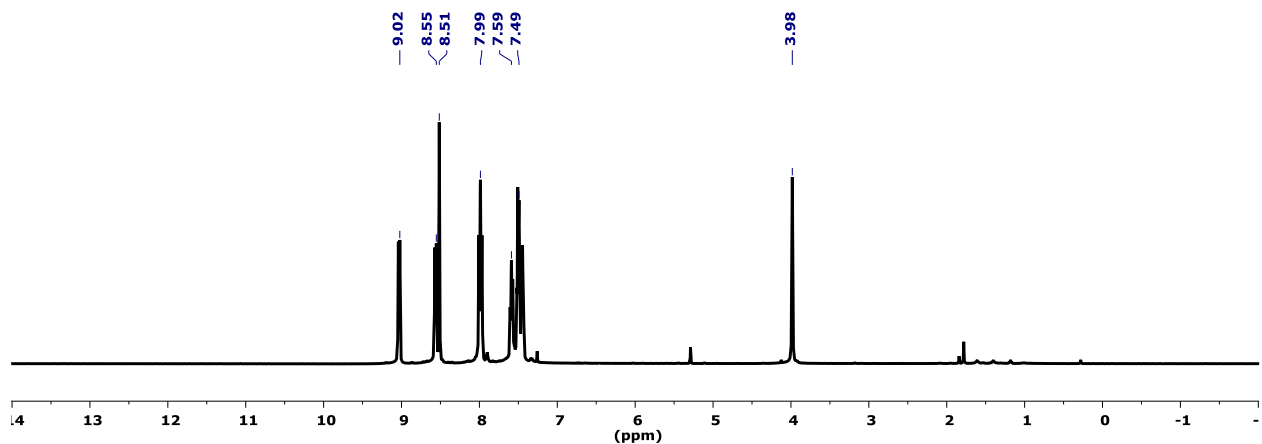


Fig. S60.  $^{13}\text{C}$  NMR Spectrum ( $^1\text{H}$  decoupled):

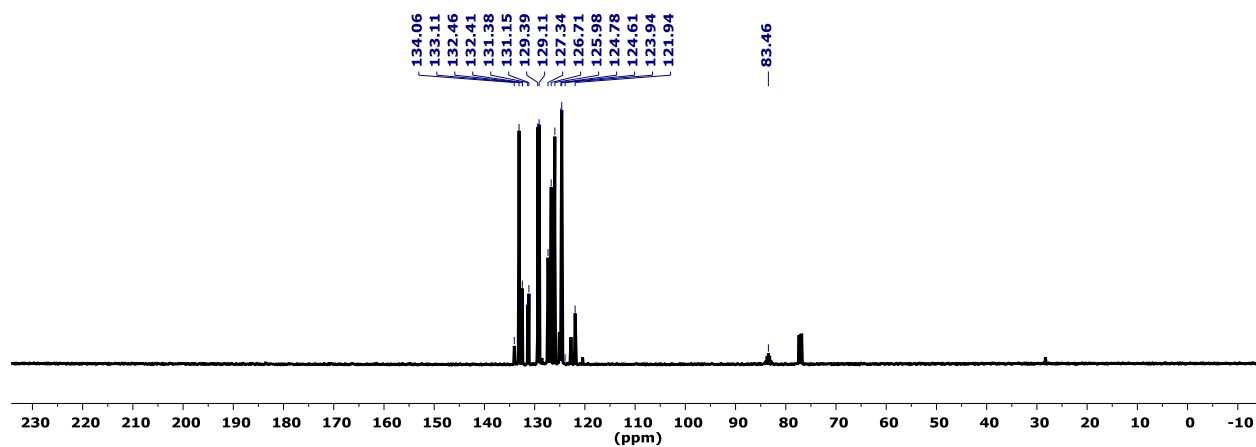


Fig. S61.  $^{13}\text{C}$  NMR Spectrum ( $^{19}\text{F}$  decoupled):

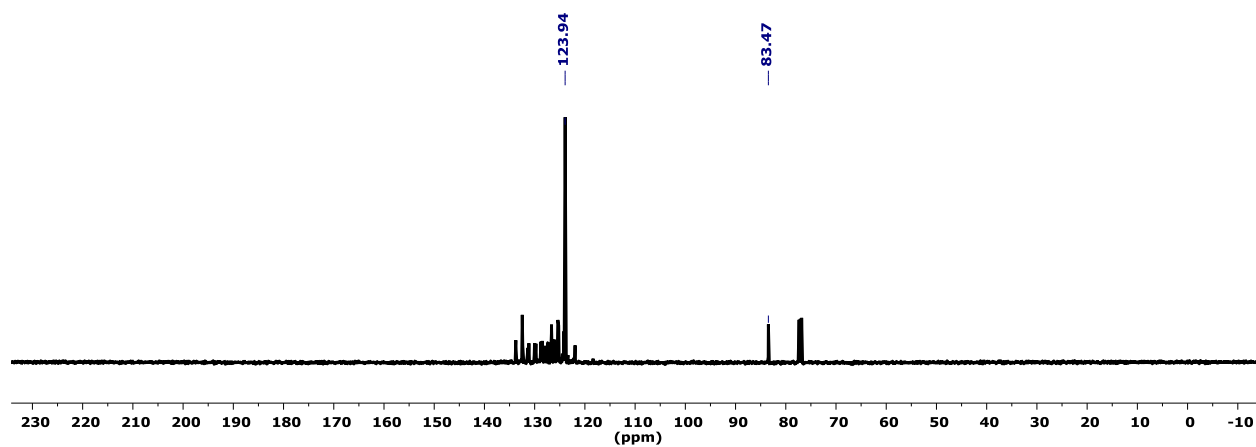
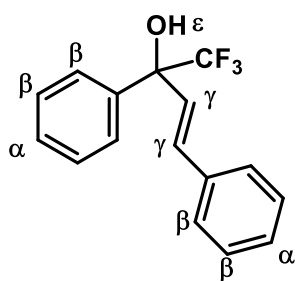
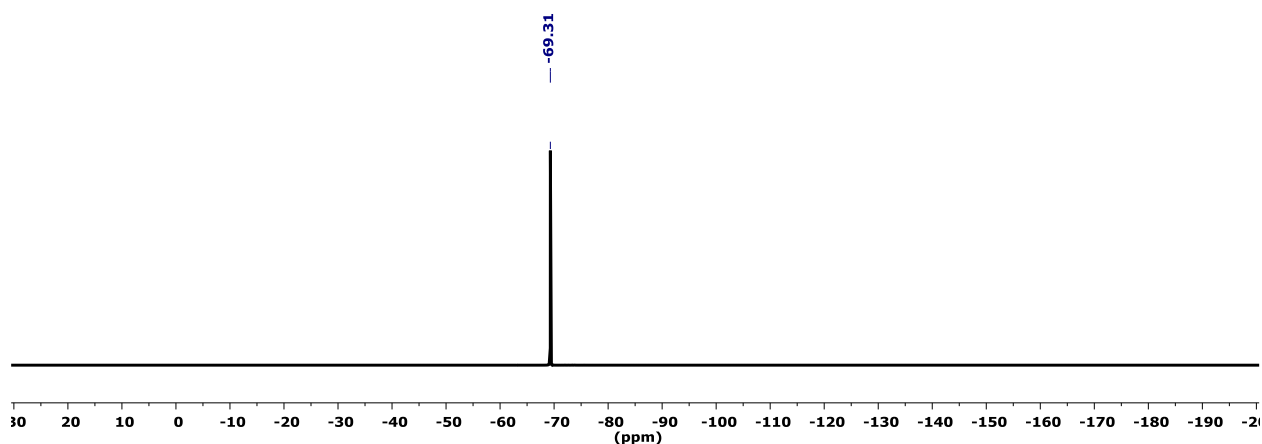


Fig. S62.  $^{19}\text{F}$  NMR Spectrum:



### 1-(*Trans*)-phenylethenyl-1-phenyl-trifluoromethylcarbinol

Substrate: *Trans*-chalcone. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 1.0 equivalents K(LA-CF<sub>3</sub>) used. 0.80 mmol substrate. Reaction time: 10 minutes. Quench: 5% HCl. Chromatography conditions: 0-100% hexane ethyl acetate, 16 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 190 mg colorless oil, 84%.  $^1\text{H-NMR}$  (CDCl<sub>3</sub>): 7.69 ( $\beta$ , 2H, (d,  $J_{\text{H-H}}=7.7$ )), 7.45 ( $\beta$ ,  $\alpha$ , 5H, m), 7.38 ( $\beta$ , 2 H, (t,  $J_{\text{H-H}}=7.4$ )), 7.33 ( $\alpha$ , 1H, (t,  $J_{\text{H-H}}=7.3$ )), 6.91 ( $\gamma$ , 1H, (d,  $J_{\text{H-H}}=16.1$ )), 6.77 ( $\gamma$ , 1H, (d,  $J_{\text{H-H}}=16.1$ )), 2.79 ( $\epsilon$ , 1H, s).  $^{13}\text{C-NMR}$ : 137.40, 135.51, 133.58, 128.84, 128.76, 128.67, 128.41, 126.95, 126.84, 126.46, 125.08(q,  $J_{13\text{C}-19\text{F}}=286$ ), 77.34(q,  $J_{13\text{C}-19\text{F}}=29$ ).  $^{19}\text{F-NMR}$ : -78.46 (s). HRMS (EI<sup>+</sup>): 278.0919(M<sup>+</sup>: 278.0918).

Fig. S63.  $^1\text{H}$  NMR Spectrum:

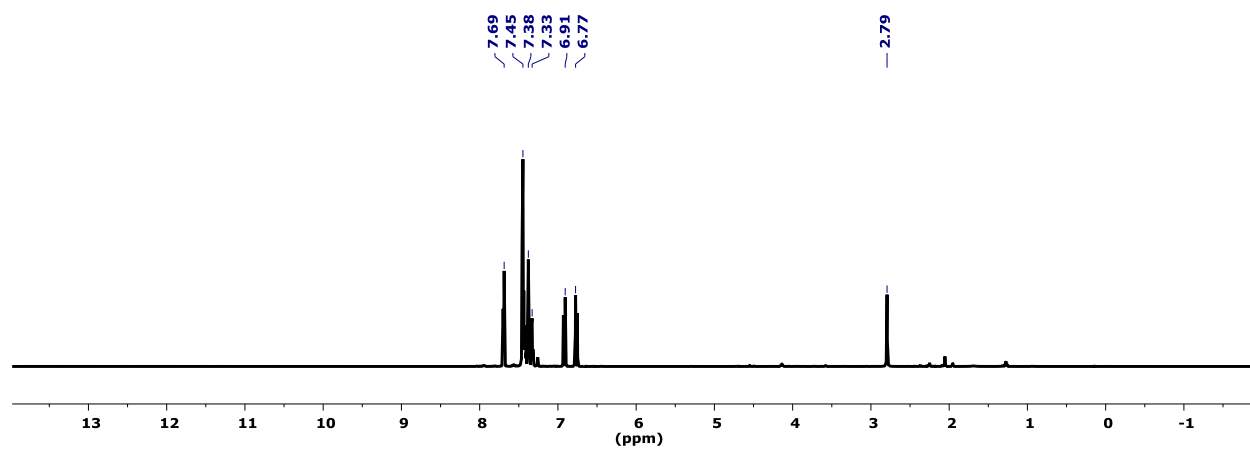


Fig. S64.  $^{13}\text{C}$  NMR Spectrum:

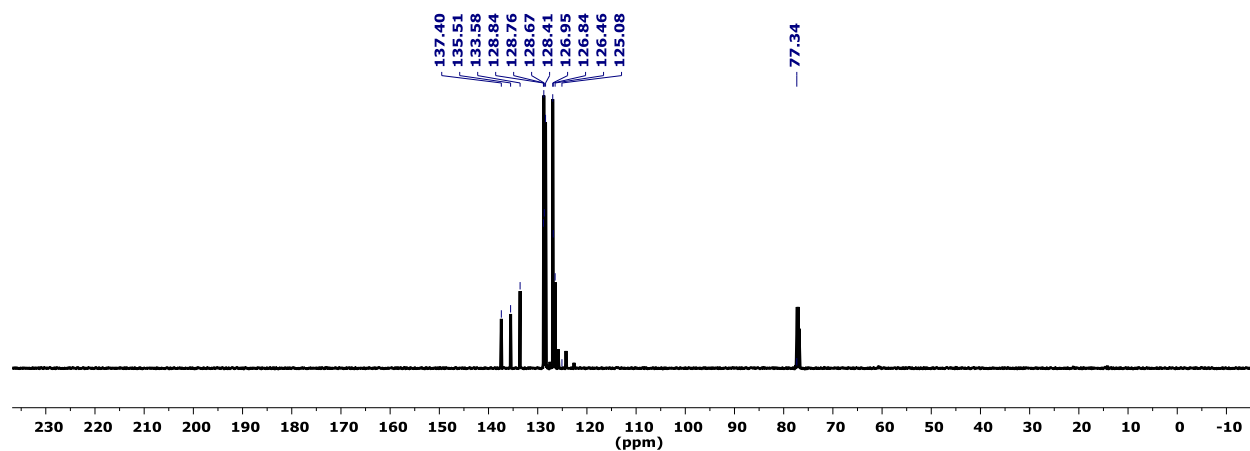
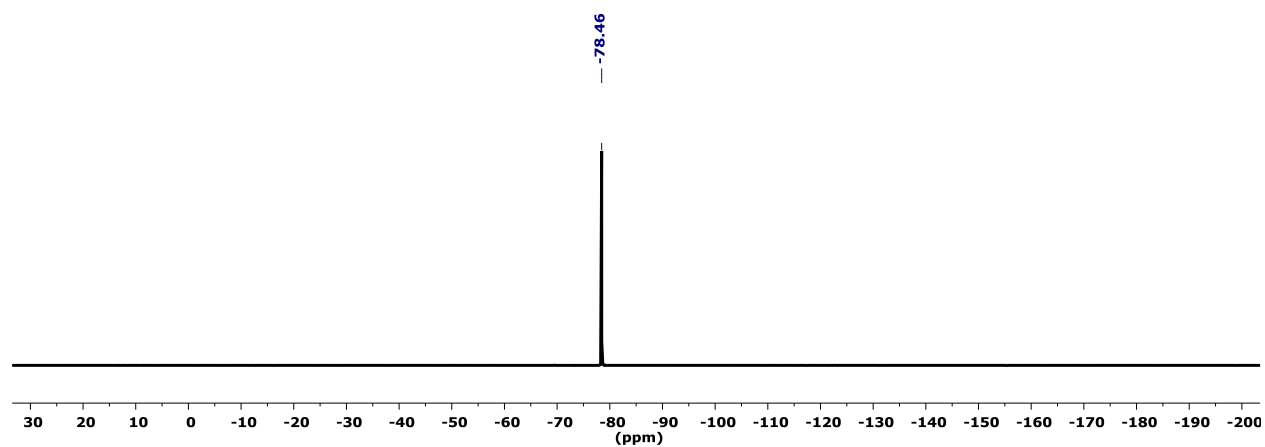
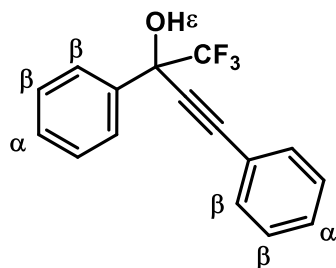


Fig. S65.  $^{19}\text{F}$  NMR Spectrum:





### 1-Phenylethynyl-1-phenyl-trifluoromethylcarbinol

Substrate: Diphenylpropynone. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 1.0 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 16 hours. Quench: saturated NH<sub>4</sub>Cl. Chromatography conditions: 0-30% hexane ethyl acetate, 16 column volumes, 50 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 45 mg orange oil, 42%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.83 (β, 2H, (d, *J*<sub>H-1H</sub>=4.8)), 7.56 (β, 2H, (d, *J*<sub>H-1H</sub>=4.8)), 7.46 (α, β, 3H, m), 7.42 (α, 1H, (p, *J*<sub>H-1H</sub>=7.4)), 7.37 (β, 2H, (t, *J*<sub>H-1H</sub>=7.4)), 3.15 (ε, 1H, s). <sup>13</sup>C-NMR: 135.26, 132.06, 129.55, 129.53, 128.47, 128.25, 127.19, 123.39(q, *J*<sub>13C-19F</sub>=286), 120.93, 88.09, 84.40, 73.36(q, *J*<sub>13C-19F</sub>=33). <sup>19</sup>F-NMR: -80.29 (s). HRMS (ESI-): 275.0683(M-H: 275.0684).

**Fig. S66. <sup>1</sup>H NMR Spectrum:**

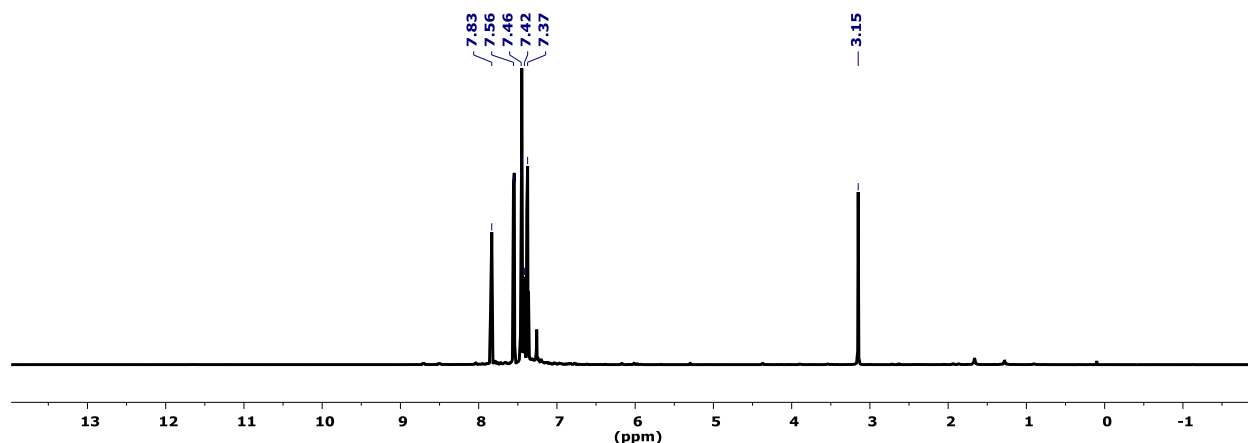


Fig. S67.  $^{13}\text{C}$  NMR Spectrum:

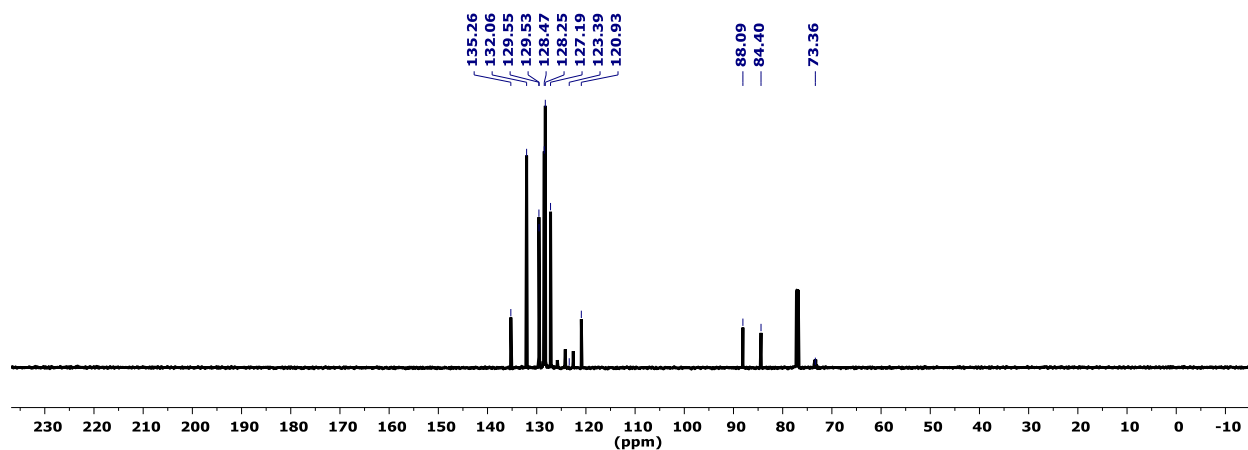
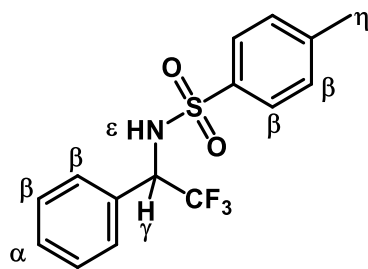
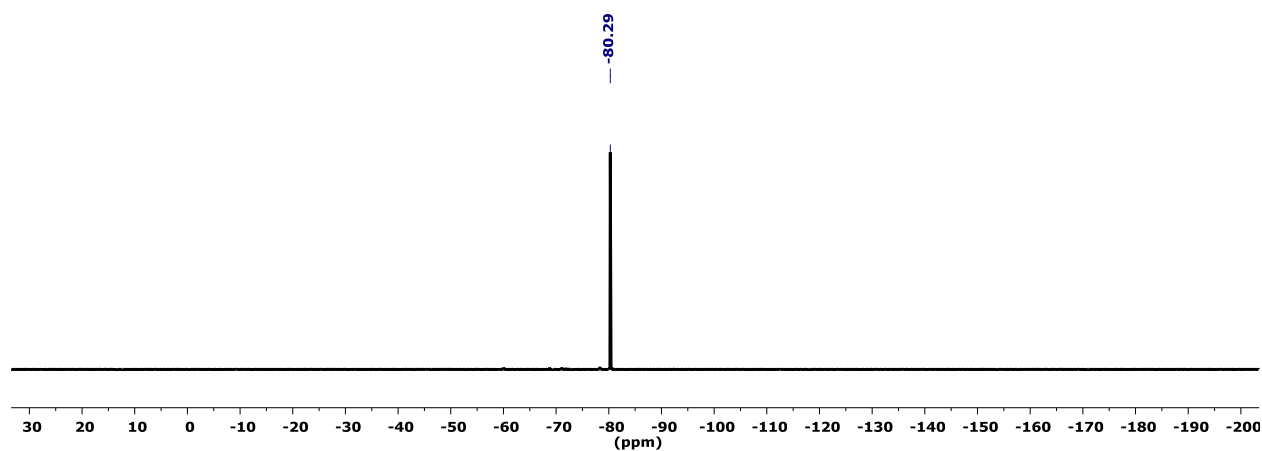


Fig. S68.  $^{19}\text{F}$  NMR Spectrum:



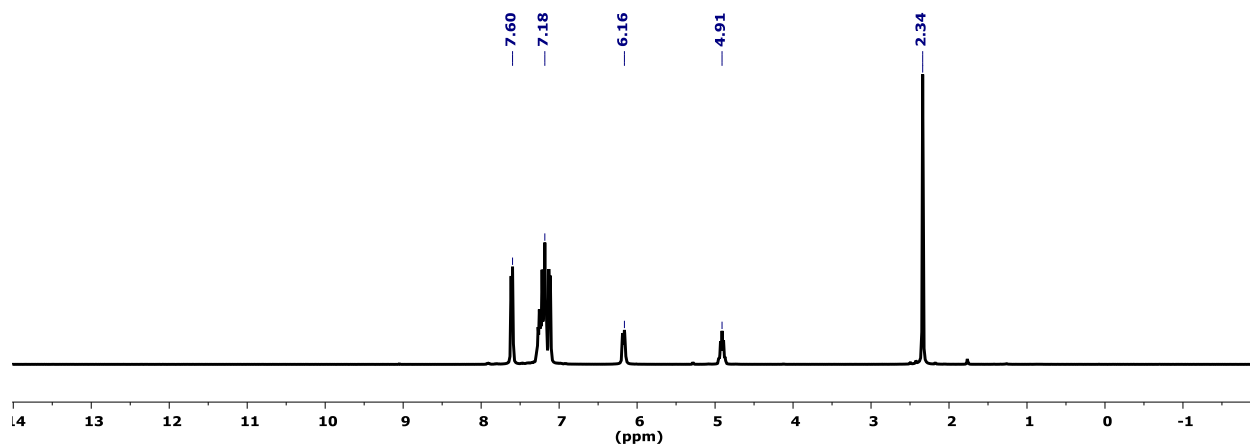
### N-tosyl-1-trifluoromethyl-benzylamine

Substrate: N-tosylbenzaldimine. Conditions: Solvent: DMSO. LA:  $\text{K}(\text{BOCH}_2\text{CH}_2\text{N})_3\text{CF}_3$ . 1.0 equivalent  $\text{K}(\text{LA}-\text{CF}_3)$  used. 0.40 mmol substrate. Reaction time: 1 hours. Quench: saturated  $\text{NH}_4\text{Cl}$ . Chromatography conditions: 0-100% hexane/ $\text{CH}_2\text{Cl}_2$ , then 0-100%  $\text{CH}_2\text{Cl}_2$ /ethyl acetate, 16 column volumes, 25 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 86 mg white solid, 65%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 7.60 ( $\beta$ , 2H, (d,  $J_{\text{H-H}}=8.2$ )), 7.18 ( $\beta$ ,  $\alpha$ , 7H, m), 6.16 ( $\epsilon$ , 1H, (d,  $J_{\text{H-H}}=9.1$ )), 4.91 ( $\gamma$ , 1H, (p,  $J_{\text{H-}^{19}\text{F}}=7.7$ )), 2.34 ( $\eta$ , 3H, s).  $^{13}\text{C}$ -NMR: 143.74, 136.89, 131.79, 129.46, 129.19,

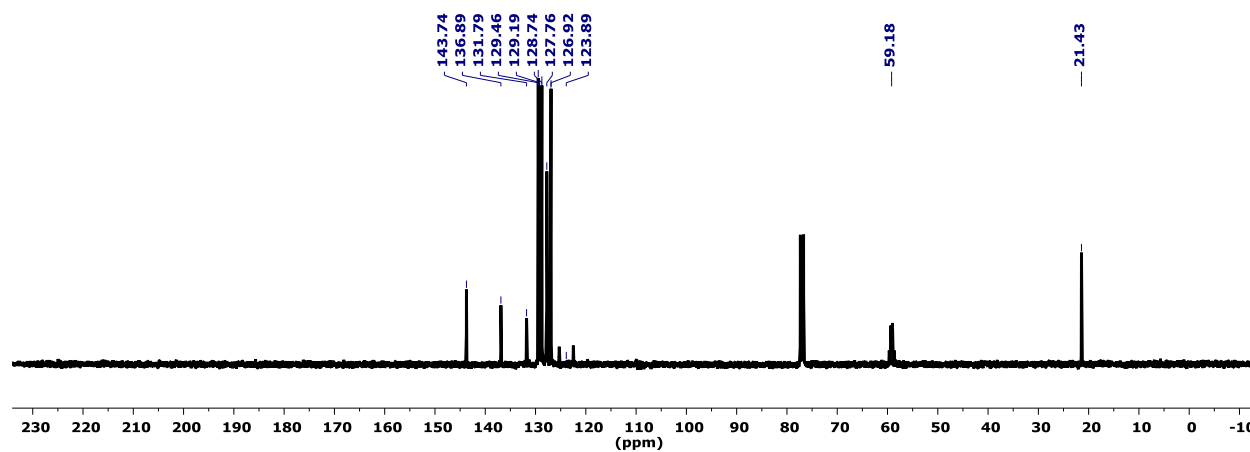


128.74, 127.76, 126.92, 123.89(q,  $J_{13C-19F}=282$ ), 59.18(q,  $J_{13C-19F}=32$ ), 21.43.  $^{19}F$ -NMR: -74.02 (d,  $J_{19F-1H}=7.4$ ). HRMS (ESI-): 328.0624(M-H: 328.0625).

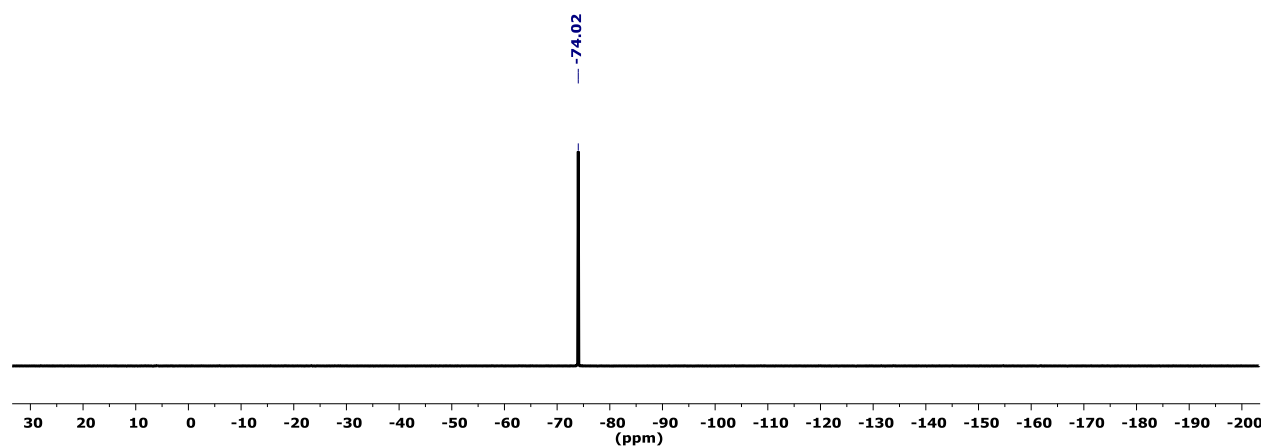
**Fig. S69.  $^1H$  NMR Spectrum:**

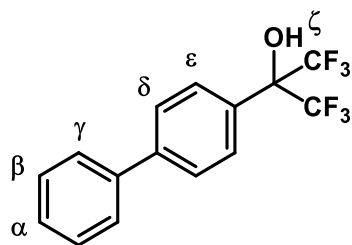


**Fig. S70.  $^{13}C$  NMR Spectrum:**



**Fig. S71.  $^{19}F$  NMR Spectrum:**





### 1,1-bis(trifluoromethyl)-1-(4-phenyl)phenyl-methanol:

Substrate: Biphenyl-4-carbonyl chloride. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 2.2 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 16 hours. Quench: 5% HCl. Chromatography conditions: 0-20% Hexane/Ethyl acetate, 8 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 107 mg white solid, 84%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.82 (ε, 2H, (d, *J*<sub>H-H</sub>=8.1)), 7.71 (δ, 2H, (d, *J*<sub>H-H</sub>=8.2)), 7.64 (γ, 2H, (d, *J*<sub>H-H</sub>=7.8)), 7.49 (β, 2H, (t, *J*<sub>H-H</sub>=7.5)), 7.41 (α, 1H, (t, *J*<sub>H-H</sub>=7.3)), 3.38 (ζ, 1H, s). <sup>13</sup>C-NMR: 143.16, 139.88, 128.90, 128.06, 127.94, 127.30, 127.20, 126.94, 122.65 (q, *J*<sub>13C-19F</sub>=288), 77.18 (p, *J*<sub>13C-19F</sub>=30.3) (overlap with CDCl<sub>3</sub>). <sup>19</sup>F-NMR: -75.58 (s). HRMS (ES<sup>+</sup>): 320.0636 (M-C<sub>3</sub>H<sub>7</sub><sup>+</sup>: 320.0636).

Fig. S72. <sup>1</sup>H NMR Spectrum:

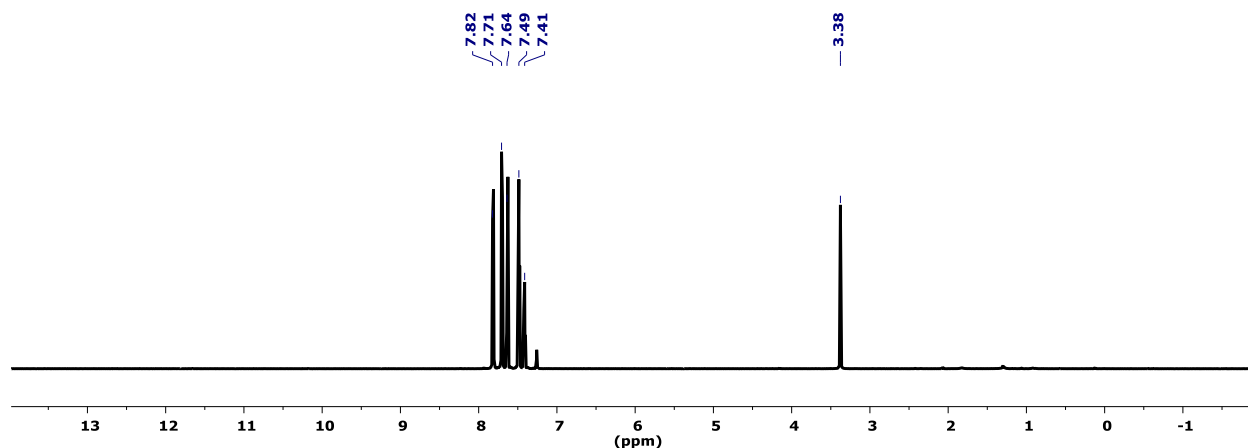


Fig. S73. <sup>13</sup>C NMR Spectrum:

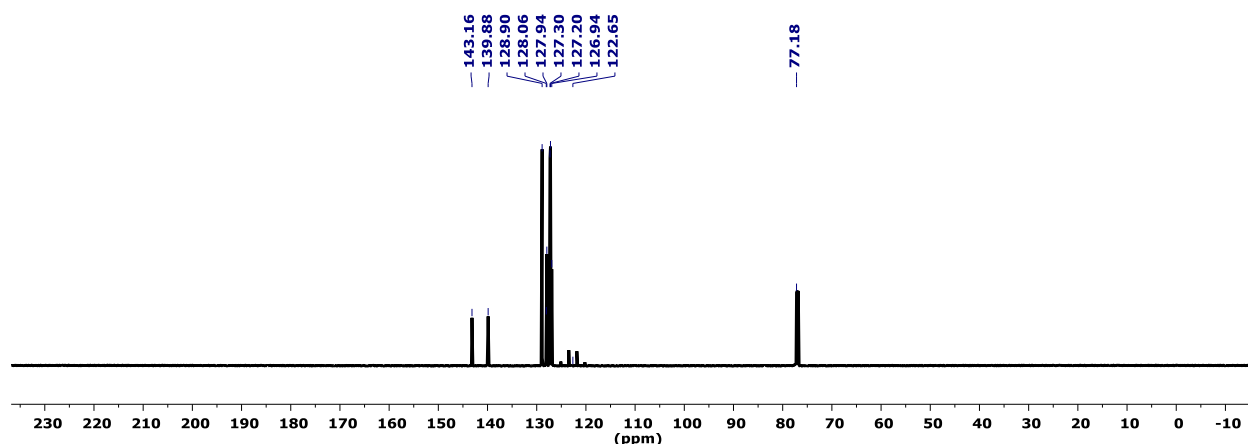


Fig. S74.  $^{19}\text{F}$  NMR Spectrum:

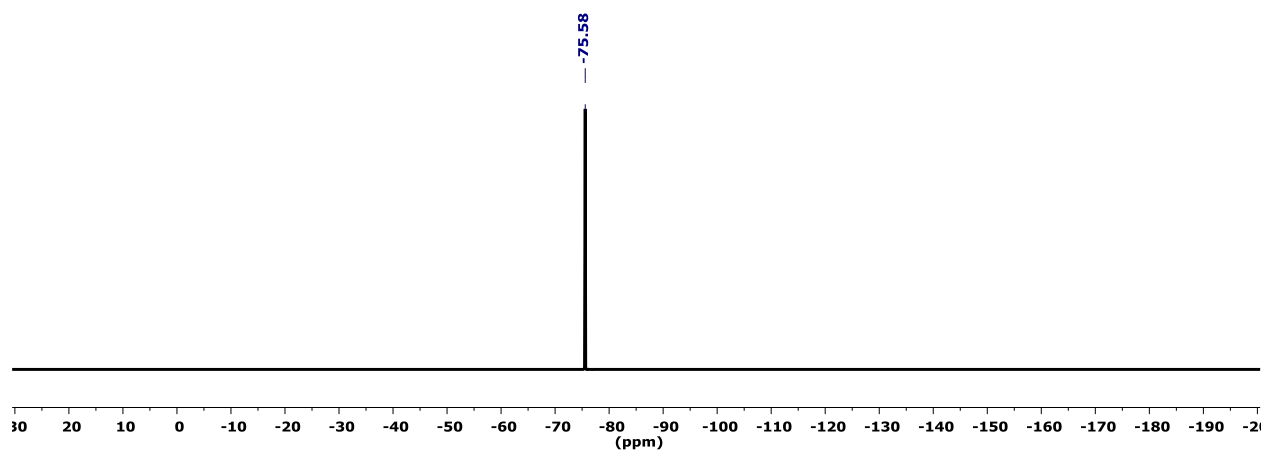


Fig. S75.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:

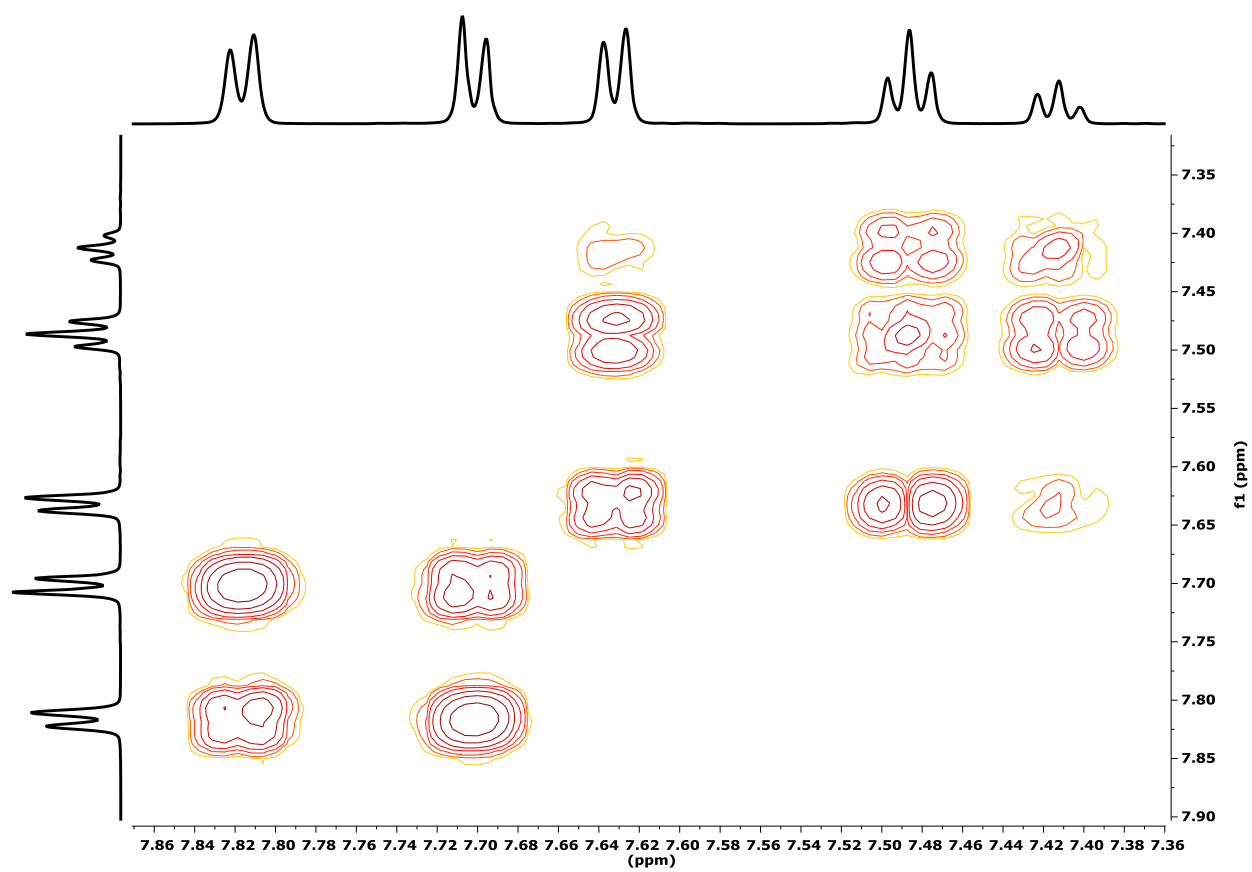


Fig. S76.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

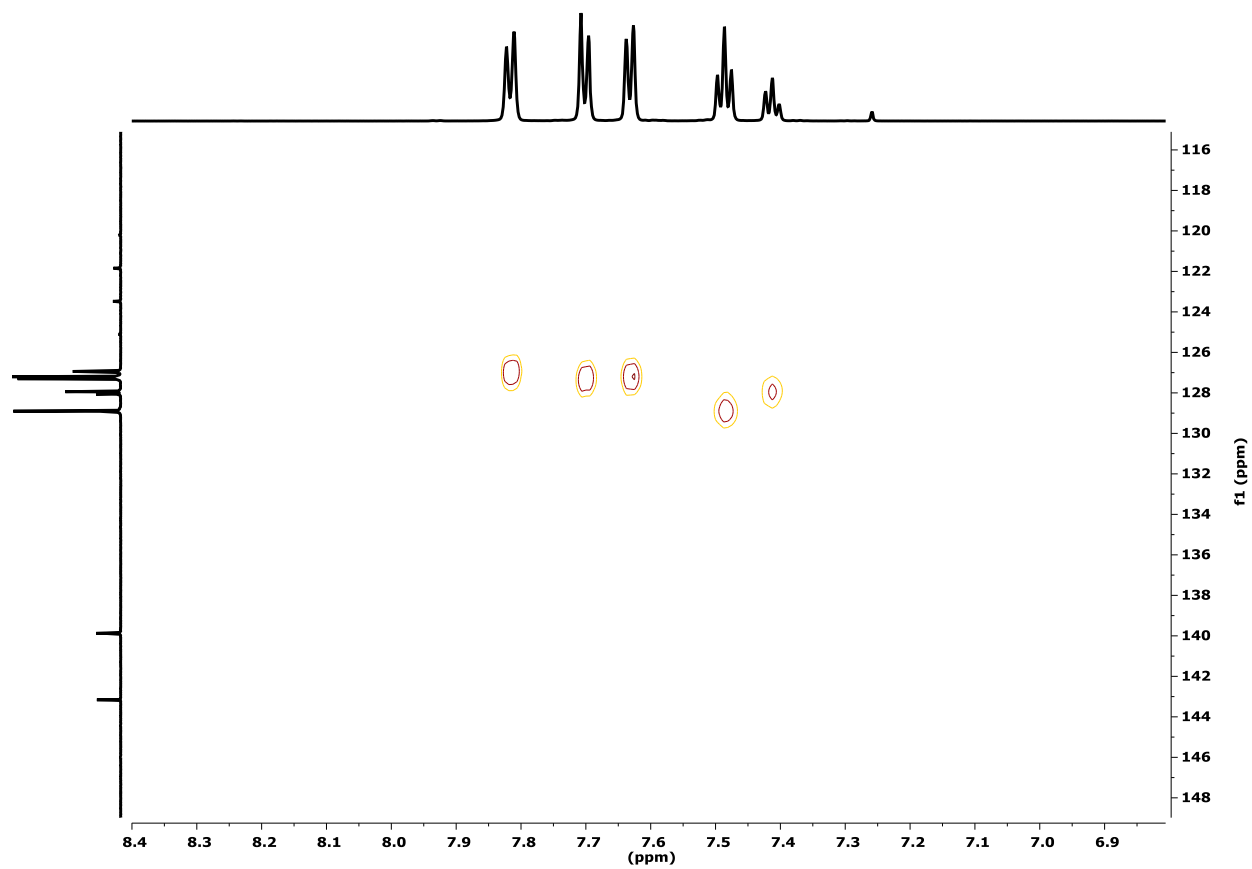


Fig. S77.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:

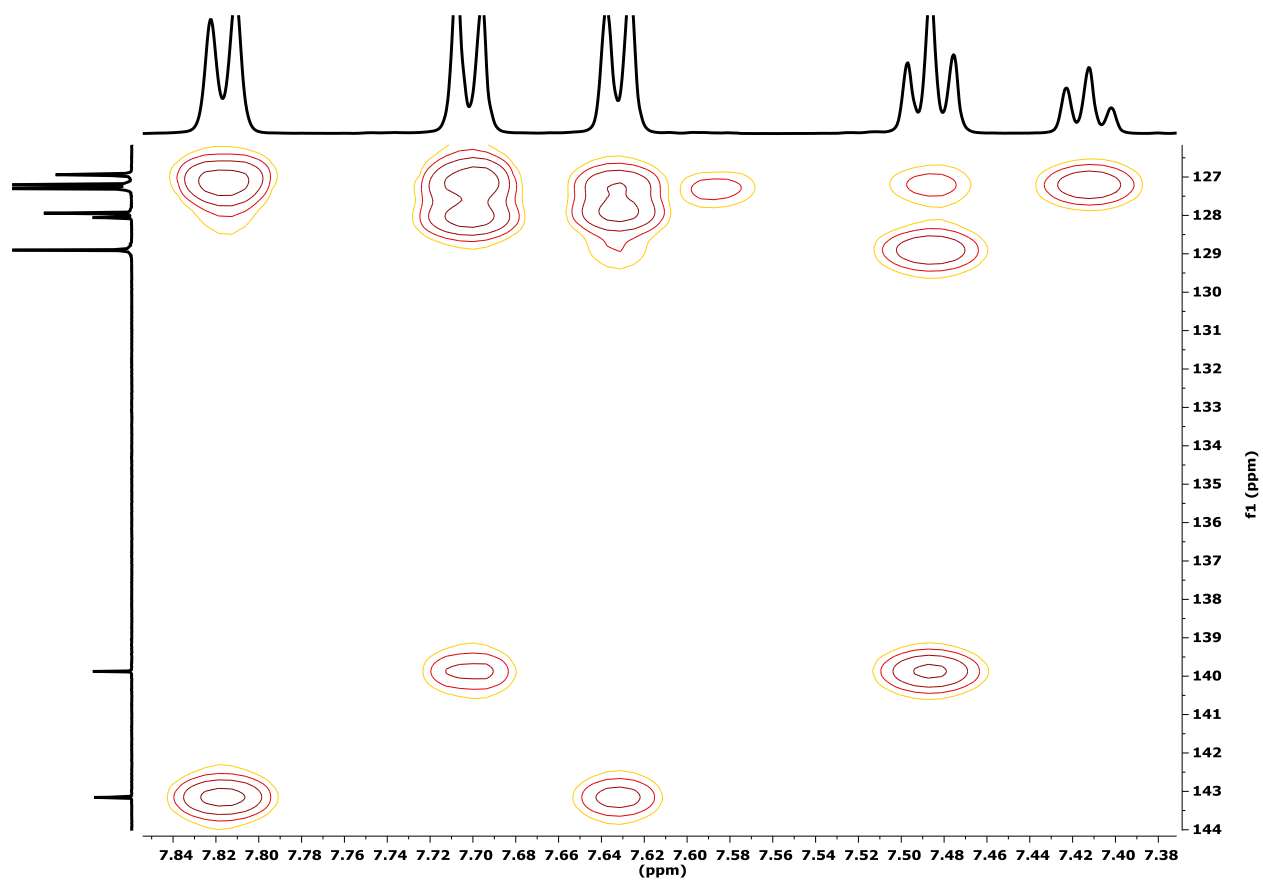


Fig. S78.  $^{19}\text{F}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

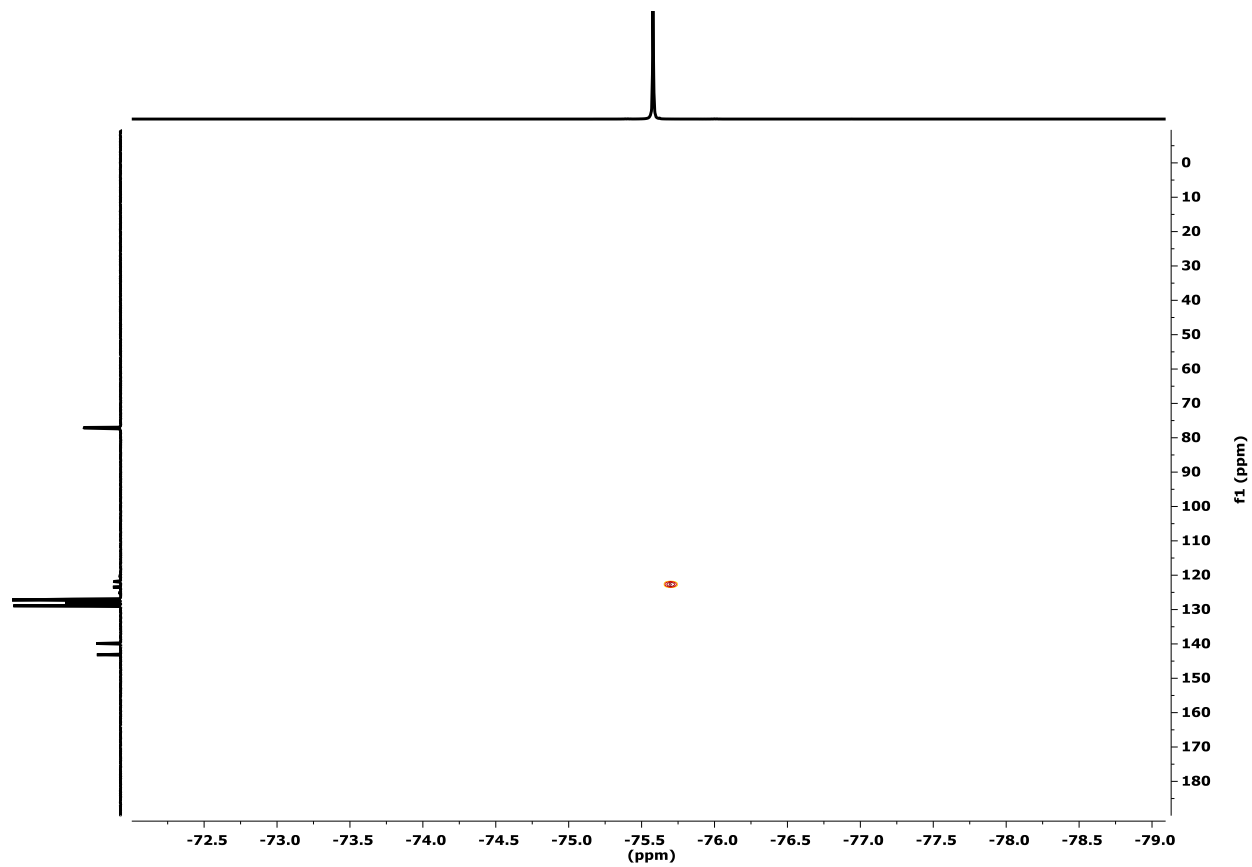
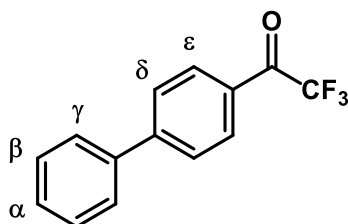
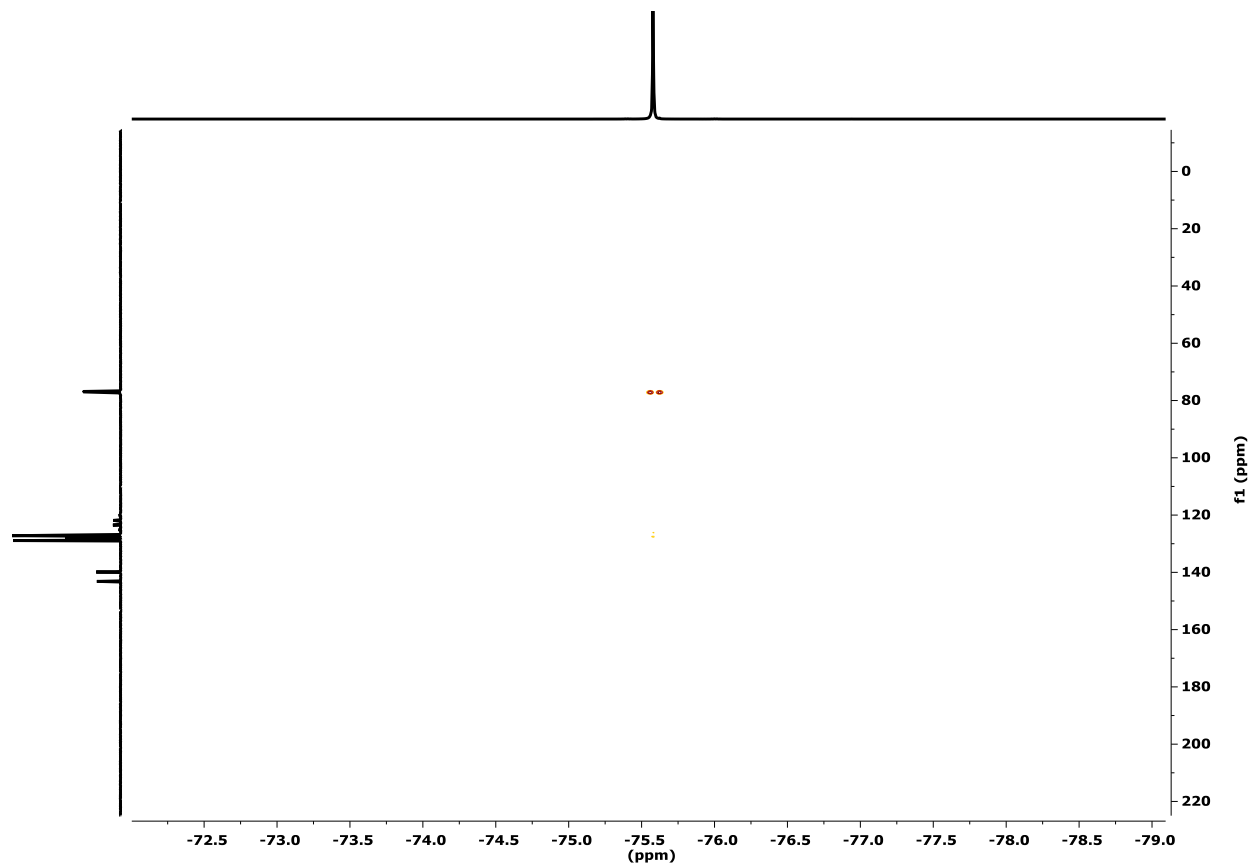


Fig. S79.  $^{19}\text{F}$ - $^{13}\text{C}$  gHMBCAD Spectrum:



**Trifluoromethyl-(4-phenyl)phenyl Ketone:**

Substrate: Methyl biphenyl-4-carboxylate. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 1.0 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 30 minutes. Quench: 5% HCl. Chromatography conditions: 0-100% Hexane/Ethyl acetate, 8 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 29 mg white solid, 29%.  $^1\text{H}$ -NMR (CDCl<sub>3</sub>): 8.17 (ε, 2H, (d,  $J_{\text{H-H}}=8.0$ )), 7.78 (δ, 2H, (d,  $J_{\text{H-H}}=8.4$ )), 7.66 (γ, 2H, (d,  $J_{\text{H-H}}=7.1$ )), 7.51 (β, 2H, (t,  $J_{\text{H-H}}=7.6$ )), 7.45 (α, 1H, (t,  $J_{\text{H-H}}=7.4$ )).  $^{13}\text{C}$ -NMR: 180.07 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=35.0$ ), 148.21, 139.11, 130.72, 129.11, 128.89, 128.56, 127.63, 127.34, 116.76 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=291$ ),  $^{19}\text{F}$ -NMR: -71.35 (s). HRMS (ES<sup>+</sup>): 250.0611 (M<sup>+</sup>: 250.0605).

Fig. S80.  $^1\text{H}$  NMR Spectrum:

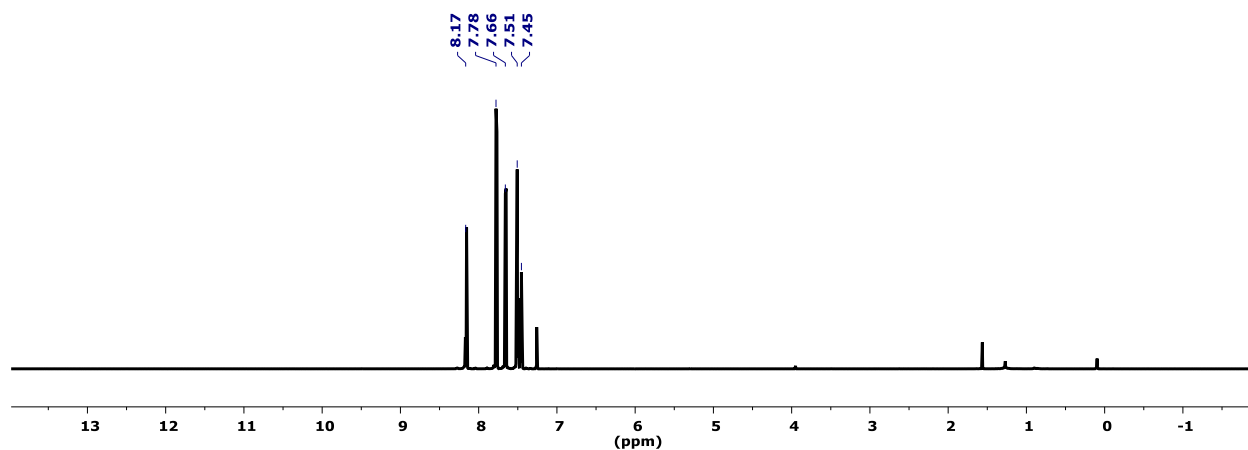


Fig. S81.  $^{13}\text{C}$  NMR Spectrum:

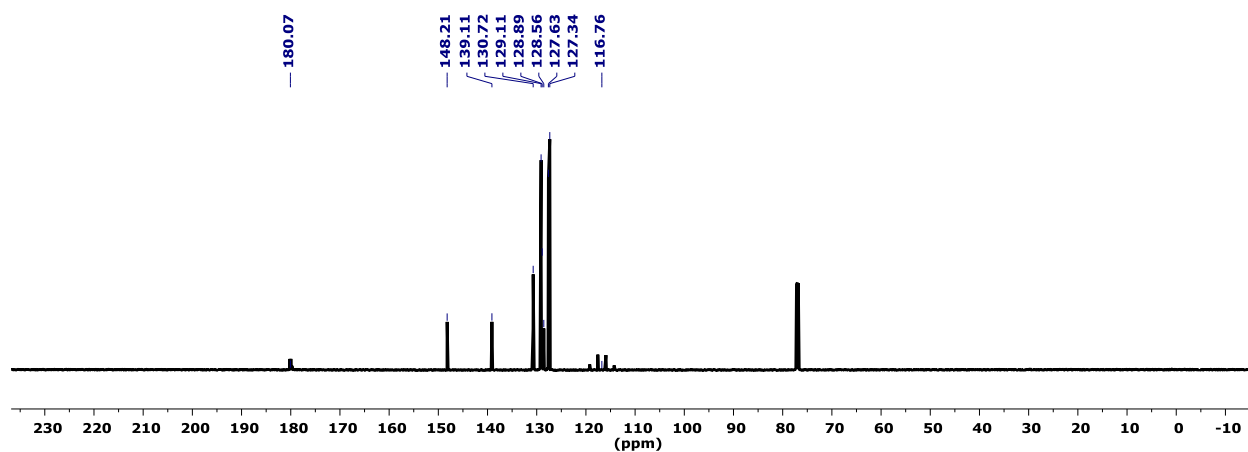
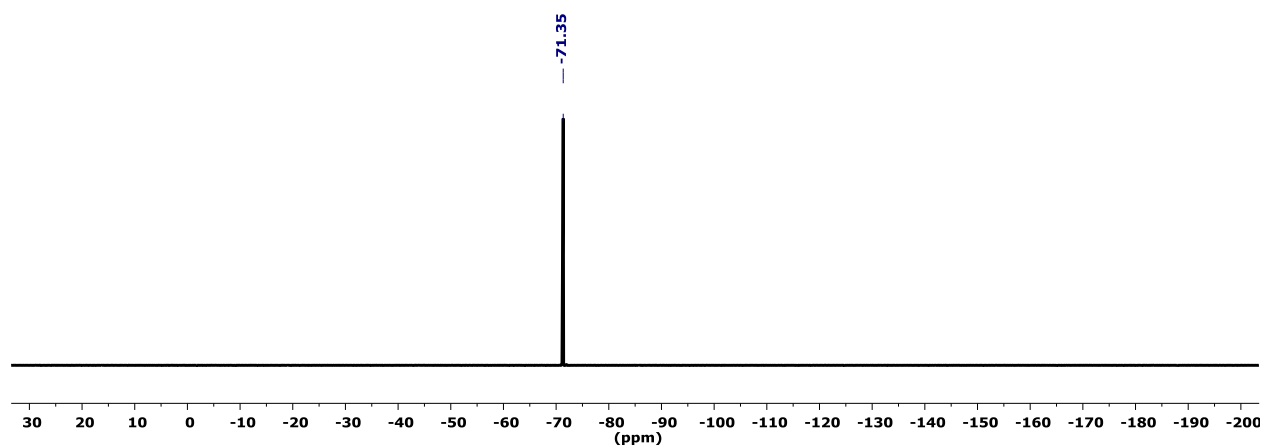
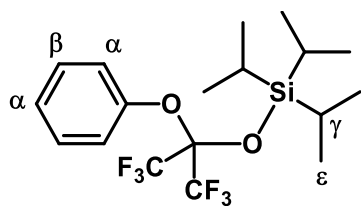


Fig. S82.  $^{19}\text{F}$  NMR Spectrum:







### Triisopropylsilyl Hexafluoro-2-phenoxypropan-2-ol

Substrate: Diphenylcarbonate. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 2.0 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 30 minutes. Quench: 2.0 equivalents triisopropylsilyl chloride were added, then the reaction stirred for 16 hours at 25 °C. The reaction mixture was then quenched with 10 mL water. Chromatography conditions: 100% Hexane, 4 column volumes, 100 g SiO<sub>2</sub>, flow rate 0.5 column volume per minute; chromatography was repeated six times to remove triisopropylsilyl phenol. 102 mg colorless oil, 61%. Boiling point: 65 °C at 0.080 Torr. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.32 (β, 2H, (t, *J*<sub>1H-1H</sub>=8.4)), 7.19 (α, 3H, m), 1.14 (γ, 3H, m), 1.05 (ε, 18H, (d, *J*<sub>1H-1H</sub>=7.2)). <sup>13</sup>C-NMR: 151.46, 129.07, 125.80, 123.58, 120.73(q, *J*<sub>13C-19F</sub>=293), 95.20 (p, *J*<sub>13C-19F</sub>=32.8), 17.43, 13.07. <sup>19</sup>F-NMR: -76.97 (s). HRMS (ES<sup>+</sup>): 373.1061 (M-C<sub>3</sub>H<sub>7</sub><sup>+</sup>: 373.1059).

**Fig. S83. <sup>1</sup>H NMR Spectrum:**

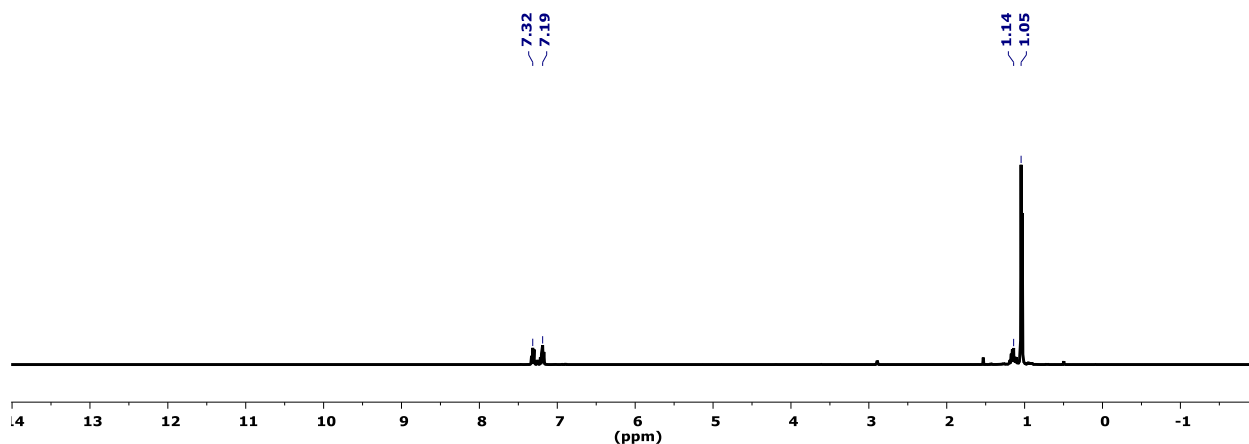


Fig. S84.  $^{13}\text{C}$  NMR Spectrum:

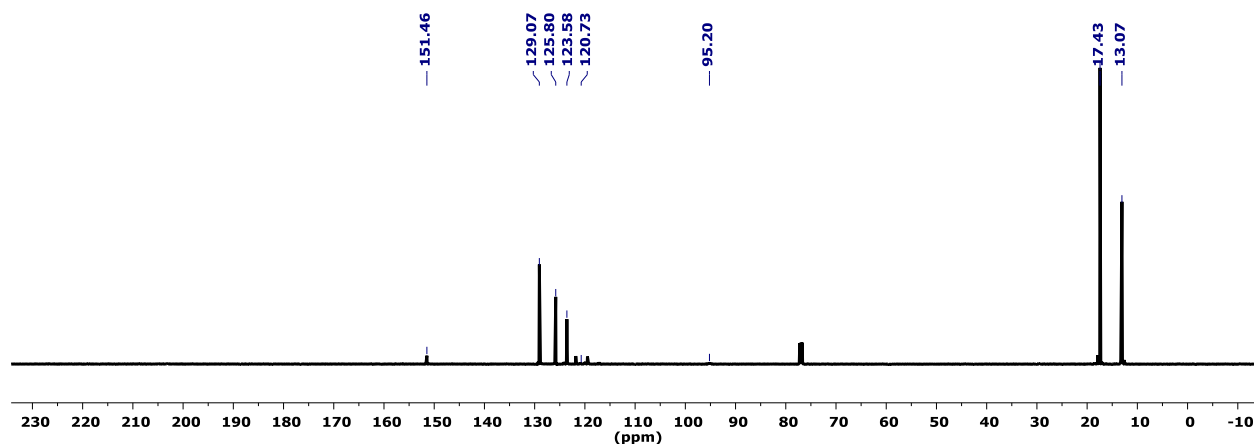
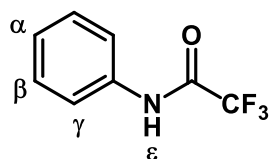
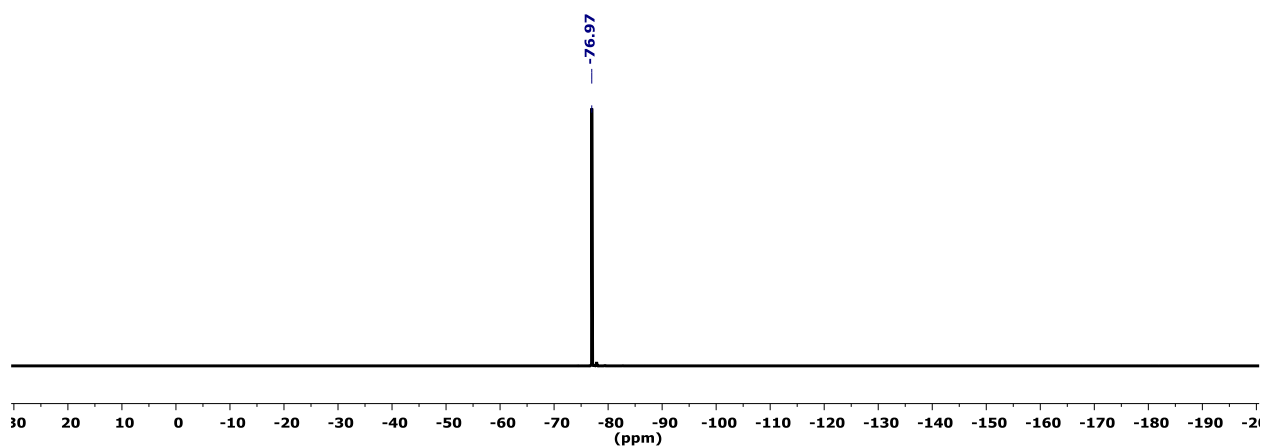


Fig. S85.  $^{19}\text{F}$  NMR Spectrum:



### Phenyl trifluoroacetamide

Substrate: Phenyl isocyanate. Conditions: Solvent: THF. LA: K(18-crown-6)( $\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3$ )(THF). 1.0 equivalents K(LA- $\text{CF}_3$ ) used. 0.80 mmol substrate. Reaction time: 1 hour. Quench: 5% HCl. Chromatography conditions: 10-50% hexane/ $\text{CH}_2\text{Cl}_2$ , 8 column volumes, 25 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 91 mg white solid, 61%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 8.03 ( $\epsilon$ , 1H, s), 7.54 ( $\gamma$ , 2H, (d,  $J_{\text{H-H}}=7.7$ )), 7.46 ( $\beta$ , 2H, (t,  $J_{\text{H-H}}=8.0$ ), 7.23 ( $\alpha$ , 1H, (t,  $J_{\text{H-H}}=7.4$ )).  $^{13}\text{C}$ -NMR: 154.87(q,  $J_{^{13}\text{C}-^{19}\text{F}}=37$ ), 135.04, 129.33, 126.39, 120.56, 115.72(q,  $J_{^{13}\text{C}-^{19}\text{F}}=288$ ).  $^{19}\text{F}$ -NMR: -75.80 (s). HRMS (ES $^+$ ): 189.0401 ( $\text{M}^+$ : 189.0401).

Fig. S86.  $^1\text{H}$  NMR Spectrum:

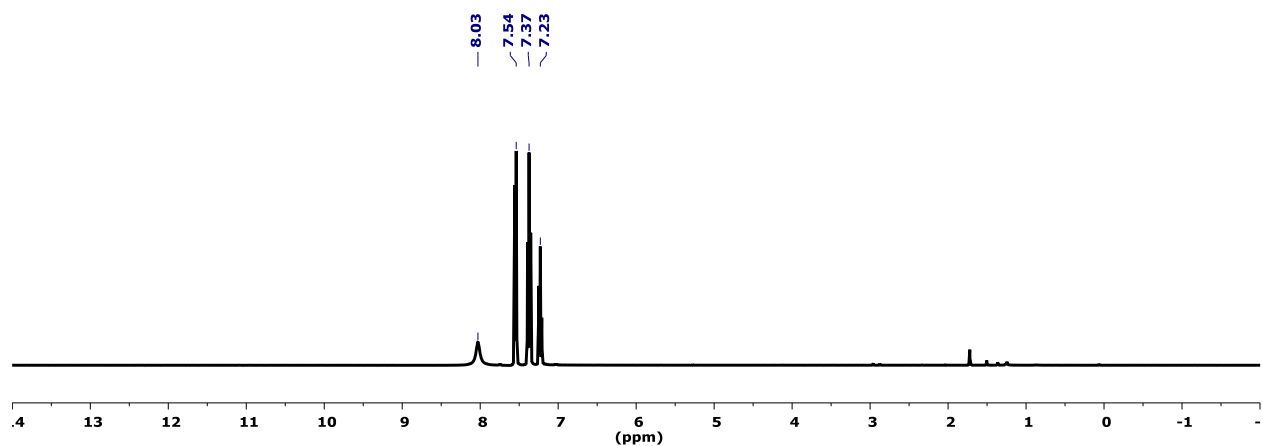


Fig. S87.  $^{13}\text{C}$  NMR Spectrum:

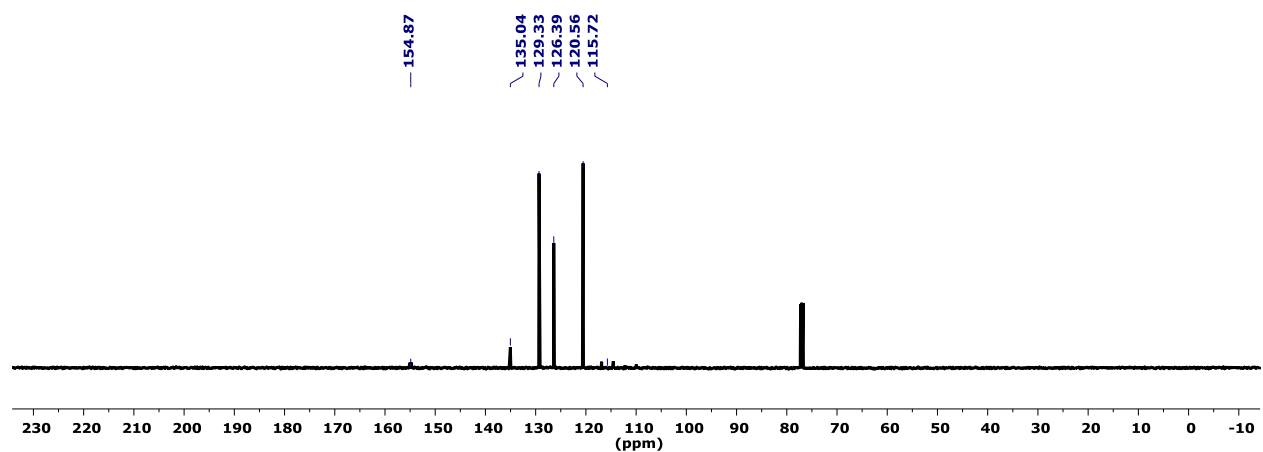
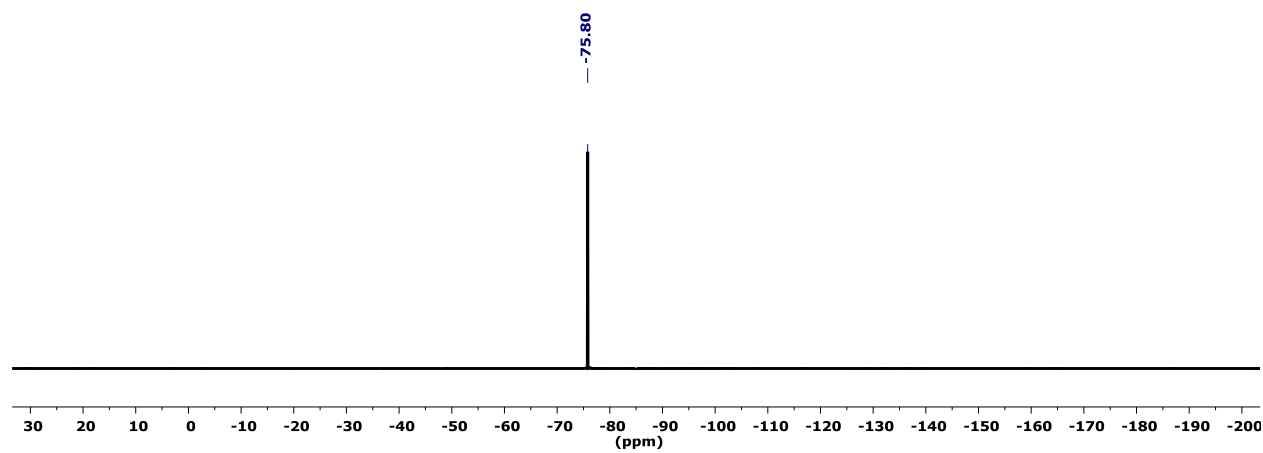
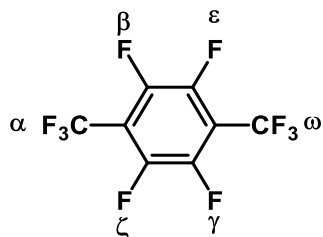


Fig. S88.  $^{19}\text{F}$  NMR Spectrum:



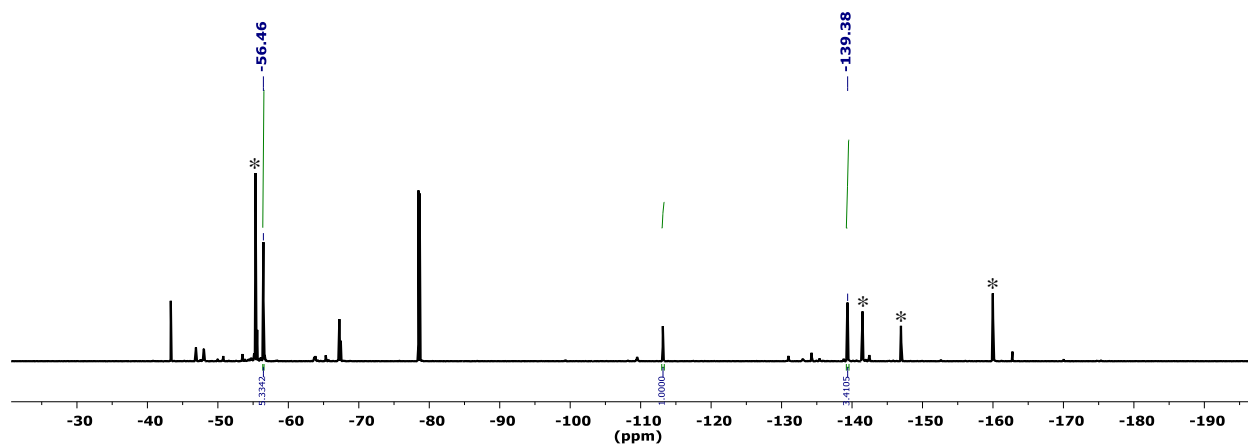
## Nucleophilic Aromatic Substitution



### Perfluoro-*p*-xylene

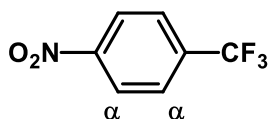
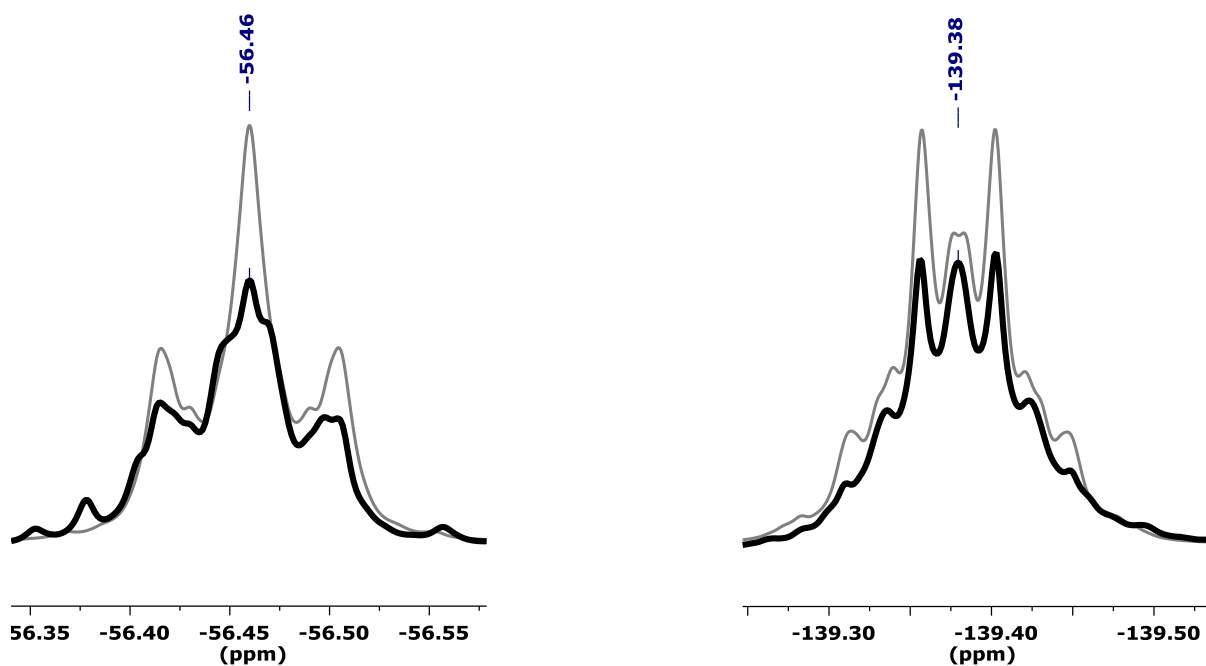
Substrate: Perfluorotoluene. Conditions: Solvent: THF. LA:  $\text{K}(\text{18-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$ . 1.0 equivalents  $\text{K}(\text{LA-CF}_3)$  used. 0.10 mmol substrate. Reaction time: 10 min. Quench: water. Characterized *in-situ*; yield determined by  $^{19}\text{F}$ -NMR spectroscopy and integrated against 0.030 mmol fluorobenzene. The product spectrum closely matched the literature chemical shifts and  $^{19}\text{F}$ - $^{19}\text{F}$  coupling constants. Because of highly complex coupling, spin simulation in MestReNova was performed using the literature coupling constants to provide comparison with the experimental *in-situ* spectrum. (Literature  $^{19}\text{F}$ -NMR (solvent not specified):  $-57.6$  ( $J_{^{19}\text{F}-^{19}\text{F}} = 22.7$  ( $\alpha$ -( $\beta/\zeta$ ),  $\omega$ -( $\epsilon/\gamma$ )),  $0.4$  ( $\alpha$ -( $\epsilon/\gamma$ ),  $\omega$ -( $\beta/\zeta$ )),  $-138.9$  ( $J_{^{19}\text{F}-^{19}\text{F}} = 18.6$  ( $\beta$ - $\epsilon$ ,  $\zeta$ - $\gamma$ ),  $13.2$  ( $\beta$ - $\gamma$ ,  $\zeta$ - $\epsilon$ ))).<sup>[28]</sup> Chemical yield: 27%. *In-Situ*  $^{19}\text{F}$ -NMR:  $-56.46$  ( $\alpha$ ,  $\omega$  6F, m),  $-139.38$  ( $\beta$ ,  $\epsilon$ ,  $\gamma$ ,  $\zeta$ , 4F, m)

Fig. S89.  $^{19}\text{F}$  NMR Spectrum:



\*: Perfluorotoluene

**Fig. S90. Superimposed Simulated (gray; from literature J-couplings) and Experimental (black; from *in-situ* generation of perfluoro-*p*-xylene) <sup>19</sup>F NMR Spectra for -CF<sub>3</sub> and -F Peaks:**



### 1-Trifluoromethyl-4-nitrobenzene

Substrate: 1,4-Dinitrobenzene. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 1.0 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 2 hour. Quench: water. Chromatography conditions: 0-100% Hexane/CH<sub>2</sub>Cl<sub>2</sub>, 8 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 64 mg white solid, 42%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.34 (α, 2H, (d, *J*<sub>1H-1H</sub>=8.4)), 7.84 (α, 2H, (d, *J*<sub>1H-1H</sub>=8.5)). <sup>13</sup>C-NMR: 150.00, 136.06 (q, *J*<sub>13C-19F</sub>=33), 126.77 (q, *J*<sub>13C-19F</sub>=3), 124.07, 122.94(q, *J*<sub>13C-19F</sub>=273), 73.36(q, *J*<sub>13C-19F</sub>=33). <sup>19</sup>F-NMR: -63.19 (s). HRMS (ES<sup>+</sup>): 191.0195 (M<sup>+</sup>: 191.0194).

Fig. S91.  $^1\text{H}$  NMR Spectrum:

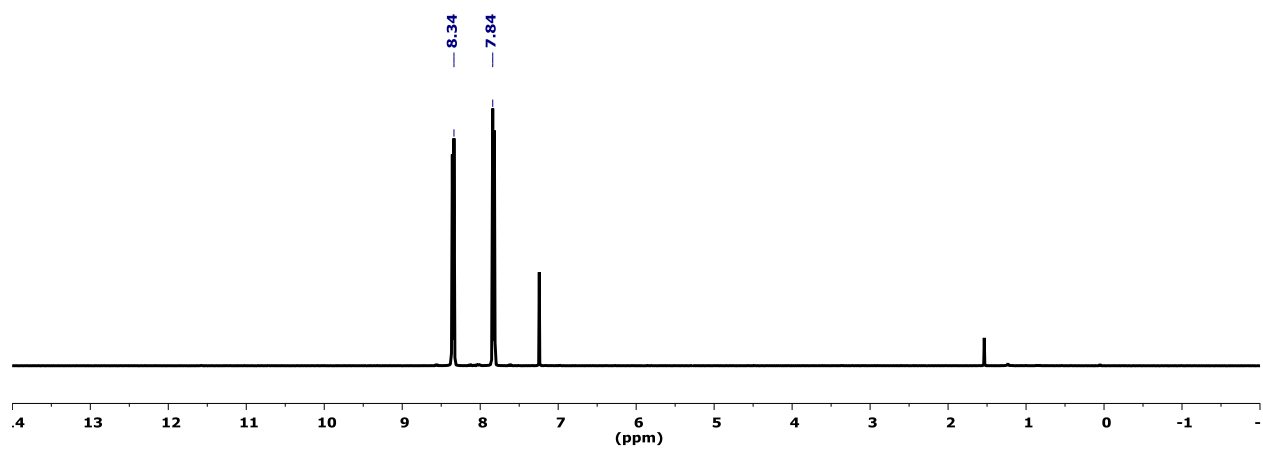


Fig. S92.  $^{13}\text{C}$  NMR Spectrum:

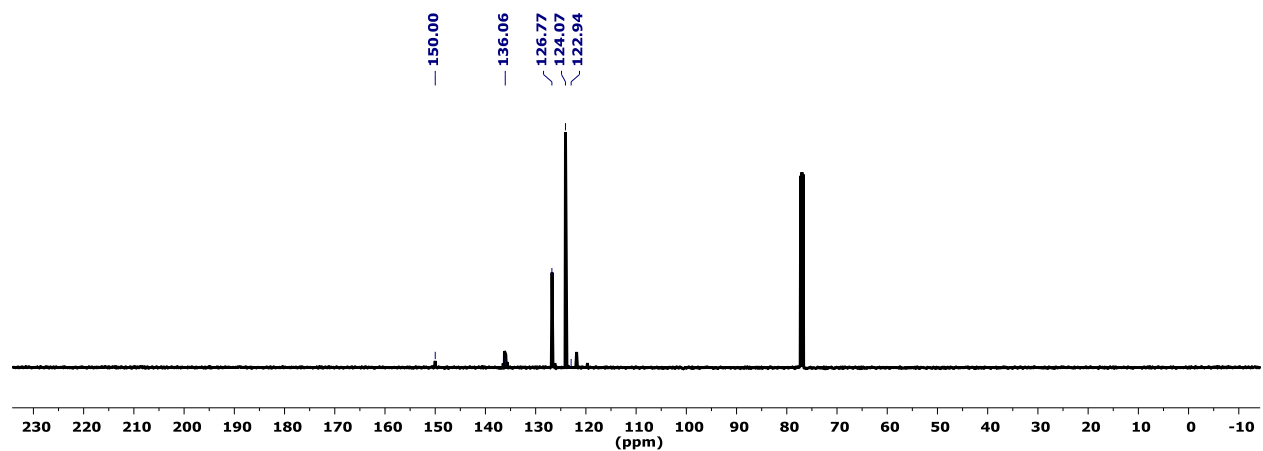
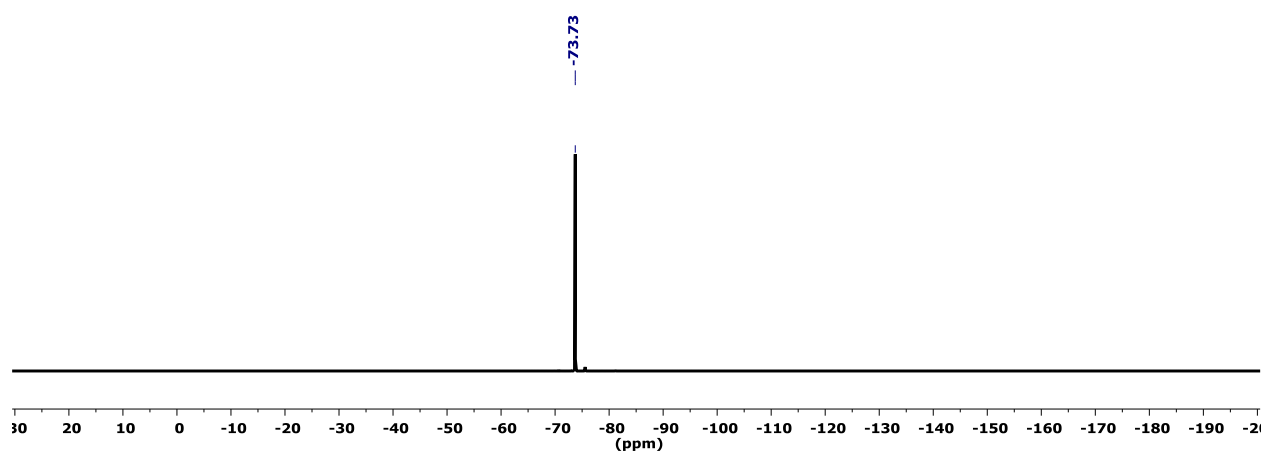
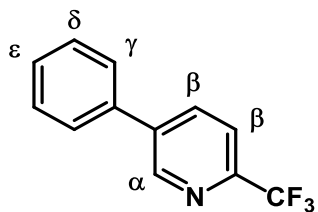


Fig. S93.  $^{19}\text{F}$  NMR Spectrum:





### 5-Phenyl-2-Trifluoromethylpyridine:

Substrate: 5-Phenyl-2-nitropyridine. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 1.0 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 2 hours. Quench: 10 mL water. Chromatography conditions: 0-30% Hexane/Ethyl acetate, 8 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 30 mg white solid, 33%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.94 (α, 1H, s), 8.04 (β, 1H, (d, *J*<sub>1H-1H</sub>=8.1)), 7.76 (β, 1H, (d, *J*<sub>1H-1H</sub>=8.1)), 7.60 (γ, 2H, (d, *J*<sub>1H-1H</sub>=8.1)), 7.53 (δ, 2H, (t, *J*<sub>1H-1H</sub>=8.1)), 7.46 (ε, 1H, (t, *J*<sub>1H-1H</sub>=6.8)). <sup>13</sup>C-NMR: 148.46, 146.77 (q, *J*<sub>13C-19F</sub>=34.7), 139.48, 136.35, 135.48, 129.32, 129.00, 127.33, 121.69 (q, *J*<sub>13C-19F</sub>=273), 120.43 (q, *J*<sub>13C-19F</sub>=2.7). <sup>19</sup>F-NMR: -71.38 (s). HRMS (ESI<sup>+</sup>): 224.0679 (M+H: 224.0682).

Fig. S94. <sup>1</sup>H NMR Spectrum:

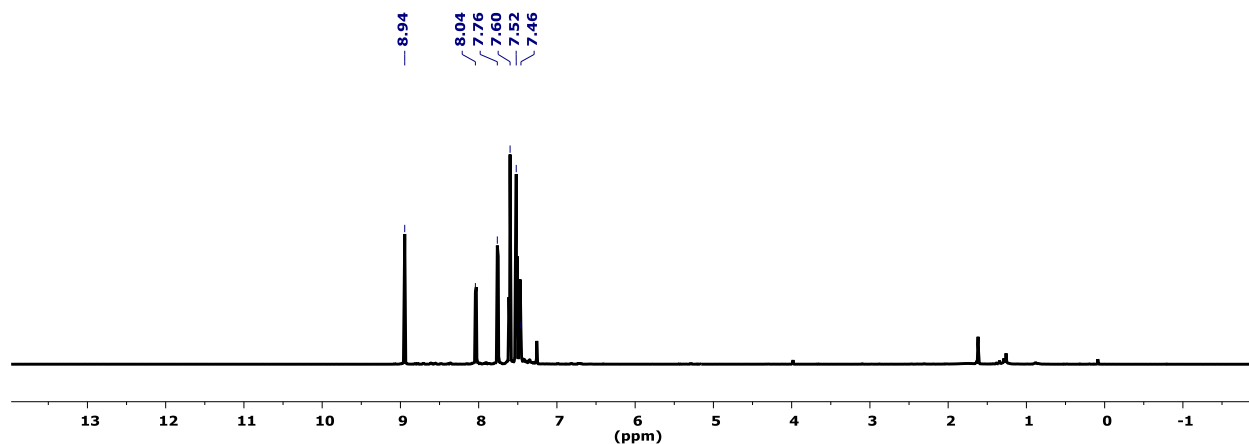


Fig. S95. <sup>13</sup>C NMR Spectrum:

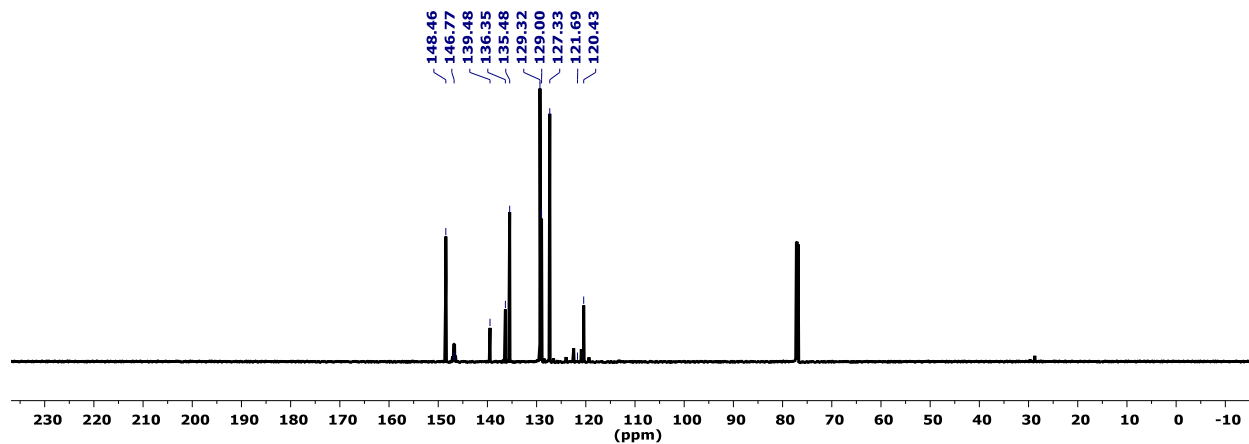
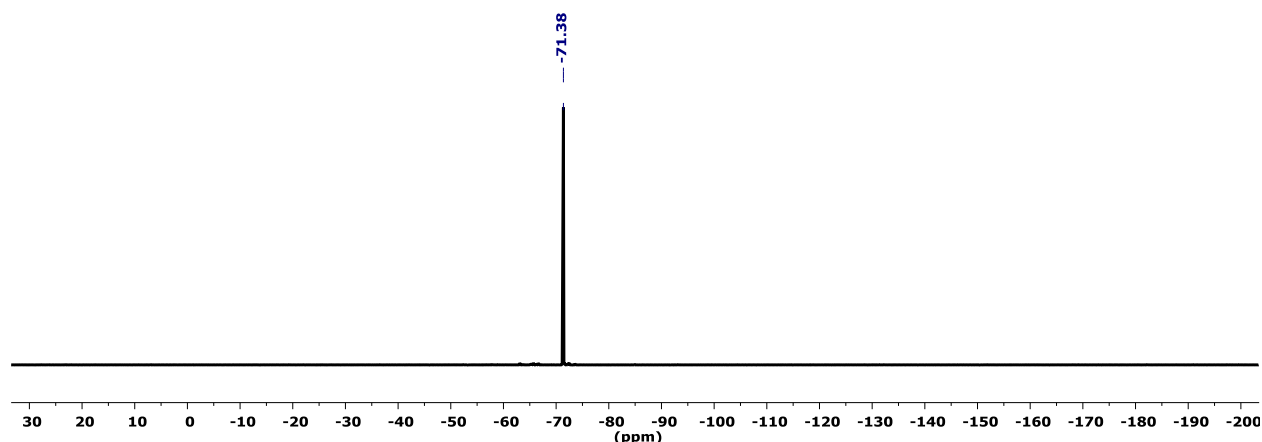
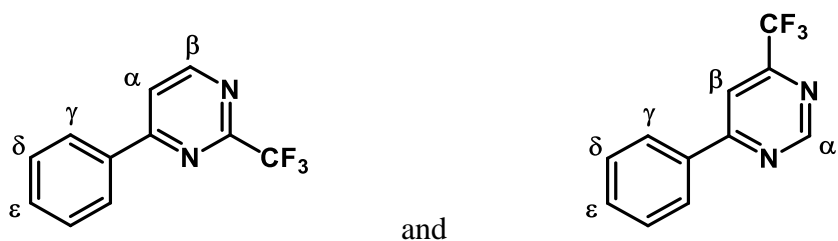


Fig. S96. <sup>19</sup>F NMR Spectrum:



### Direct Nucleophilic Addition/Oxidation



### 6-Phenyl-(2-/4-)trifluoromethylpyrimidine:

6-Phenylpyrimidine (93.7 mg, 0.600 mmol) was dissolved in 3 mL THF. K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF) (3.00 mL, 0.2 M in THF, 0.600 mmol) was then added. After 72 hours, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (135 mg, 0.600 mmol) was added and the mixture stirred for five minutes. NMR spectra showed a mixture of two trifluoromethylated products. The reaction mixture was quenched with water. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 x 2 mL), the CH<sub>2</sub>Cl<sub>2</sub> extract was dried and concentrated, and the crude oil was purified by flash silica chromatography. Chromatography conditions: 0-40% Hexane/DCM, 12 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. Chromatography afforded separated -2 and -4 substituted products. 6-Phenyl-2-trifluoromethylpyrimidine: 9.2 mg white solid, 7%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.91 (β, 1H, (d, *J*<sub>1H-1H</sub>=5.3)), 8.17 (γ, 2H, (dd, *J*<sub>1H-1H</sub>=8.1, 1.4)), 7.88 (α, 1H, (d, *J*<sub>1H-1H</sub>=5.3)), 7.57 (ε, 1H, m), 7.55 (δ, 2H, m) <sup>13</sup>C-NMR: 165.28, 158.30, 157.05 (q, *J*<sub>13C-19F</sub>=36.5), 135.04, 132.04, 129.22, 127.45, 119.63 (q, *J*<sub>13C-19F</sub>=275), 118.23 <sup>19</sup>F-NMR: -70.65 (s). HRMS (ESI+): 225.0635 (M+H: 225.0640). 6-Phenyl-4-trifluoromethylpyrimidine: 39.5 mg white solid, 29%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 9.39 (α, 1H, s), 8.15 (γ, 2H, (d, *J*<sub>1H-1H</sub>=6.9)), 8.03 (β, 1H, s), 7.58 (ε, 1H, m), 7.55 (δ, 2H, m) <sup>13</sup>C-NMR: 166.51, 159.40, 156.16 (q, *J*<sub>13C-19F</sub>=36.0), 135.34, 132.10, 129.26, 127.40, 120.66 (q, *J*<sub>13C-19F</sub>=275), 112.54 <sup>19</sup>F-NMR: -73.70 (s). HRMS (ESI+): 225.0635 (M+H: 225.0640).

6-Phenyl-2-trifluoromethylpyrimidine:



Fig. S97.  $^1\text{H}$  NMR Spectrum:

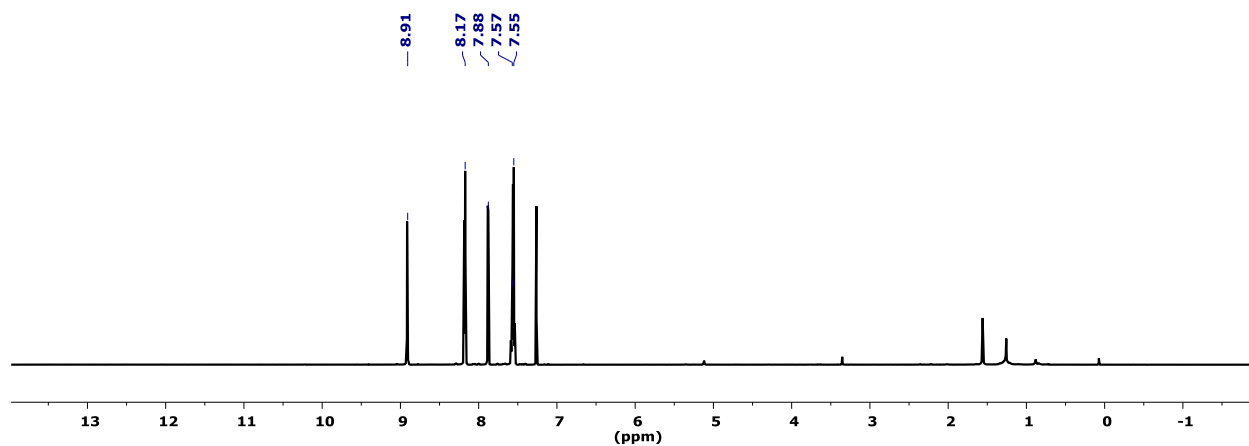


Fig. S98.  $^{13}\text{C}$  NMR Spectrum:

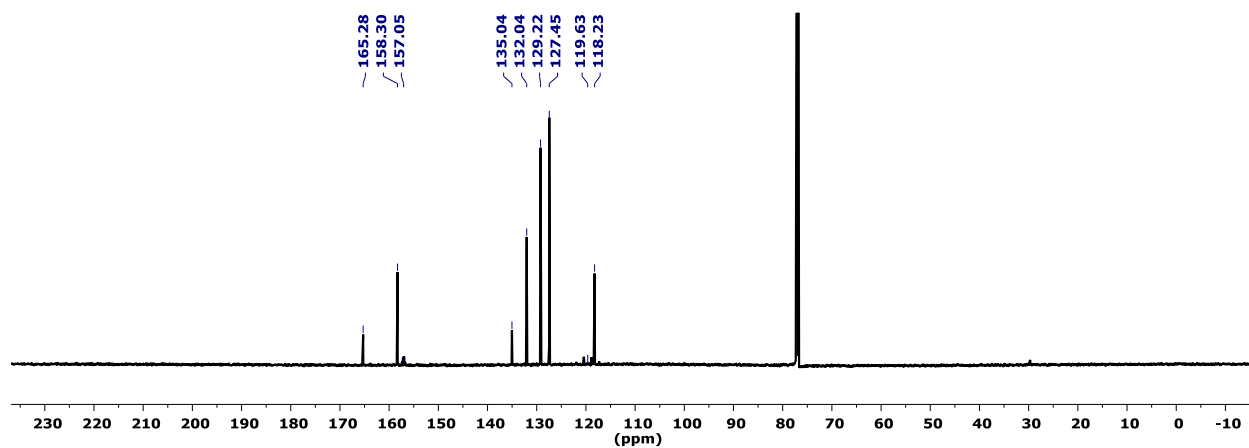
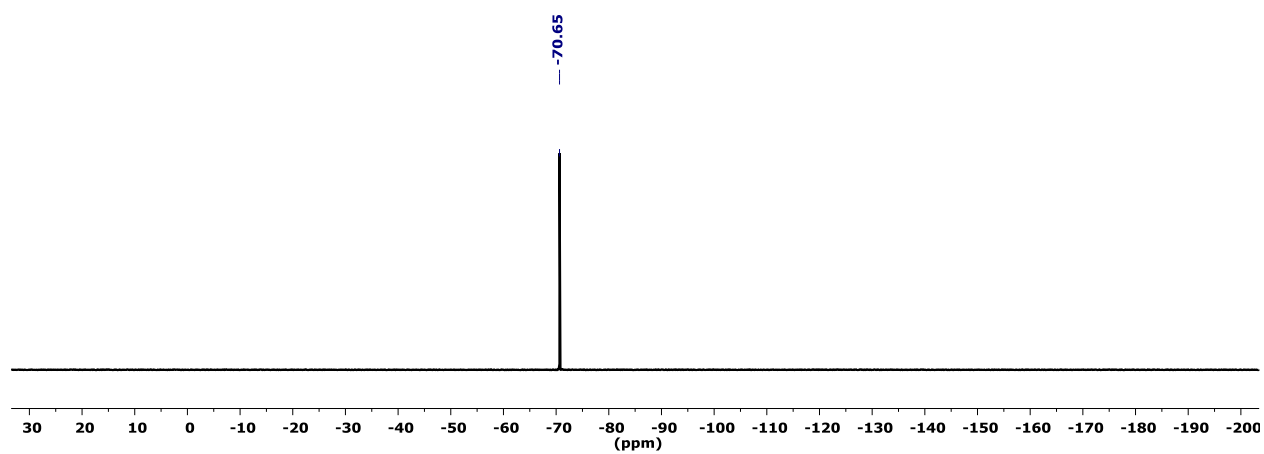


Fig. S99.  $^{19}\text{F}$  NMR Spectrum:



**Fig. S100.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:**

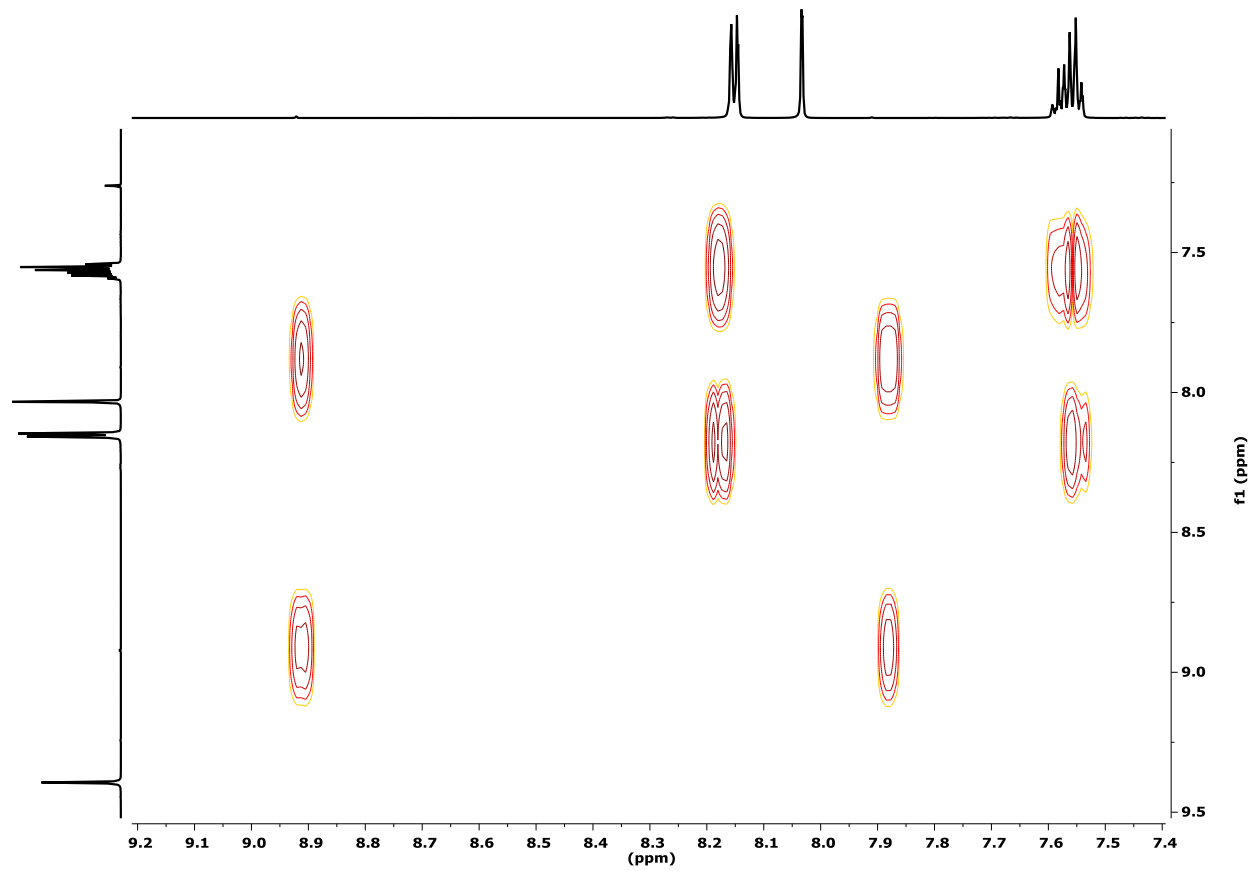


Fig. S101.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

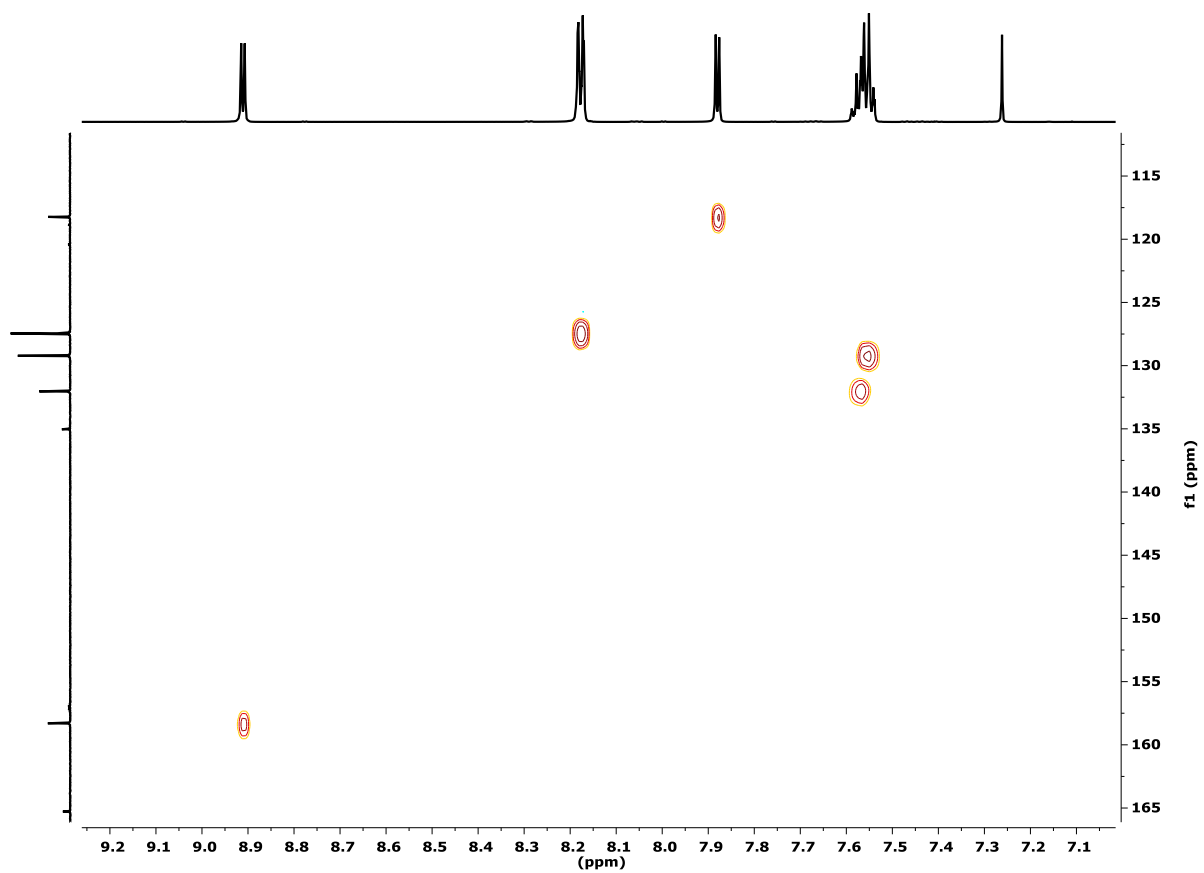
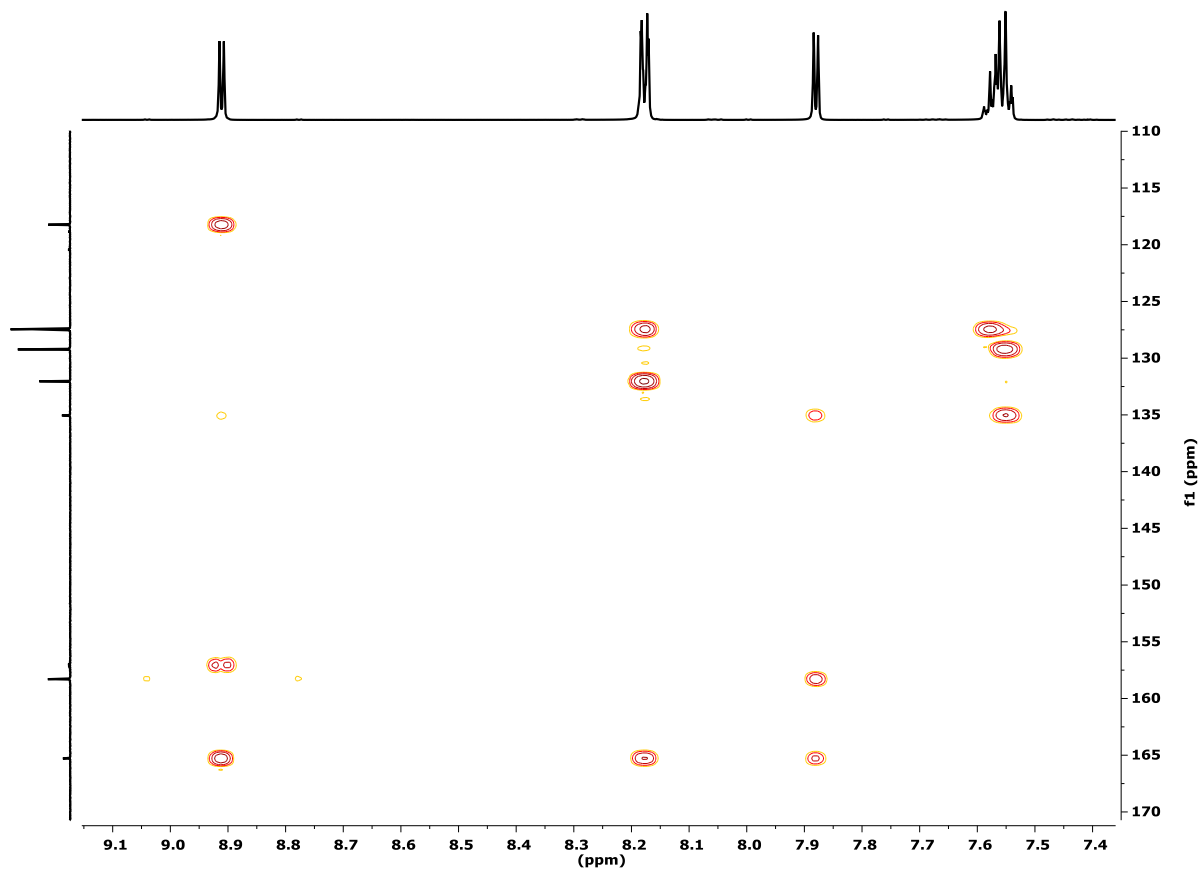


Fig. S102.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:



6-Phenyl-4-trifluoromethylpyrimidine:

Fig. S103.  $^1\text{H}$  NMR Spectrum:

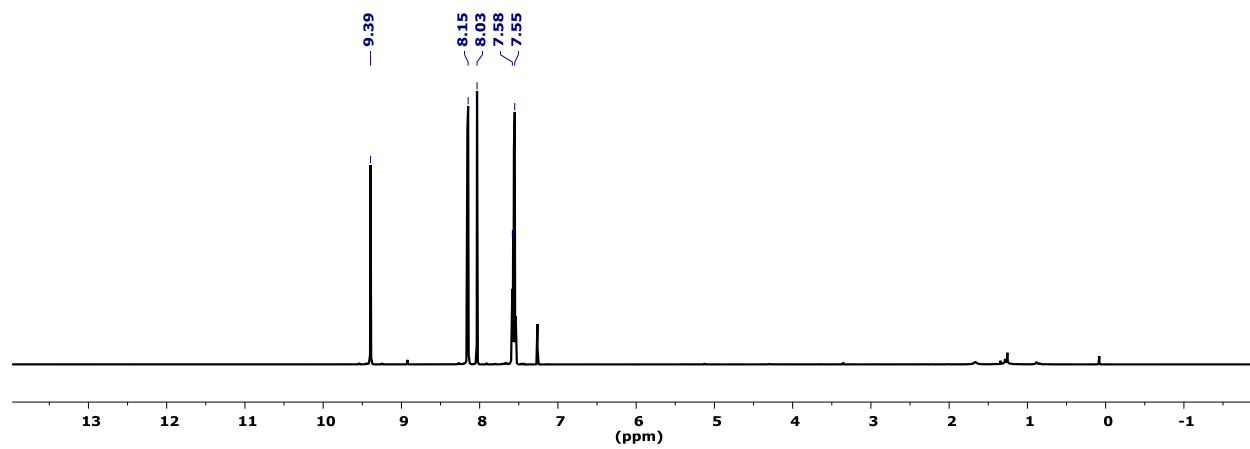


Fig. S104.  $^{13}\text{C}$  NMR Spectrum:

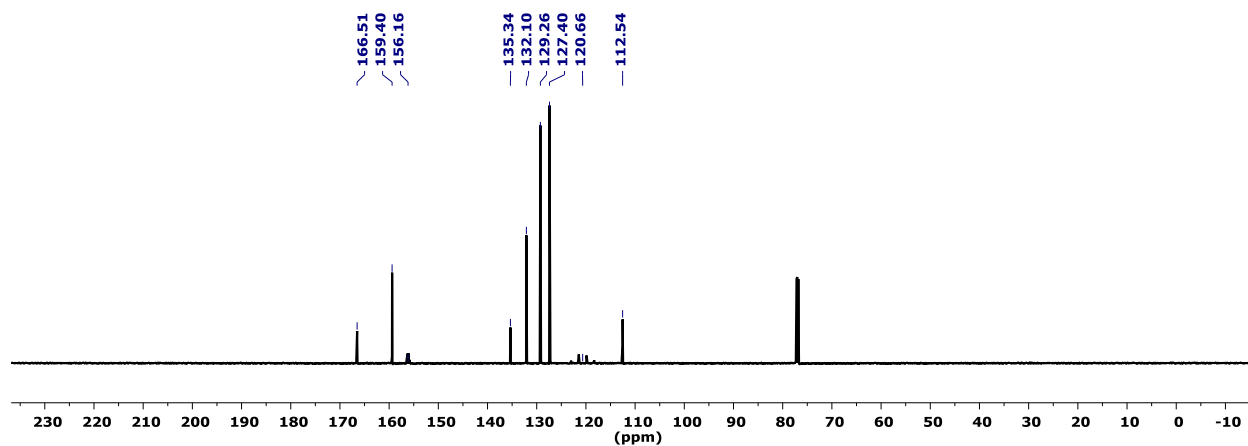


Fig. S105.  $^{19}\text{F}$  NMR Spectrum:

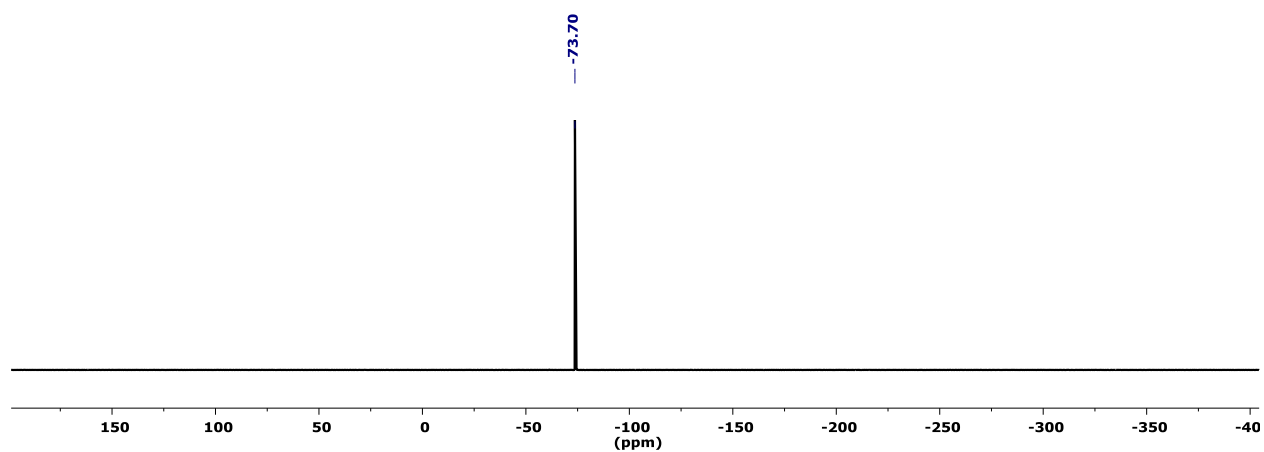


Fig. S106.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:

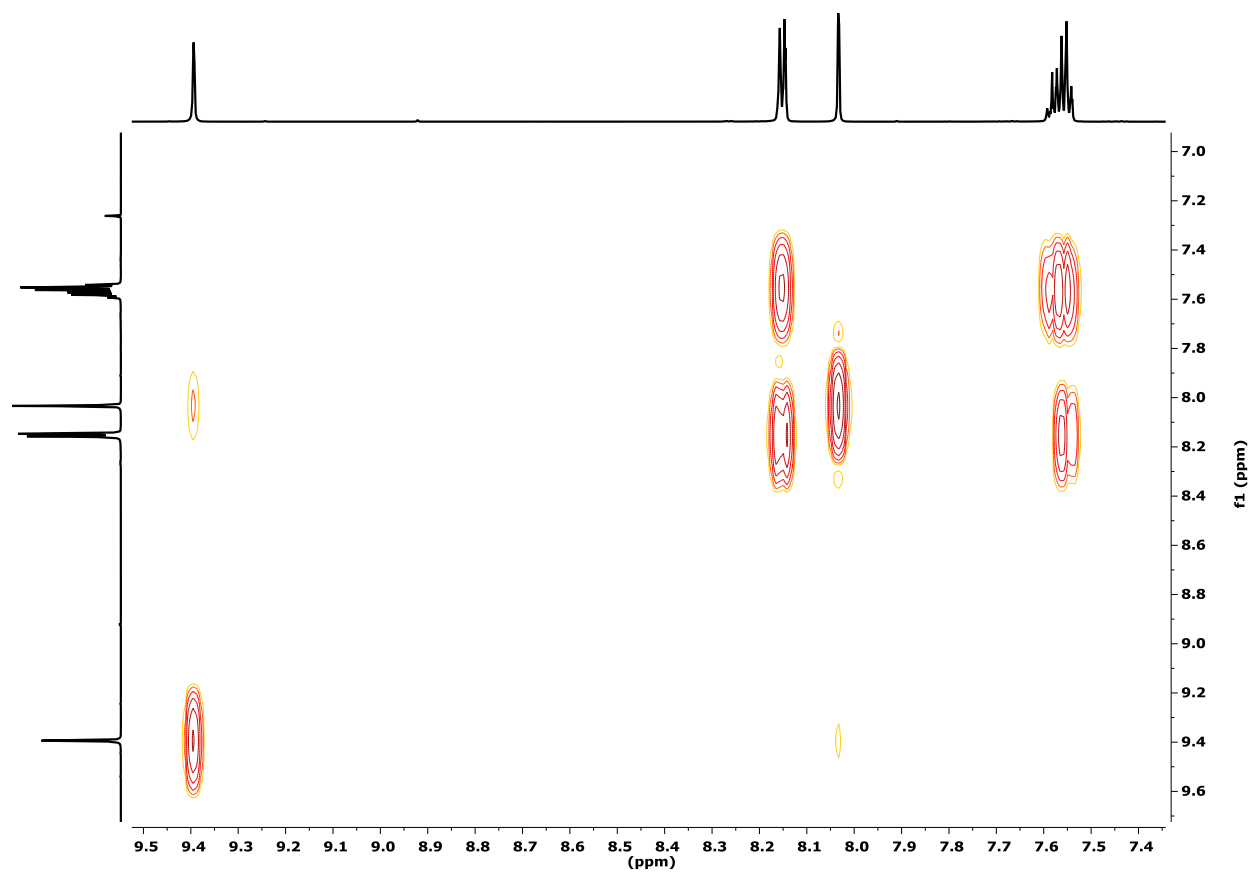


Fig. S107.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

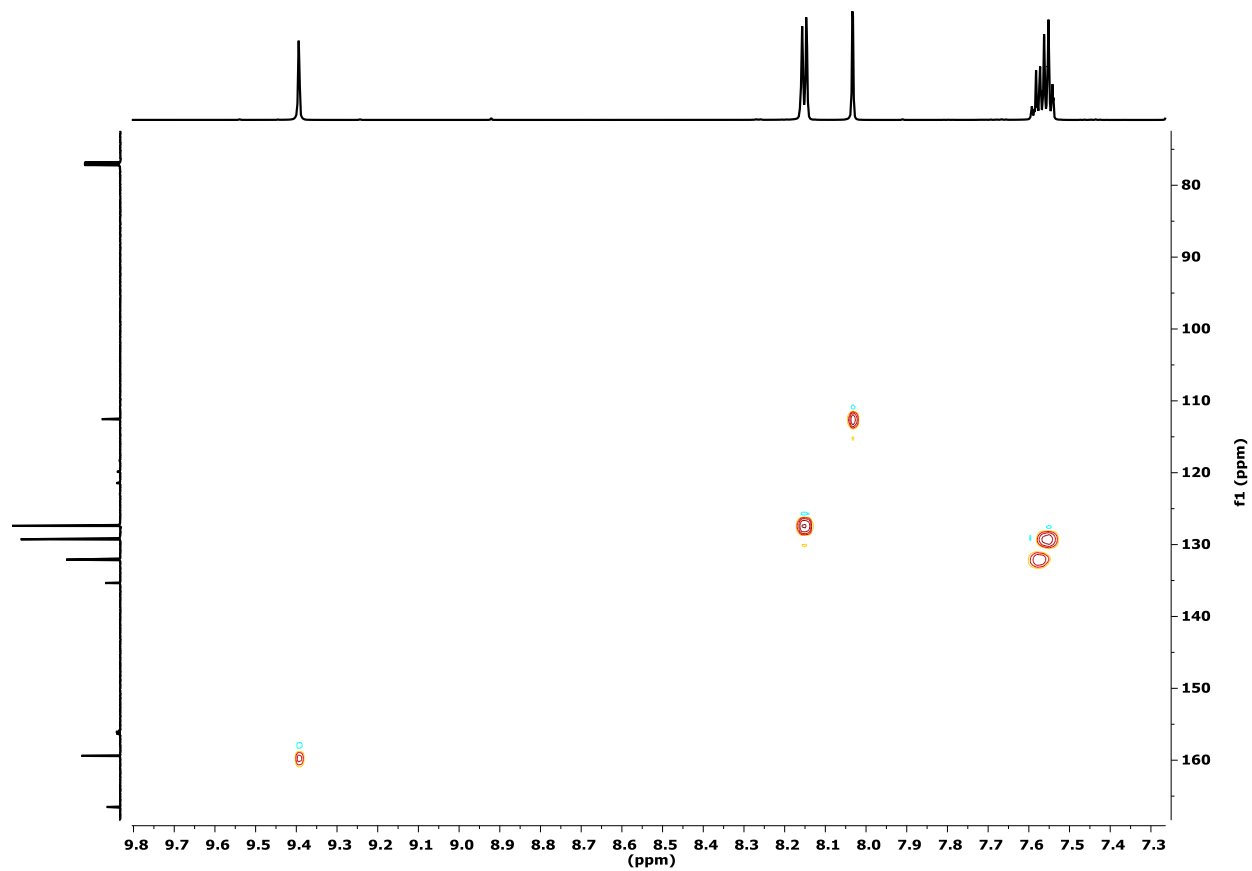
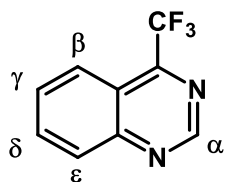
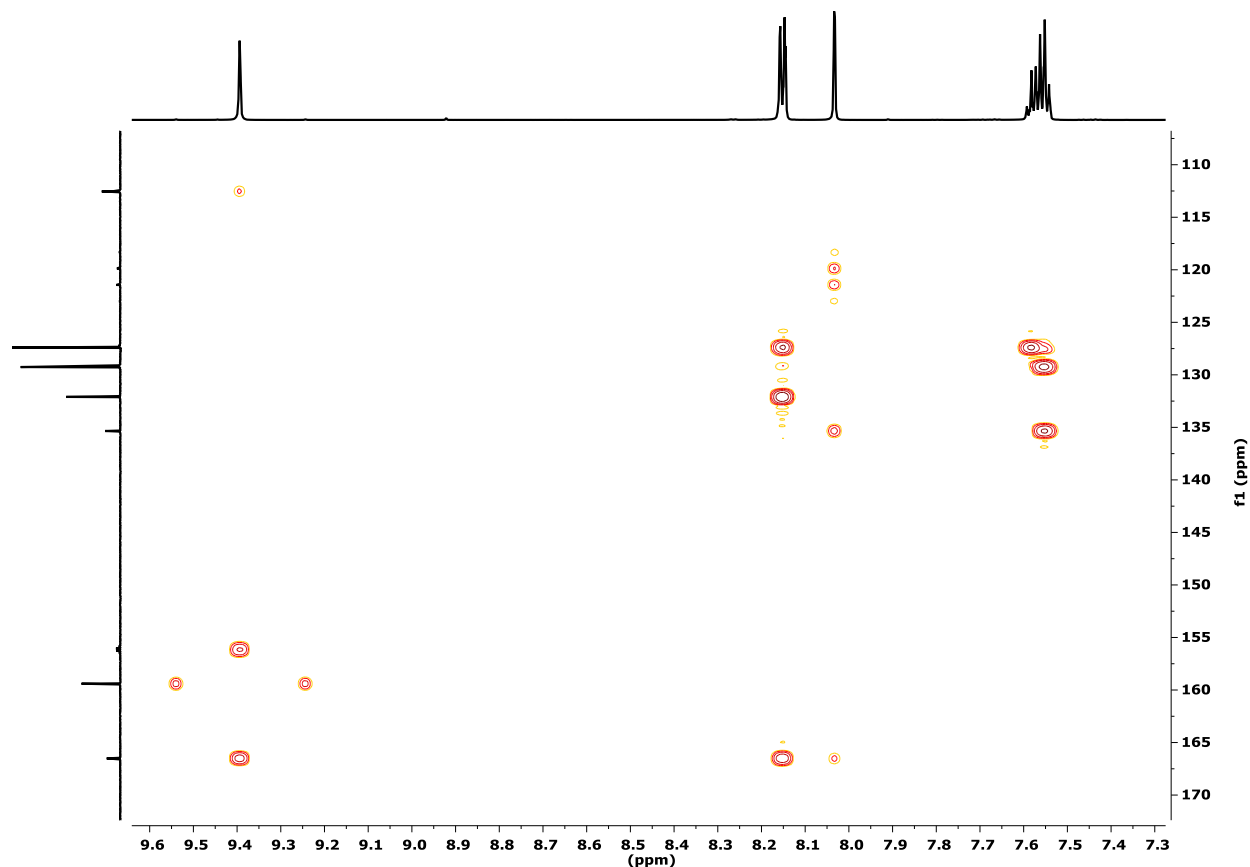


Fig. S108.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:



#### 4-Trifluoromethylquinazoline:

Quinazoline (78 mg, 0.600 mmol) was dissolved in 3 mL THF. K(18-crown-6)( $\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3$ )(THF) (3.00 mL, 0.2 M in THF, 0.600 mmol) was then added. After 1 hour, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (135 mg, 0.600 mmol) was added and the mixture stirred for one hour. NMR spectra showed a single product. The reaction mixture was quenched with water. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL), the  $\text{CH}_2\text{Cl}_2$  extract was dried and concentrated, and the crude oil was purified by flash silica chromatography. Chromatography conditions: 0-20% Hexane/Ethyl Acetate, 16 column volumes, 25 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 4-Trifluoromethylquinazoline: 64.0 mg yellow oil, 53%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 9.44 ( $\alpha$ , 1H, s), 8.25 ( $\beta$ , 1H, (d,  $J_{\text{H-H}}=8.5$ )), 8.18 ( $\epsilon$ , 1H, (d,  $J_{\text{H-H}}=8.5$ )), 8.03 ( $\delta$ , 1H, (t,  $J_{\text{H-H}}=8.3$ )), 7.55 ( $\gamma$ , 1H, (t,  $J_{\text{H-H}}=7.7$ )).  $^{13}\text{C}$ -NMR: 154.57 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=34.9$ ), 153.50, 151.86, 134.88, 129.50, 129.40, 124.27 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=2.7$ ), 121.24 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=277$ ), 120.28  $^{19}\text{F}$ -NMR: -64.55 (s). HRMS (ESI $^+$ ): 199.0478 (M+H: 199.0483).



Fig. S109.  $^1\text{H}$  NMR Spectrum:

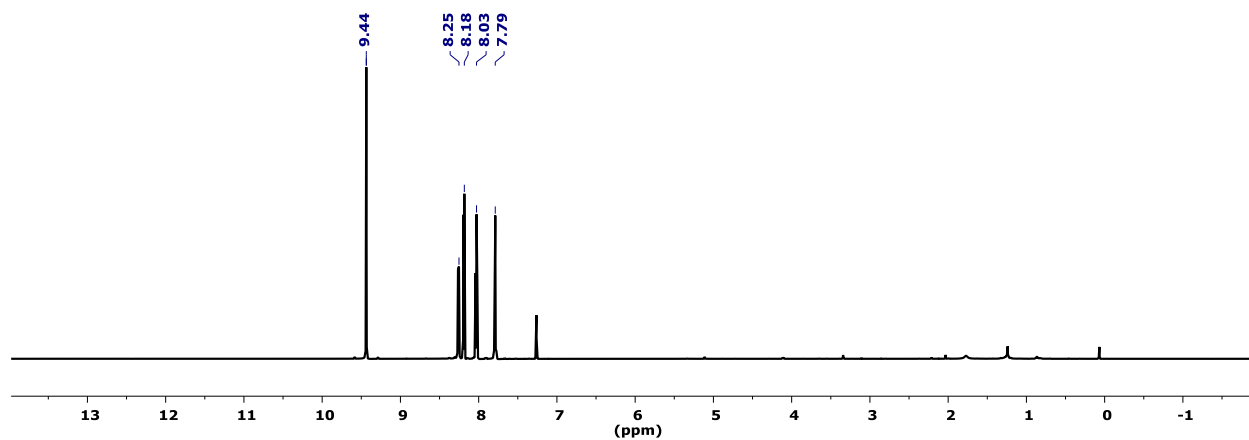


Fig. S110.  $^{13}\text{C}$  NMR Spectrum:

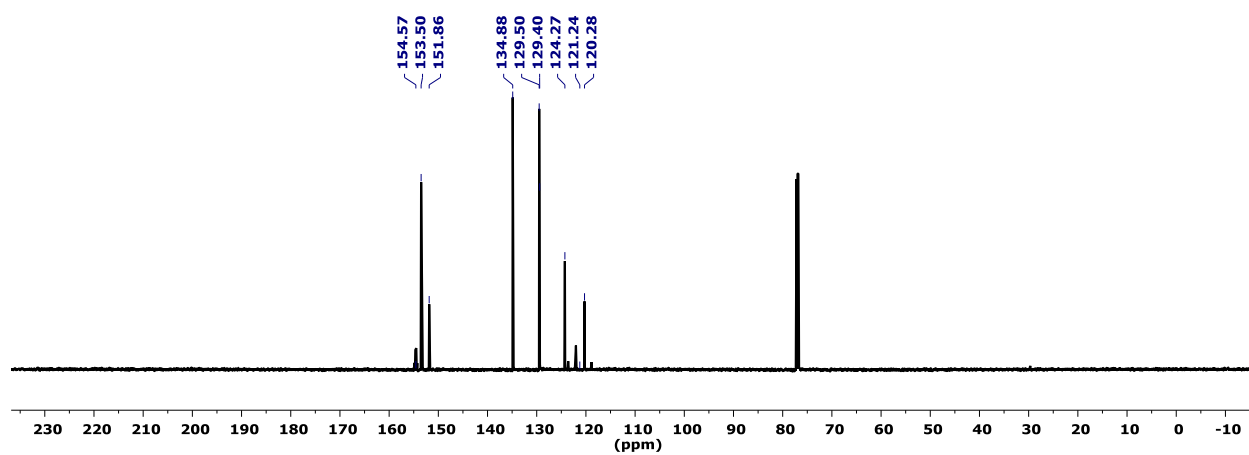


Fig. S111.  $^{19}\text{F}$  NMR Spectrum:

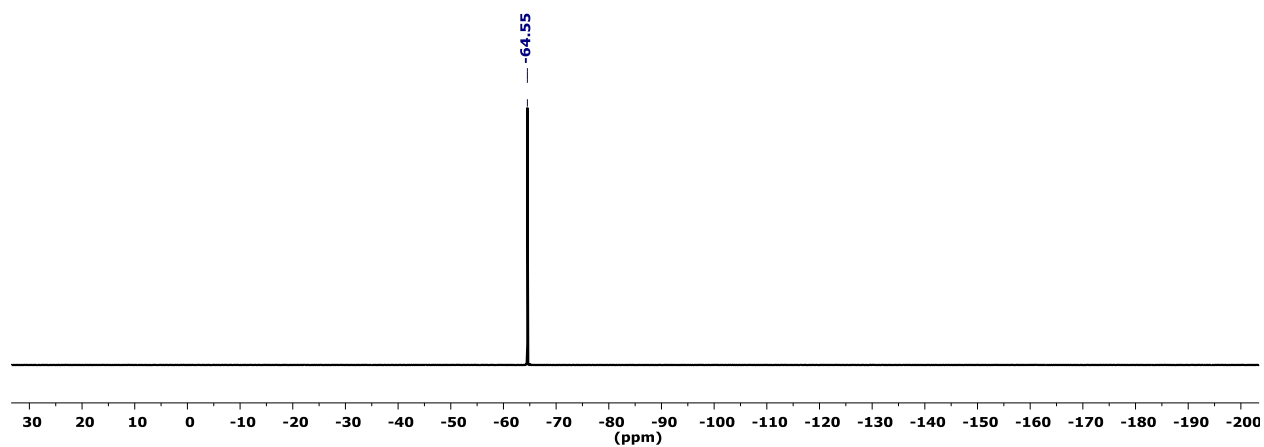


Fig. S112.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:

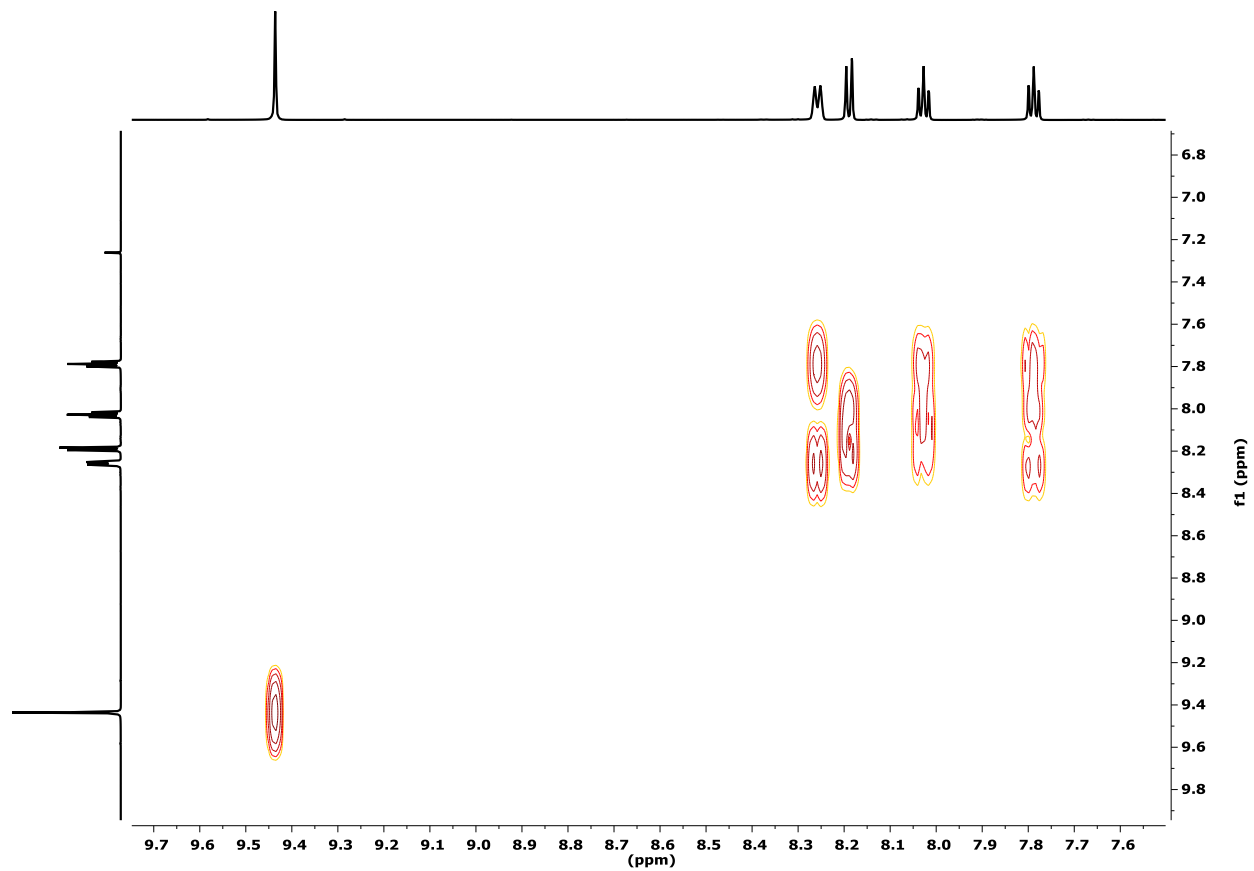


Fig. S113.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

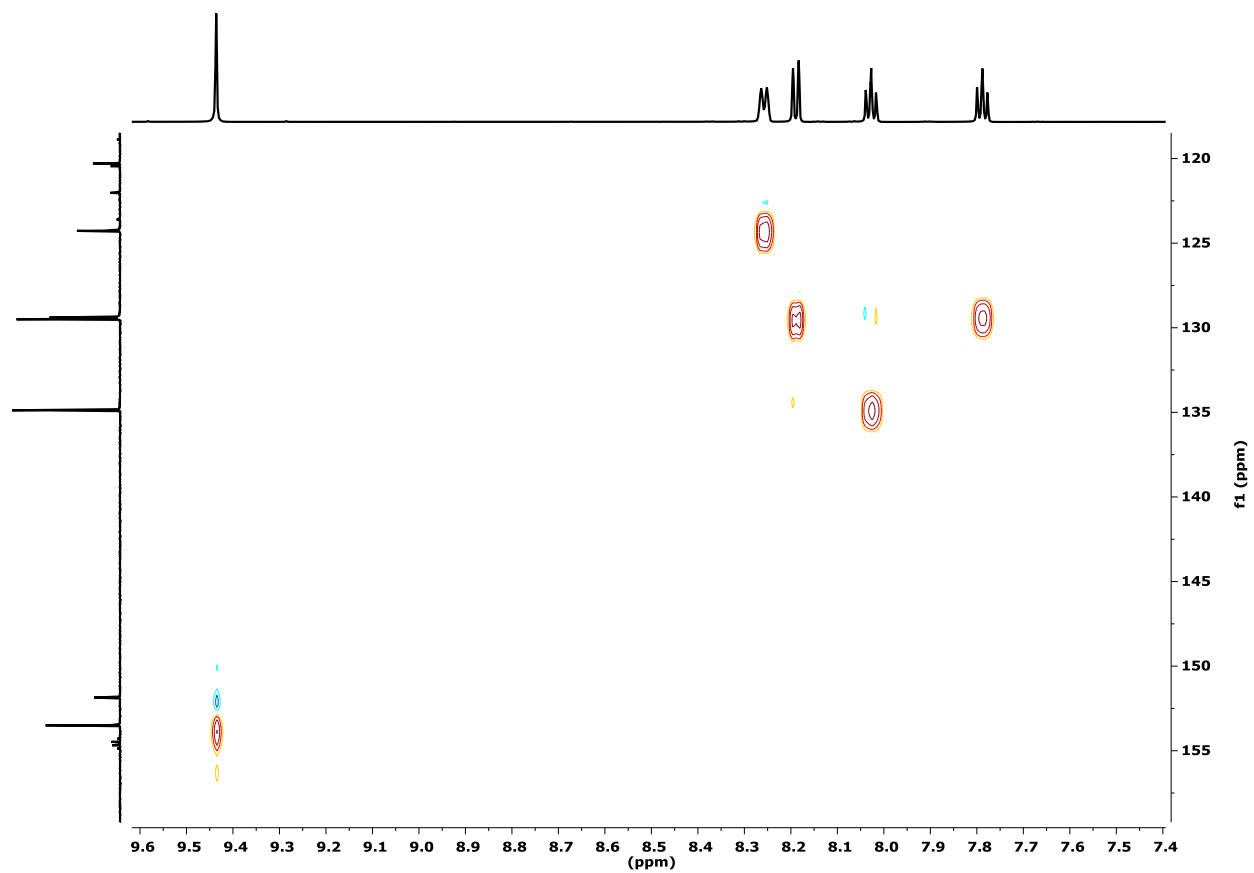
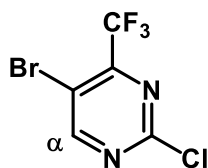
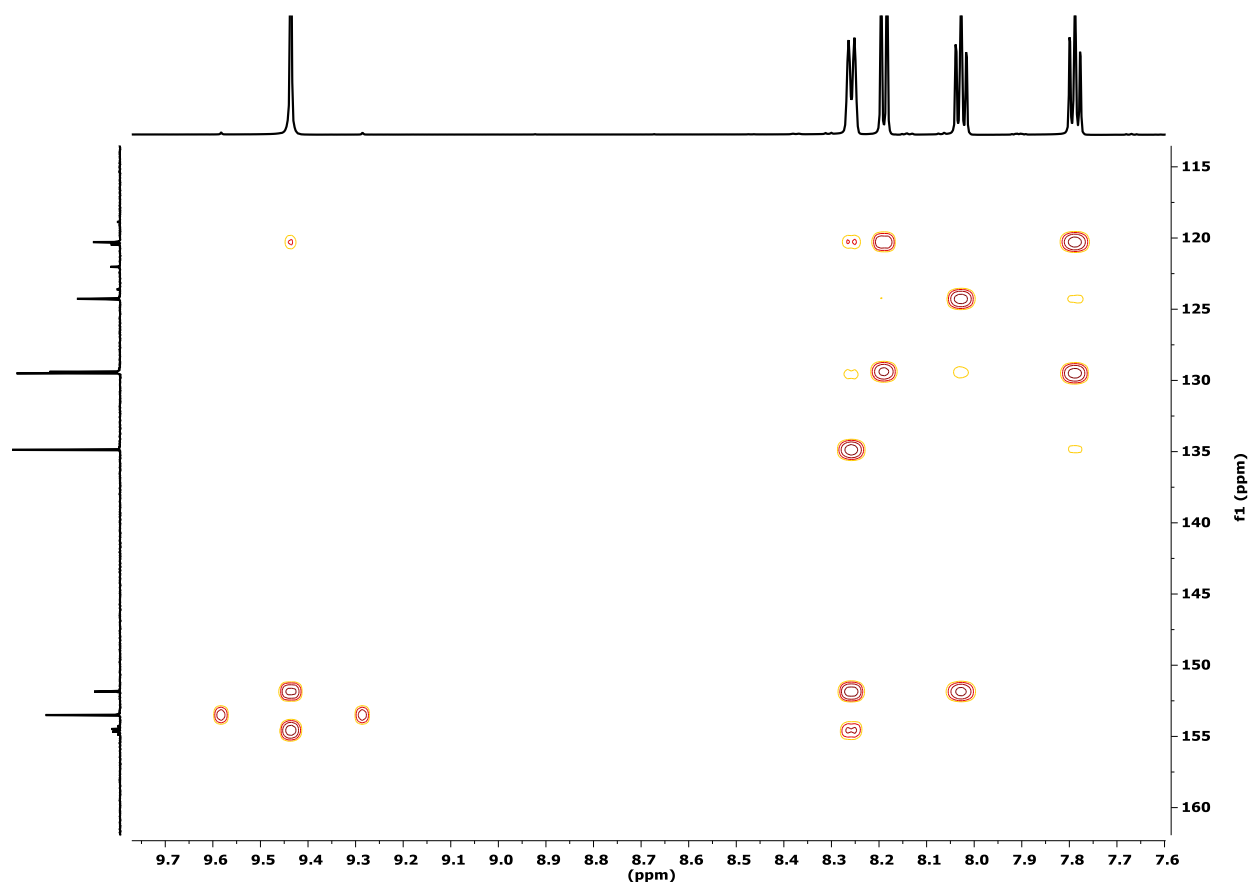


Fig. S114.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:



#### 4-Trifluoromethyl-5-bromo-2-chloro-pyrimidine:

5-Bromo-2-chloro-pyrimidine (154 mg, 0.800 mmol) was dissolved in 4 mL THF. K(18-crown-6)( $\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3$ )(THF) (4.00 mL, 0.2 M in THF, 0.800 mmol) was then added. After 5 minutes, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (135 mg, 0.600 mmol) was added and the mixture stirred for one hour. NMR spectra showed a single product. The reaction mixture was quenched with water. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL), the  $\text{CH}_2\text{Cl}_2$  extract was dried and concentrated, and the crude oil was purified by flash silica chromatography. Chromatography conditions: 0-20% Hexane/DCM, 12 column volumes, 25 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 4-Trifluoromethyl-5-bromo-2-chloro-pyrimidine: 102.3 mg colorless oil, 49%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 8.94 ( $\alpha$ , 1H, s).  $^{13}\text{C}$ -NMR: 164.56, 159.61, 155.21 (q,  $J_{13\text{C}-19\text{F}}=36.7$ ), 119.28 (q,  $J_{13\text{C}-19\text{F}}=277$ ), 115.35  $^{19}\text{F}$ -NMR: -68.22 (s). HRMS (EI+): 259.8966 ( $\text{M}^+$ : 259.8964).

Fig. S115.  $^1\text{H}$  NMR Spectrum:

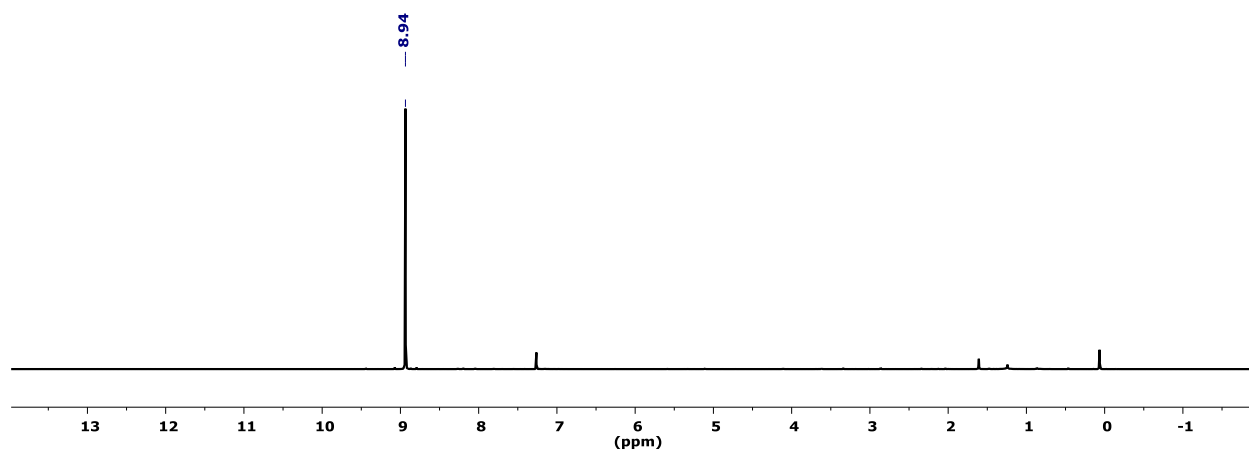


Fig. S116.  $^{13}\text{C}$  NMR Spectrum:

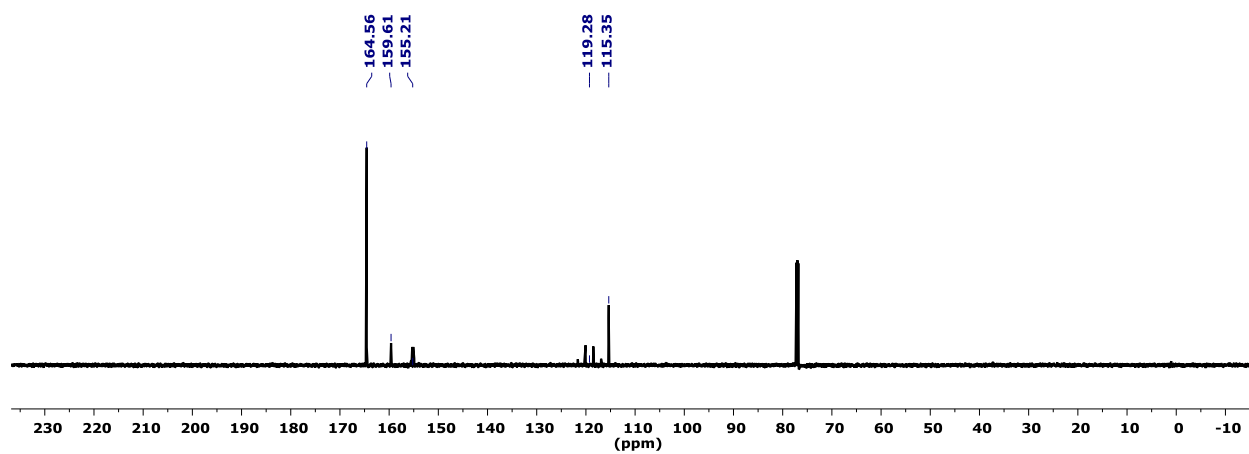


Fig. S117.  $^{19}\text{F}$  NMR Spectrum:

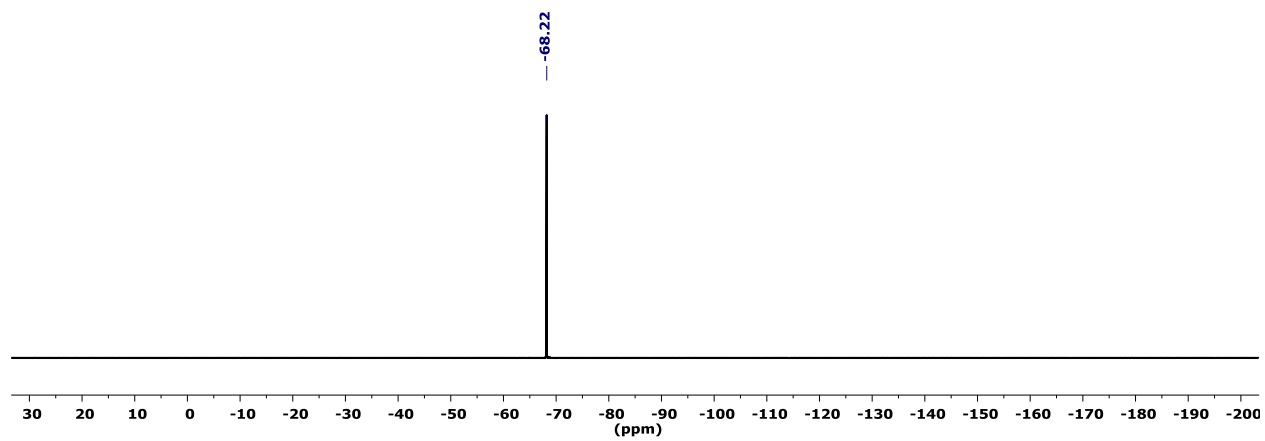


Fig. S118.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

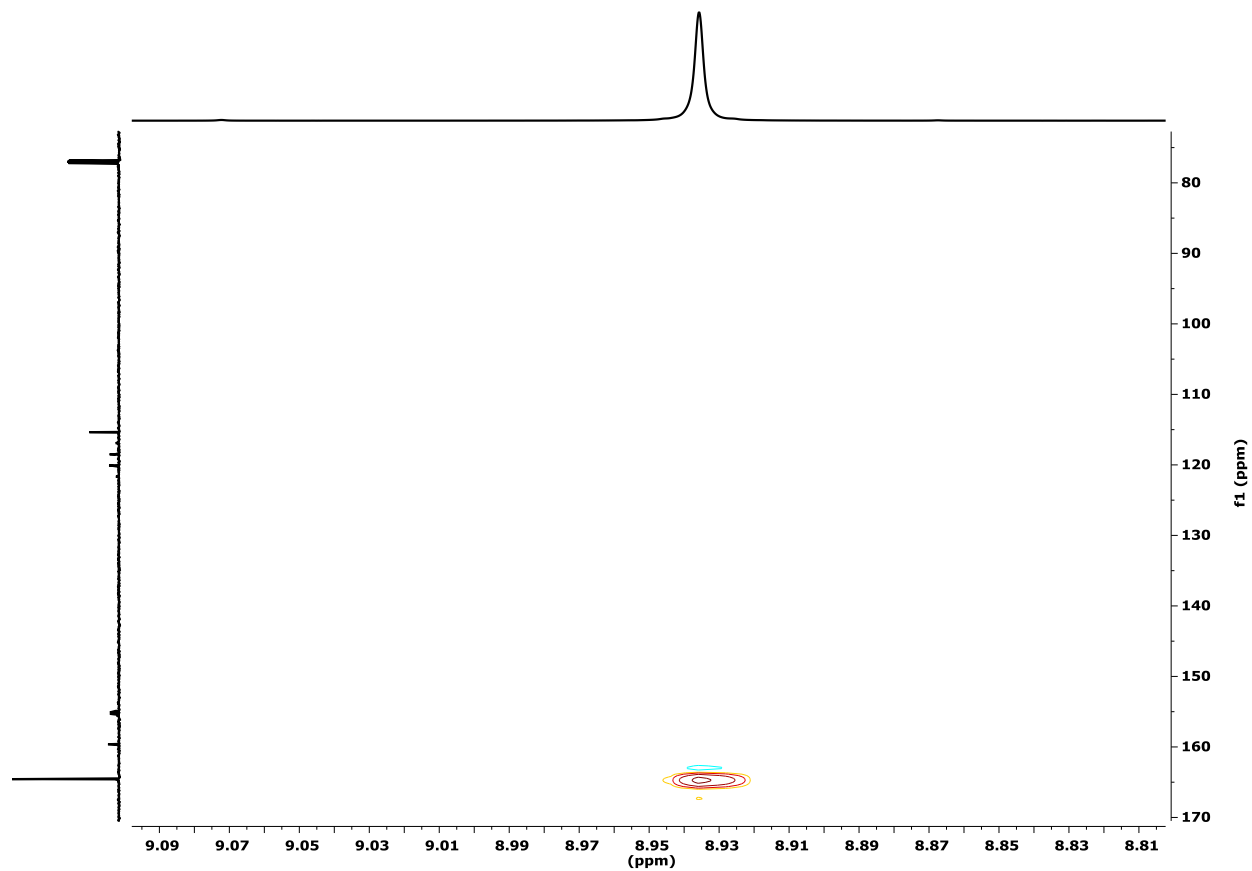
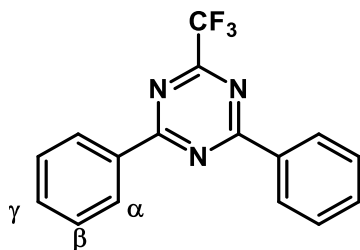
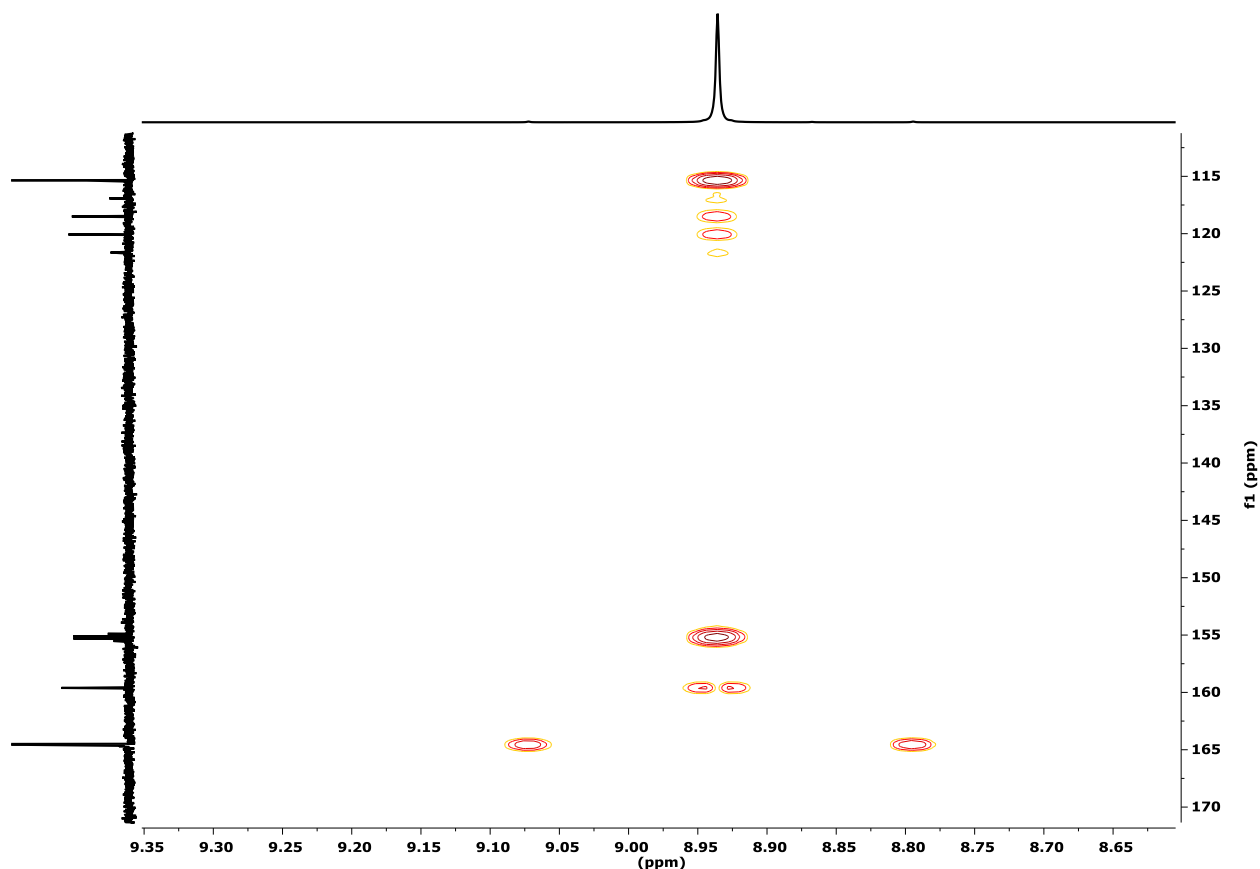


Fig. S119.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:

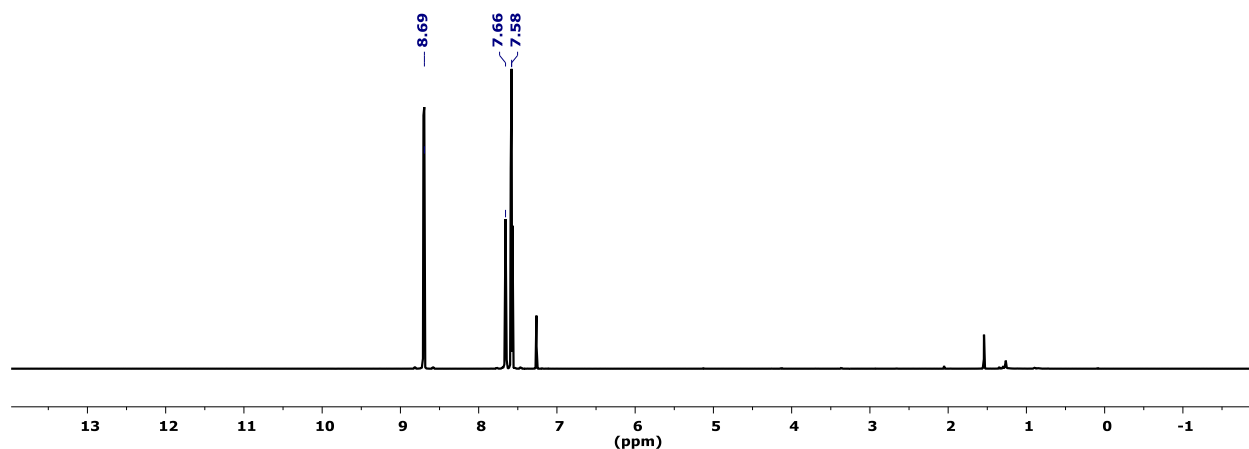


#### 4-Trifluoromethyl-2,6-diphenyltriazine:

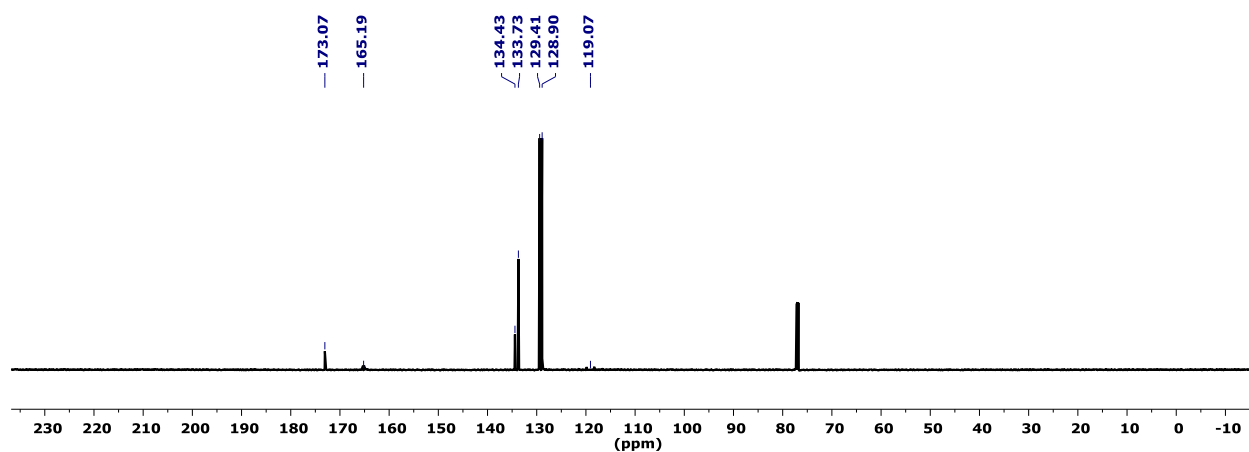
2,6-Diphenyltriazine<sup>[29]</sup> (0.4 mg, 0.800 mmol) was dissolved in 2 mL THF. K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF) (4.00 mL, 0.2 M in THF, 0.800 mmol) was then added. After 5 minutes, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (135 mg, 0.600 mmol) was added and the mixture stirred for one hour. NMR spectra showed a single product. The reaction mixture was quenched with water. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 x 2 mL), the CH<sub>2</sub>Cl<sub>2</sub> extract was dried and concentrated, and the crude oil was purified by flash silica chromatography. Chromatography conditions: 2-15% Hexane/DCM, 8 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 4-Trifluoromethyl-5-bromo-2-chloro-pyrimidine: 52.5 mg white solid, 43%.  $^1\text{H}$ -NMR (CDCl<sub>3</sub>): 8.69 ( $\alpha$ , 4H, (d,  $J_{\text{H-H}}=8.4$ )), 7.66 ( $\gamma$ , 2H, (t,  $J_{\text{H-H}}=7.3$ )), 7.58 ( $\beta$ ,

4H, (t,  $J_{1H-1H}=7.7$ )).  $^{13}C$ -NMR: 173.07, 165.19 (q,  $J_{13C-19F}=37.7$ ), 134.43, 133.73, 129.41, 128.90, 119.07 (q,  $J_{13C-19F}=277$ )  $^{19}F$ -NMR: -72.28 (s). HRMS (ESI+): 302.0897 (M+H: 302.0905).

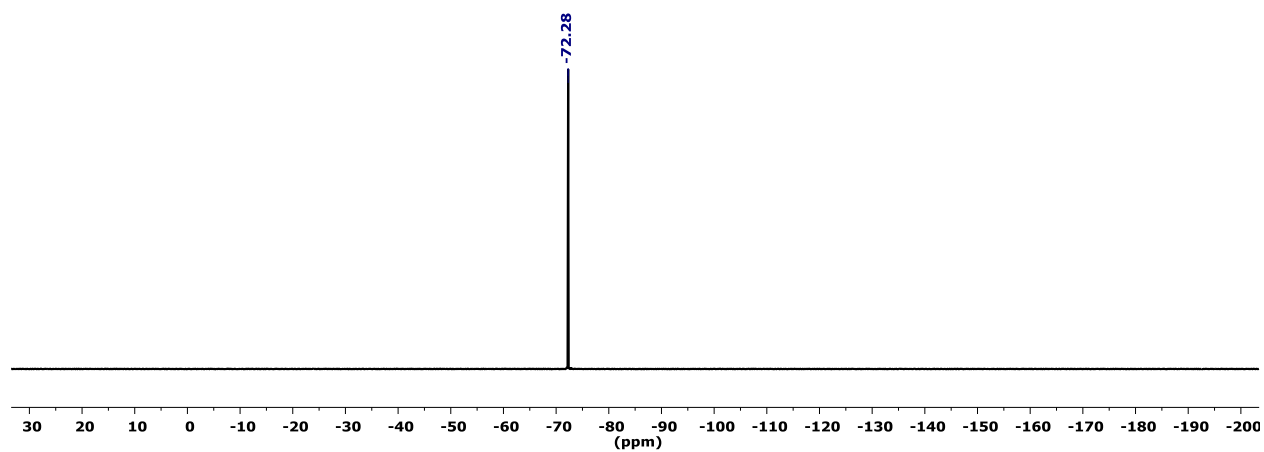
**Fig. S120.  $^1H$  NMR Spectrum:**



**Fig. S121.  $^{13}C$  NMR Spectrum:**

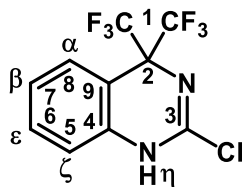


**Fig. S122.  $^{19}F$  NMR Spectrum:**





## Geminal Bistrifluoromethylations



### 4,4-Bistrifluoromethyl-2-chloro-3-hydroquinazoline

Substrate: Dichloroquinazoline. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 1.5 equivalents K(LA-CF<sub>3</sub>) used. 0.80 mmol substrate. Reaction time: 30 minutes. Quench: 10 mL 5% NaOH, then brought to pH 7 with glacial acetic acid. Chromatography conditions: 0-100% hexane/ethyl acetate, 16 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 146 mg light yellow solid, 60%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.22 (η, 1H, s), 7.58 (α, 1H, (d, *J*<sub>1H-1H</sub>=8.0)), 7.41 (ε, 1H, (t, *J*<sub>1H-1H</sub>=7.7)), 7.22 (β, 1H, (t, *J*<sub>1H-1H</sub>=7.7)), 6.88 (ζ, 1H, (d, *J*<sub>1H-1H</sub>=8.0)). <sup>13</sup>C-NMR: 145.84 (3), 135.58 (4), 131.34 (6), 128.19 (8), 125.66 (7), 122.42(1, q, *J*<sub>13C-19F</sub>=288), 115.09 (5), 108.67 (9), 73.36(2, p, *J*<sub>13C-19F</sub>=29). <sup>19</sup>F-NMR: -73.73 (s). HRMS (ESI+): 303.0114 (M+H: 303.0124).

The trifluoromethyl groups were assigned based on crosspeaks in 2D NMR experiments and a septet for carbon #2 in the <sup>13</sup>C NMR spectrum. HSQC was used to identify the carbon atoms associated with hydrogen atoms α, β, ε, and ζ. <sup>19</sup>F-<sup>13</sup>C HMBC was then used to identify one bond coupling with carbon 1, two bond coupling with carbon 2, four bond coupling with carbon 3, and four bond coupling with carbon 8. Carbon 3 was assigned based on its lack of long-range coupling with any protons and high shift. The positions of carbons 9 and 4 were assigned based on their long-range coupling with hydrogen atoms α, β, ε, and ζ. The position of carbon 8 was based on its proximity to the <sup>19</sup>F group. Finally, the position of acidic hydrogen η and confirmation of the assignment was obtained through single-crystal X-Ray diffraction. A single crystal was obtained by allowing a concentrated solution of 4,4-Bistrifluoromethyl-2-chloro-3-hydroquinazoline in chloroform to slowly evaporate.

**Fig. S123. <sup>1</sup>H NMR Spectrum:**

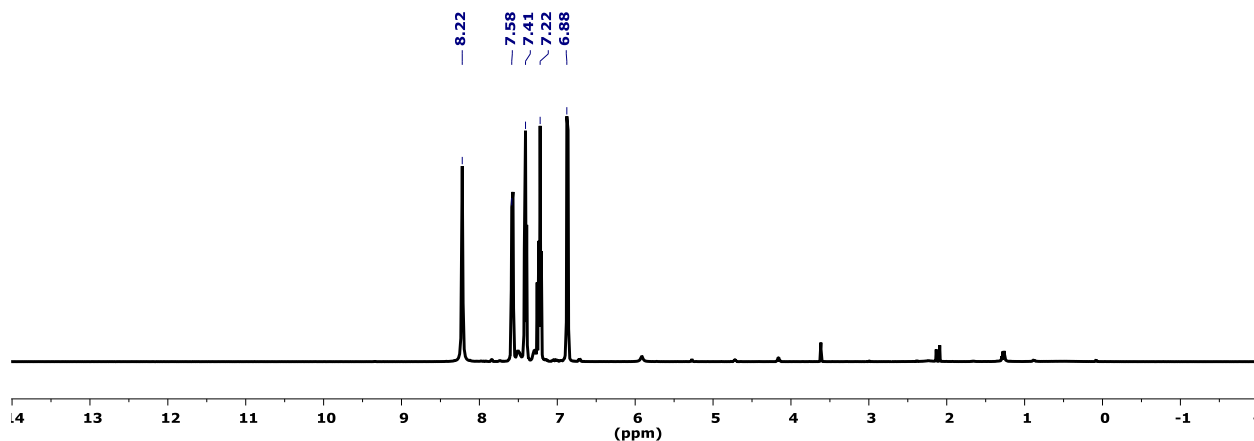


Fig. S124.  $^{13}\text{C}$  NMR Spectrum:

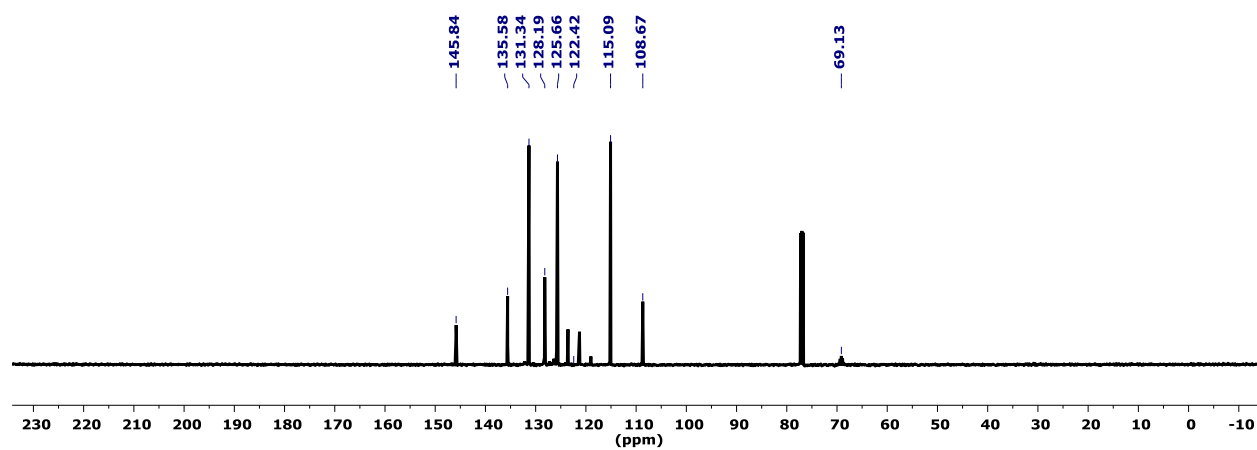


Fig. S125.  $^{19}\text{F}$  NMR Spectrum:

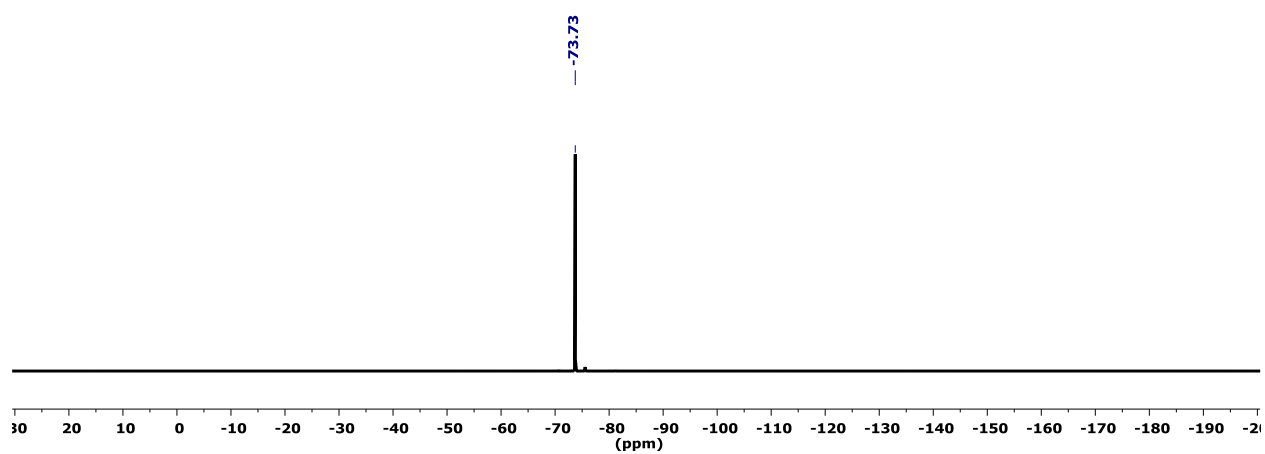


Fig. S126.  $^{19}\text{F}$ - $^{13}\text{C}$  Crisis2 HMBC Spectrum:

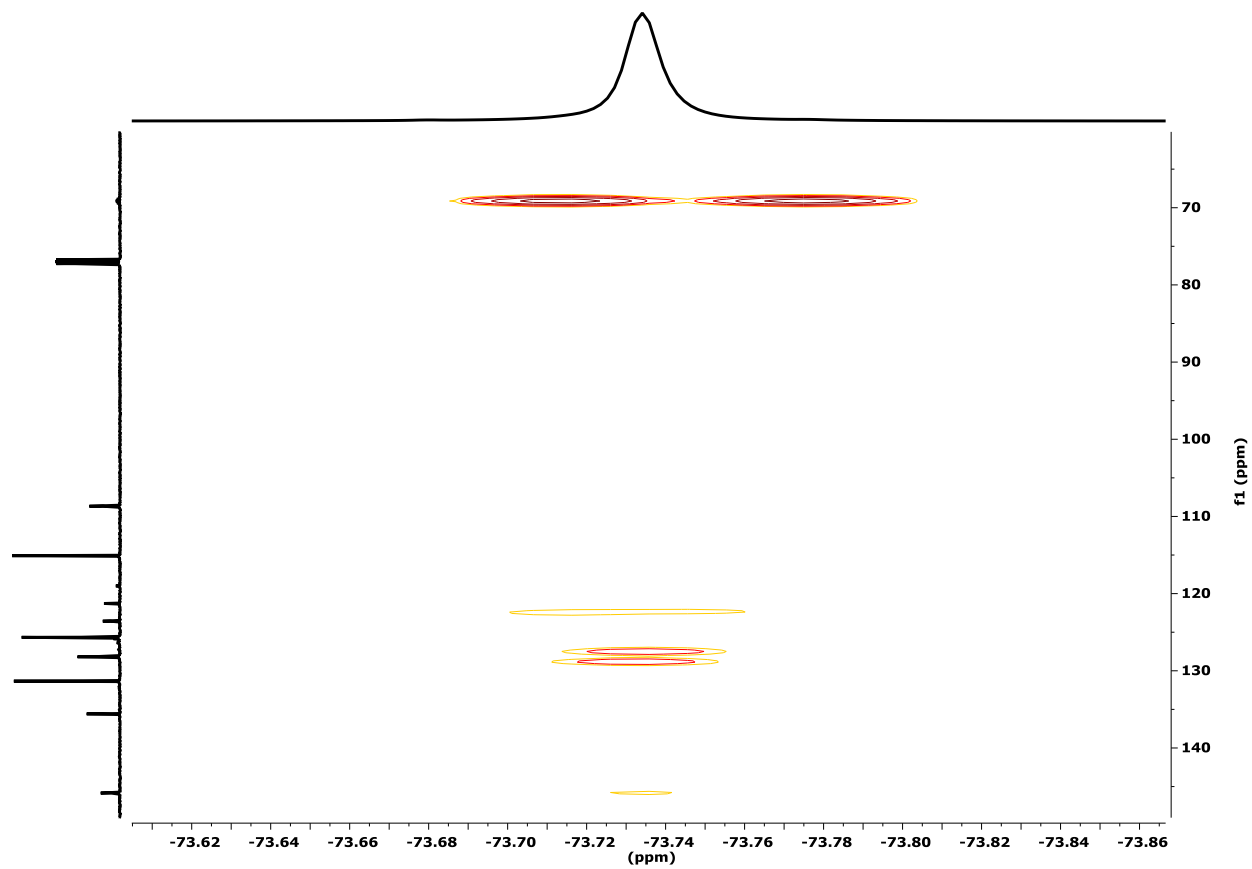


Fig. S127.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:

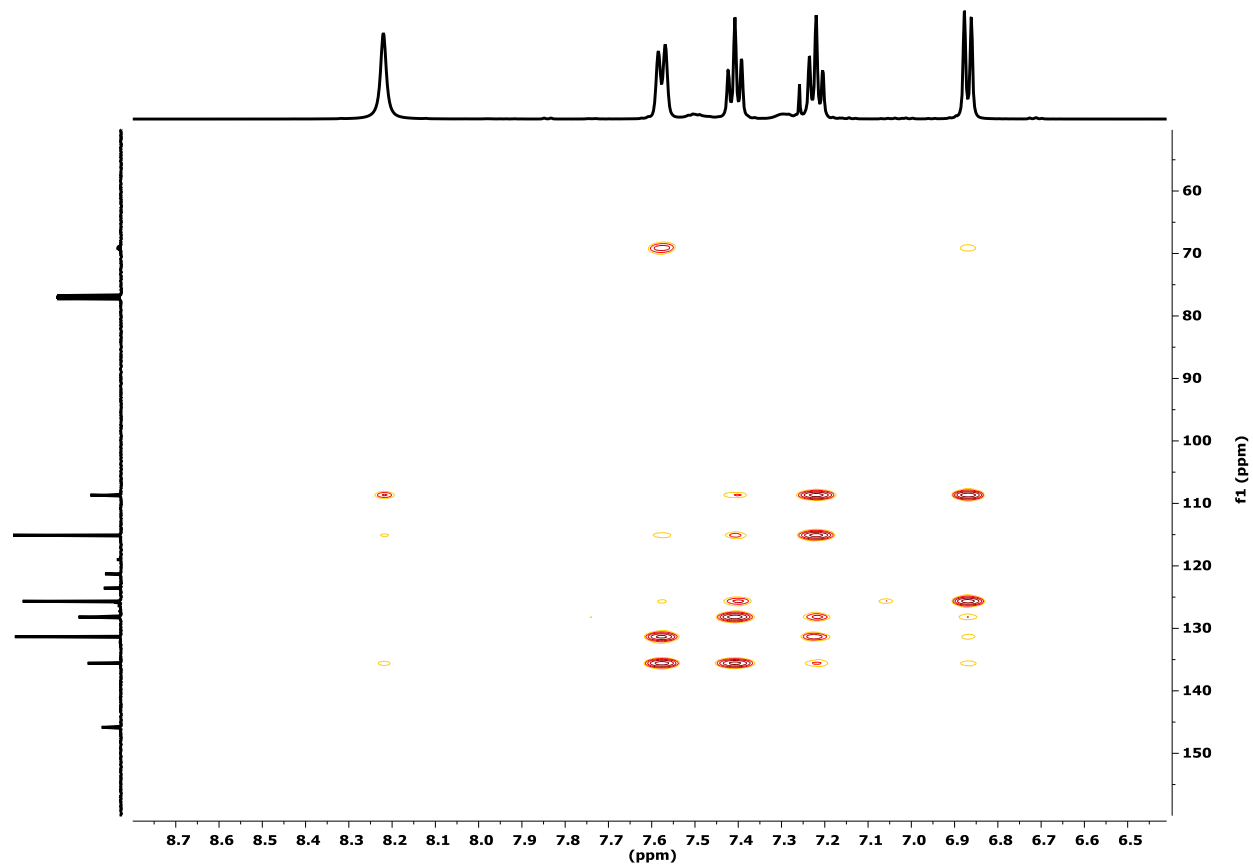


Fig. S128.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

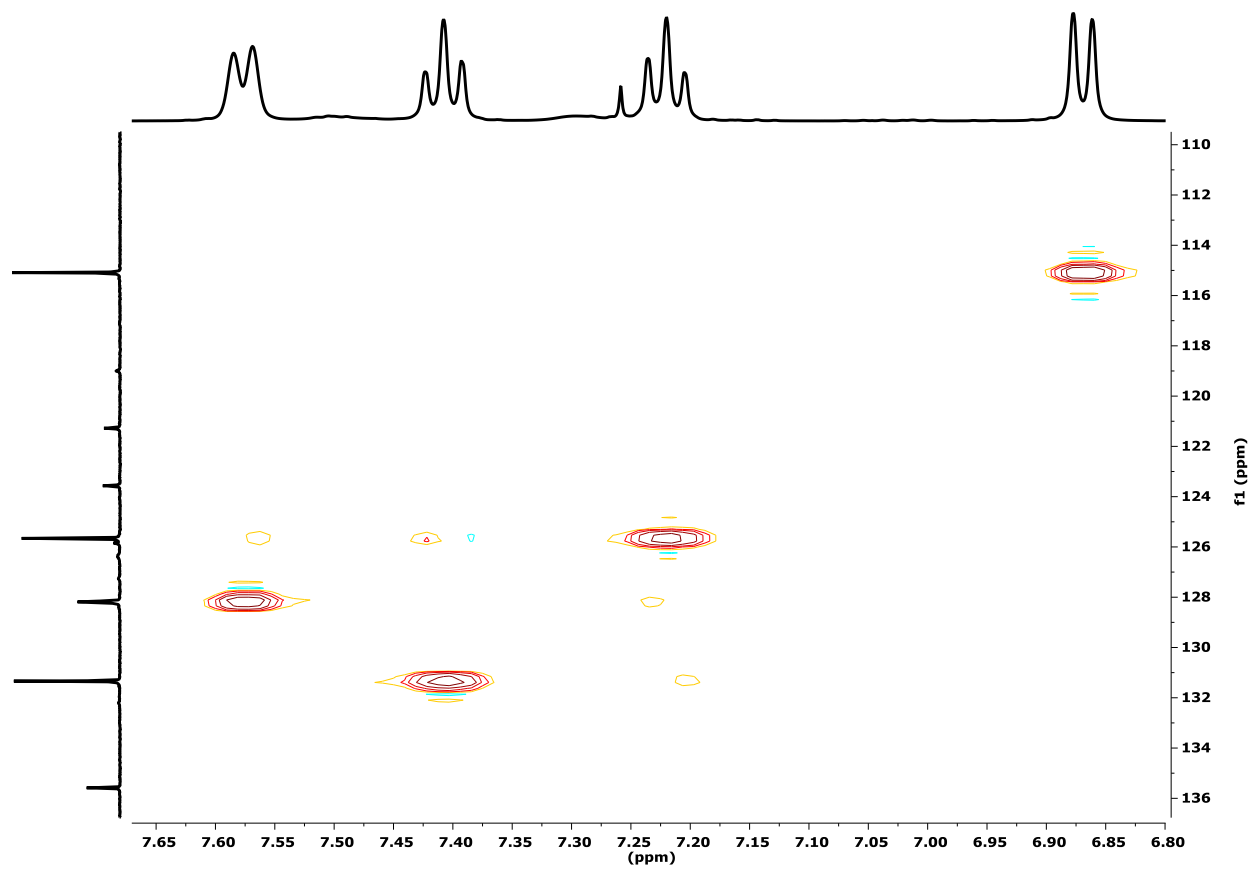
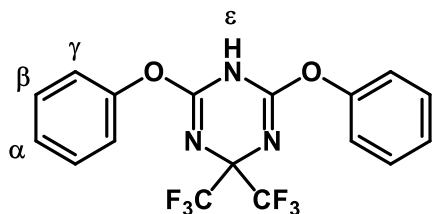
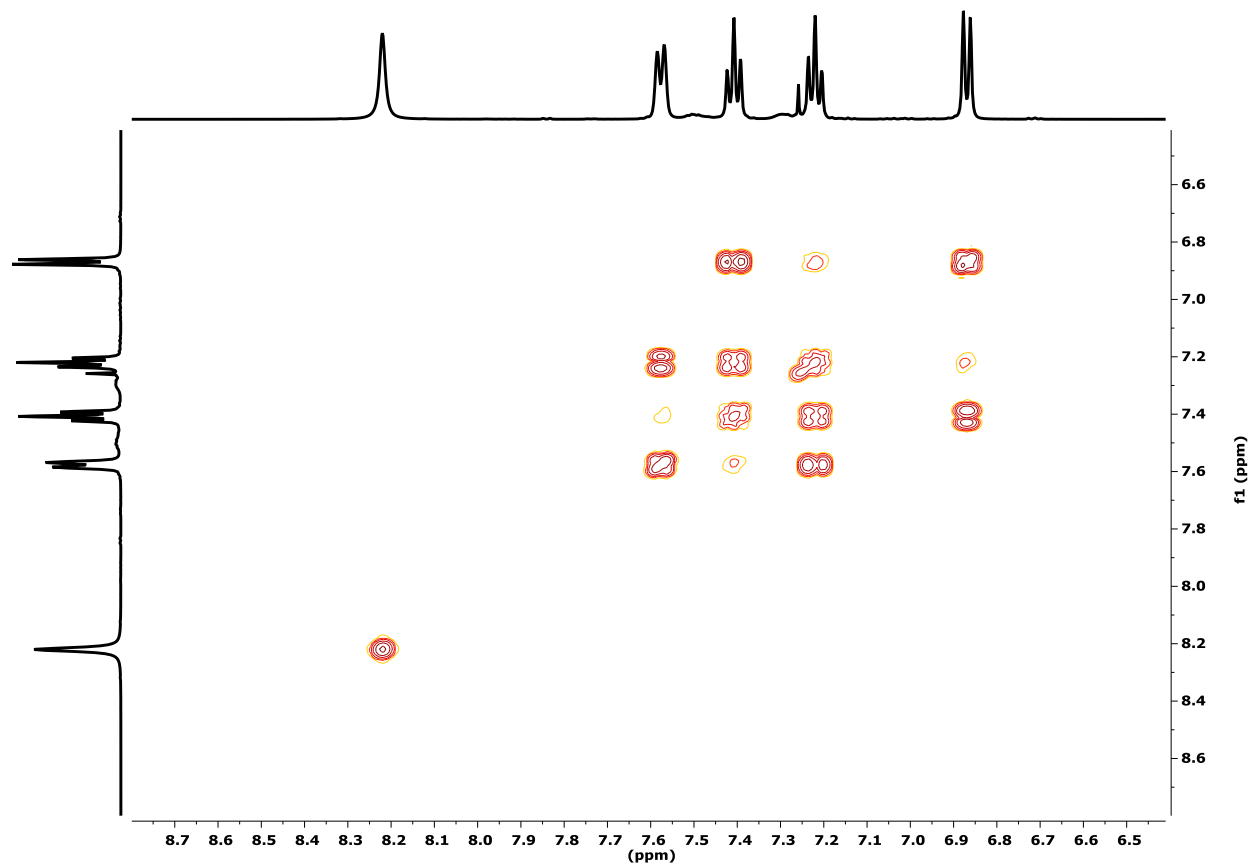


Fig. S129.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:



### 2,4-Phenoxy-6,6-bistrifluoromethyl-3-hydro-triazine

Substrate: 2,4-diphenoxy-6-chlorotriazine. Solvent: THF. Conditions: LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 2.0 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 2 hour. Quench: water. Chromatography conditions: 0-50% Hexane/Ethyl acetate, 8 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 123 mg white solid, 76%.  $^1\text{H}$ -NMR (DMSO-*d*<sub>6</sub>): 12.36 ( $\epsilon$ , 1H, s), 7.84 ( $\beta$ , 2H, (t, 4H, (t,  $J_{\text{H-H}}=7.8$ ))), 7.27 ( $\alpha$ , 2H, (t,  $J_{\text{H-H}}=7.3$ )), 7.21 ( $\gamma$ , 4H, (d,  $J_{\text{H-H}}=8.0$ )).  $^{13}\text{C}$ -NMR (DMSO-*d*<sub>6</sub>): 155.74, 151.04, 130.12, 126.60, 122.09(q,  $J_{13\text{C}-19\text{F}}=288$ ), 121.63, 81.02 (p,  $J_{13\text{C}-19\text{F}}=29.5$ ).  $^{19}\text{F}$ -NMR: -79.44 (s). HRMS (ES<sup>+</sup>): 403.0759 (M<sup>+</sup>: 403.0755).

Fig. S130.  $^1\text{H}$  NMR Spectrum:

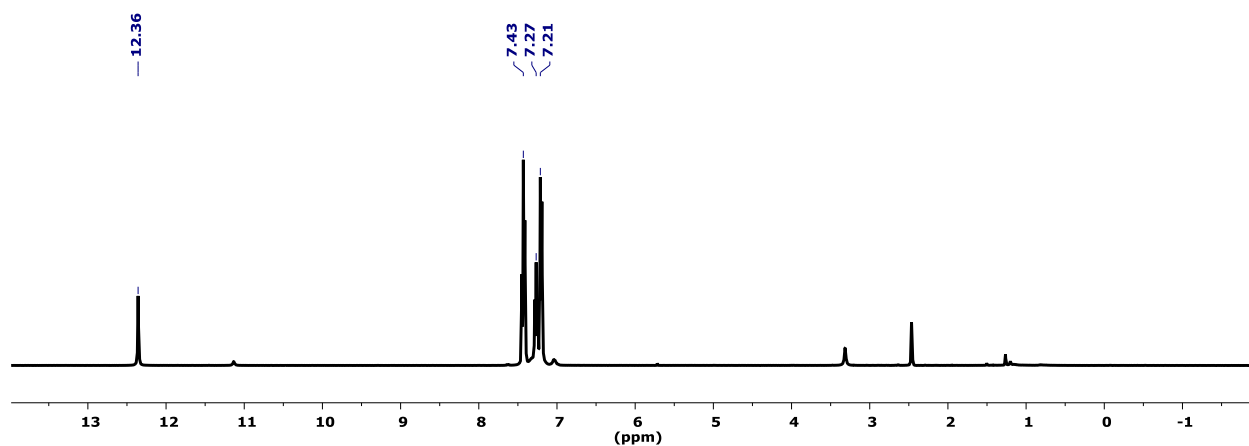


Fig. S131.  $^{13}\text{C}$  NMR Spectrum:

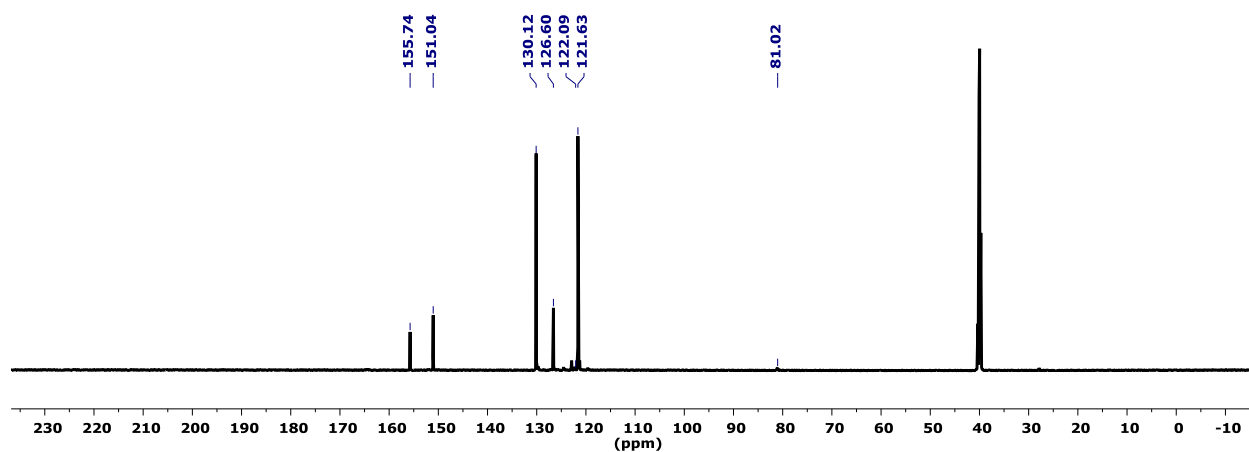
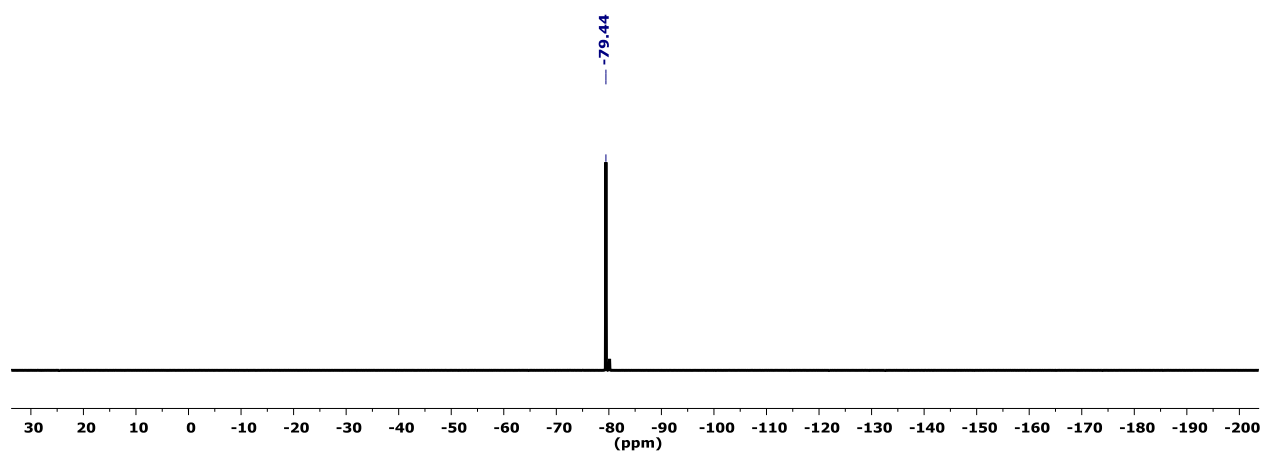
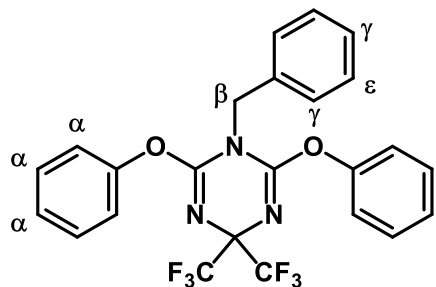


Fig. S132.  $^{19}\text{F}$  NMR Spectrum:





### 2,4-Phenoxy-6,6-bistrifluoromethyl-3-benzyl-triazine

Substrate: 2,4-diphenoxy-6-chlorotriazine. Conditions: Solvent: THF. LA: K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF). 2.0 equivalents K(LA-CF<sub>3</sub>) used. 0.40 mmol substrate. Reaction time: 30 minutes. Quench: 1 equiv. benzyl bromide was added under nitrogen, then the reaction stirred for 16 hours at 25 °C. The reaction mixture was then quenched with 10 mL water. Chromatography conditions: 0-100% Hexane/Ethyl acetate, 16 column volumes, 25 g SiO<sub>2</sub>, flow rate 1 column volume per minute. 108 mg white solid, 55%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.37 (α, 10H, m), 7.24 (ε, 2H, (t, *J*<sub>H-H</sub>=7.4)), 7.11 (γ, 3H, m), 5.21 (β, 2H, s). <sup>13</sup>C-NMR: 153.07, 151.25, 136.53, 129.33, 128.92, 127.95, 126.86, 126.02, 121.59(q, *J*<sub>13C-19F</sub>=288), 121.11, 78.83(p, *J*<sub>13C-19F</sub>=30.3), 46.00. <sup>19</sup>F-NMR: -80.41 (s). HRMS (ES<sup>+</sup>): 493.1229 (M<sup>+</sup>: 493.1225).

**Fig. S133. <sup>1</sup>H NMR Spectrum:**

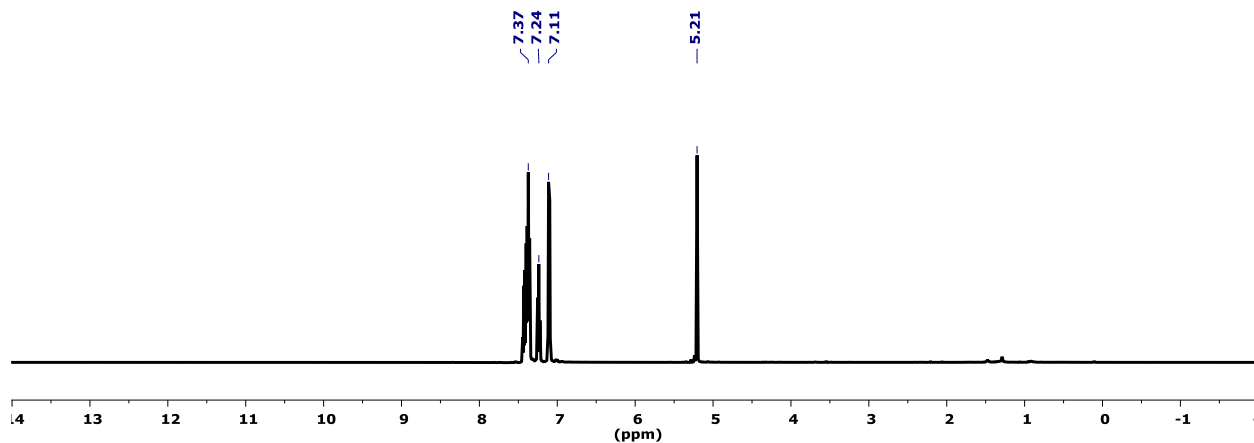




Fig. S134.  $^{13}\text{C}$  NMR Spectrum:

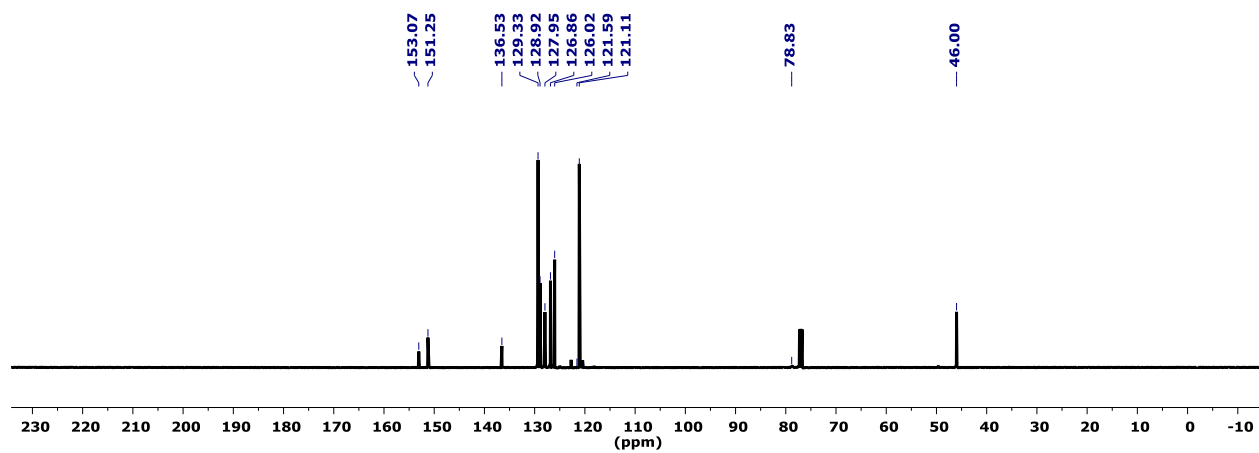
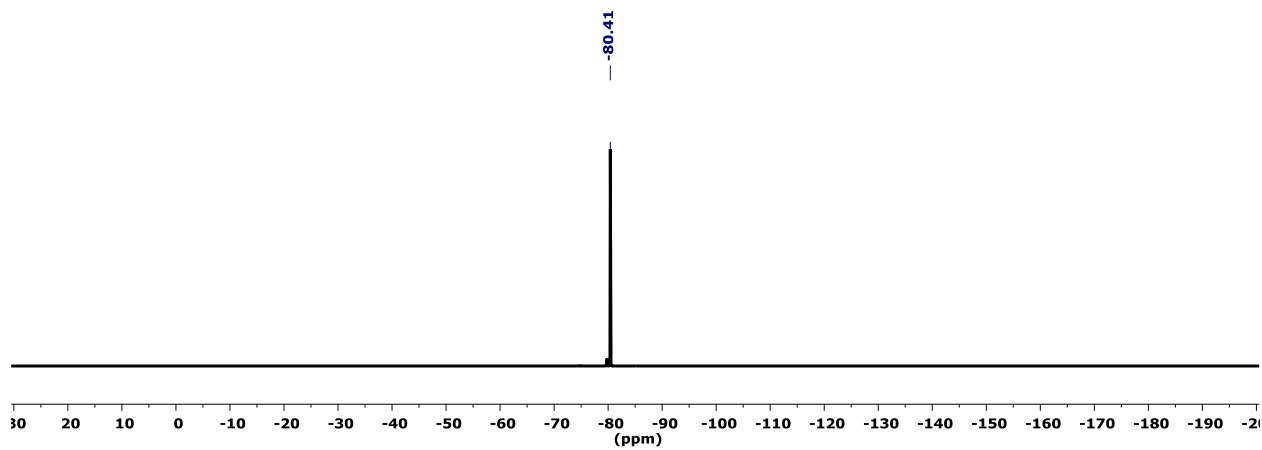
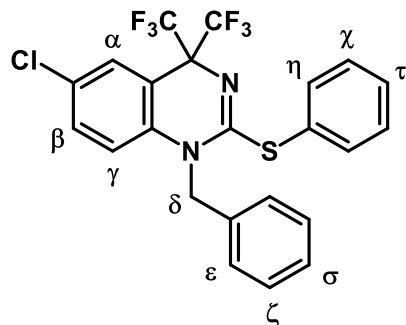


Fig. S135.  $^{19}\text{F}$  NMR Spectrum:





### 1-benzyl-6-chloro-2-(phenylthio)-4,4-bis(trifluoromethyl)-1,4-dihydroquinazoline:

Substrate: Trichloroquinazoline. Experimental: Trichloroquinazoline (0.400 mmol, 93.4 mg) was combined with 2 equivalents K(18-crown-6)(B<sub>3</sub>N<sub>3</sub>Me<sub>6</sub>CF<sub>3</sub>)(THF) (0.800 mmol, 4.00 mL, 0.2M solution in THF) and stirred for 30 minutes at 25 °C. One equivalent benzyl bromide (0.400 mmol, 68.4 mg) was then added, and the mixture stirred at 70 °C for 24 hours. The reaction was then cooled to 25 °C, and 1 equivalent sodium thiophenolate (0.400 mmol, 52.8 mg) was added. The reaction was then heated to 70 °C and stirred for 24 hours. The THF solvent was then removed by rotary evaporation, and the crude solid purified by flash chromatography (conditions: 25g SiO<sub>2</sub> column, 0-50% CH<sub>2</sub>Cl<sub>2</sub>/Hexane over 16 column volumes at a flow rate of 1 column volume per minute) to afford 120 mg of white solid (60%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.55 (η, 2H, overlap), 7.54 (1H, α, overlap), 7.41 (5H, χ, τ, ζ, overlap), 7.34 (1H, σ, (t, *J*<sub>H-H</sub>=7.4)), 7.28 (2H, ε, (d, *J*<sub>H-H</sub>=7.7)), 7.24 (1H, (d(d), (*J*<sub>H-H</sub>=8.8, 2.1)), 6.75 (1H, γ, (d, *J*<sub>H-H</sub>=9.0)), 5.27 (2H, δ, s). <sup>13</sup>C-NMR: 158.99, 136.80, 135.69, 134.95, 130.81, 129.48, 129.37, 129.21, 128.73, 128.08, 127.93, 125.76, 122.46 (q, *J*<sub>13C-19F</sub>=288), 115.67, 113.23, 66.80(p, *J*<sub>13C-19F</sub>=28.7), 50.36. <sup>19</sup>F-NMR: -73.92 (s). HRMS (ESI+): 501.0619 (M+H: 501.0621). A single crystal was obtained for X-Ray diffraction by allowing a concentrated solution in chloroform to slowly evaporate.

Fig. S136. <sup>1</sup>H NMR Spectrum:

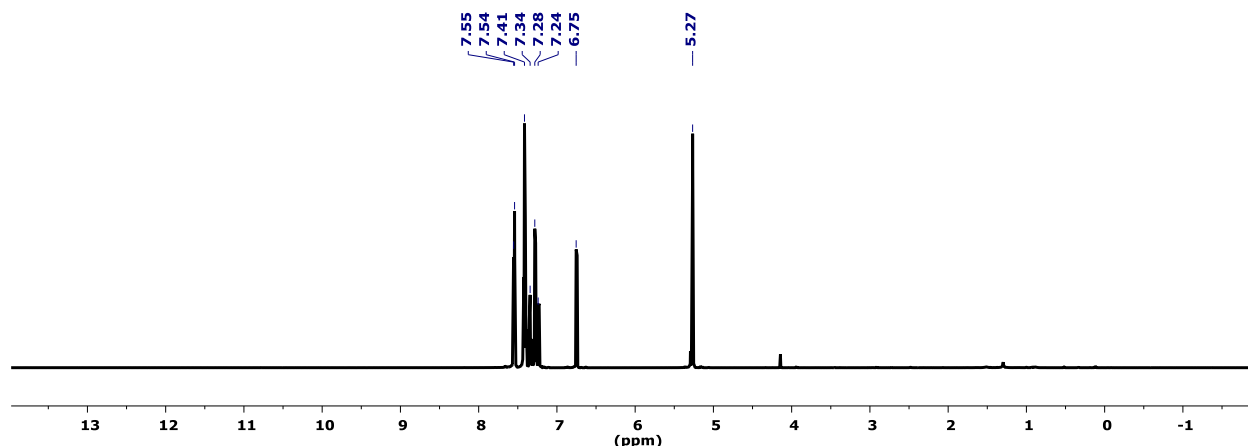


Fig. S137.  $^{13}\text{C}$  NMR Spectrum:

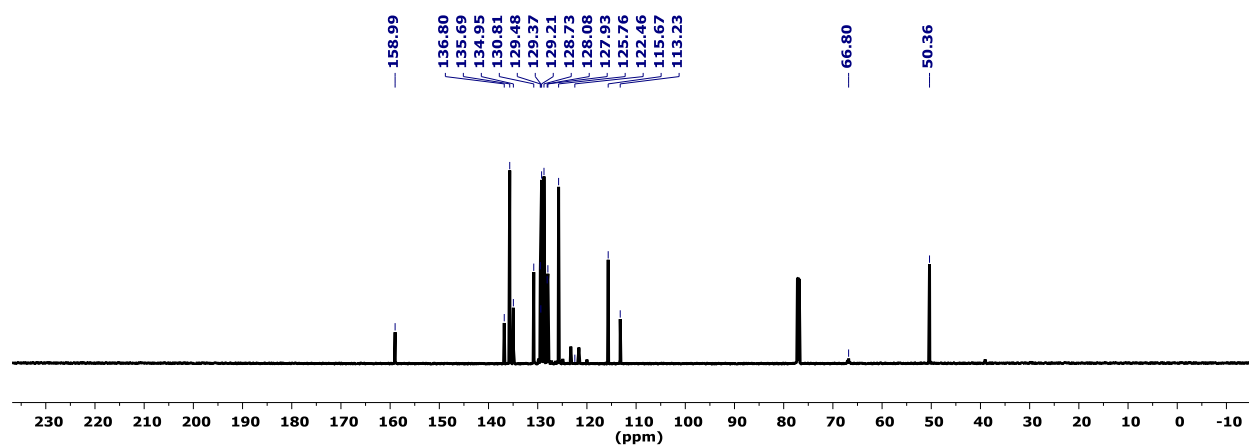


Fig. S138.  $^{19}\text{F}$  NMR Spectrum:

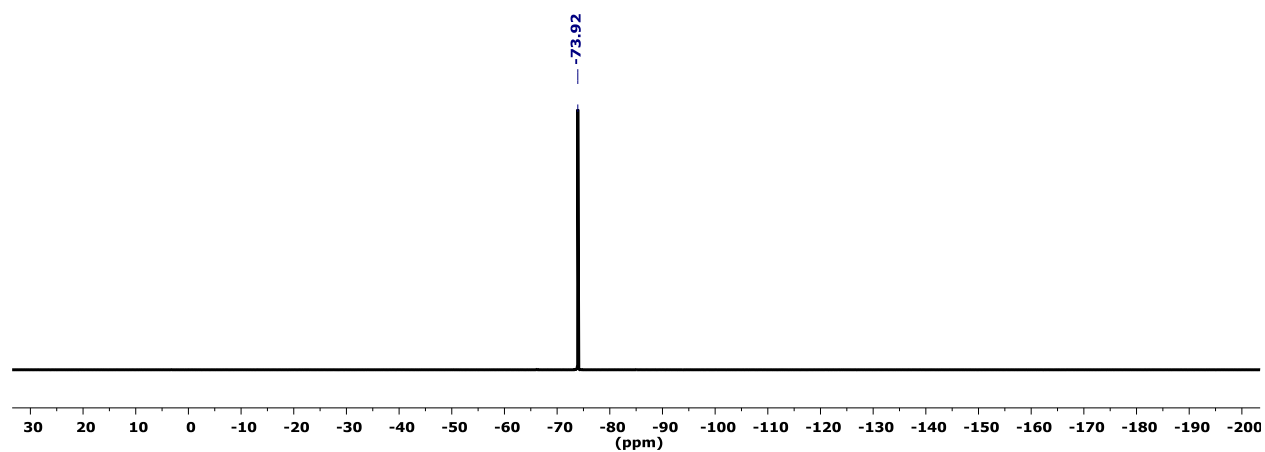


Fig. S139.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:

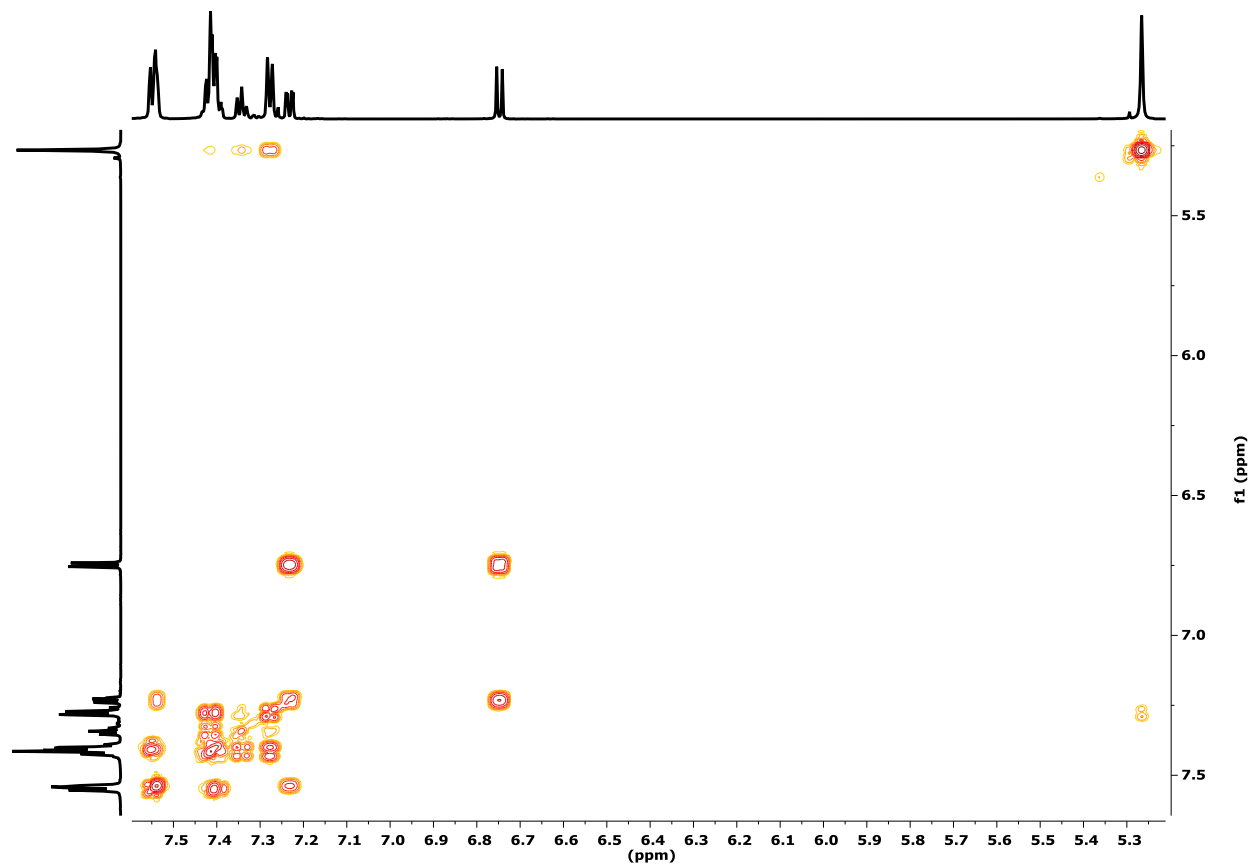


Fig. S140.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

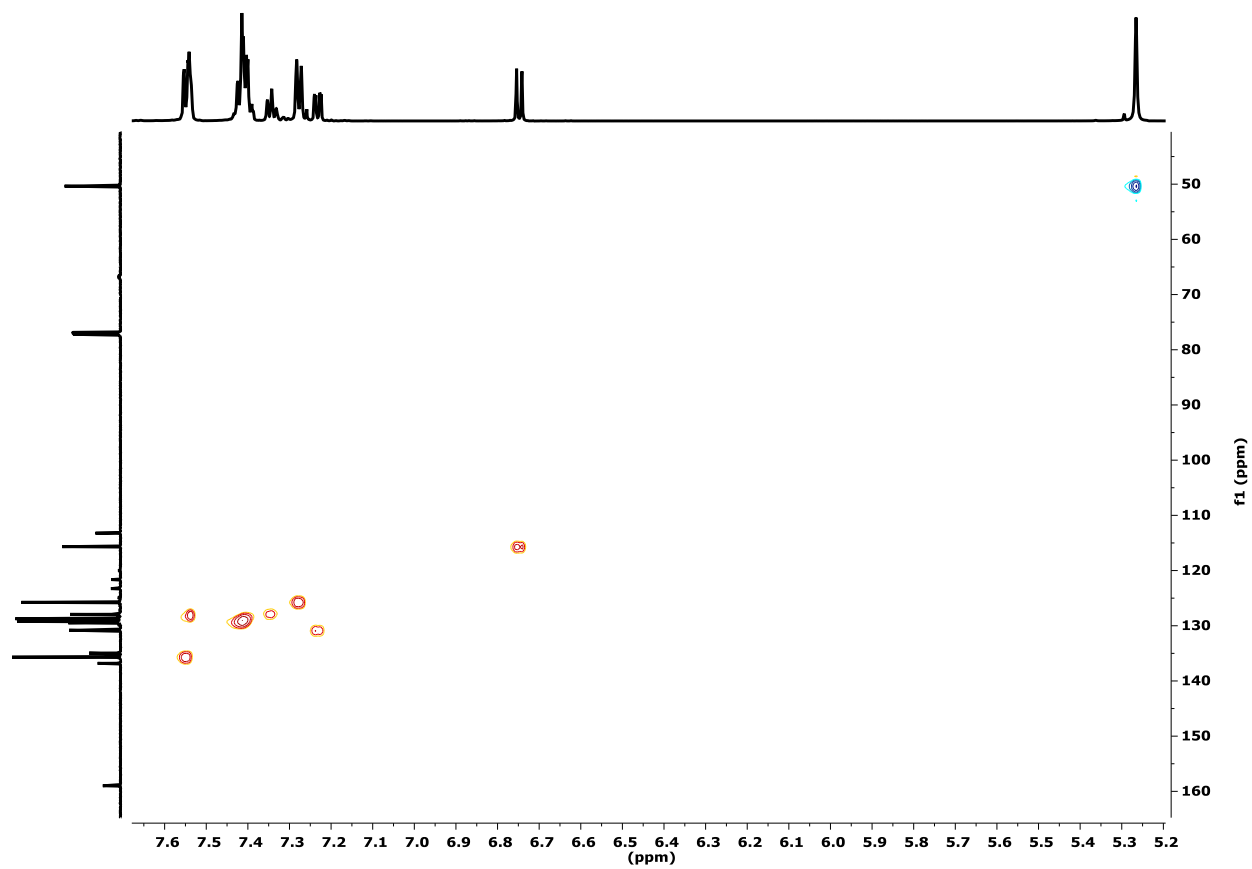
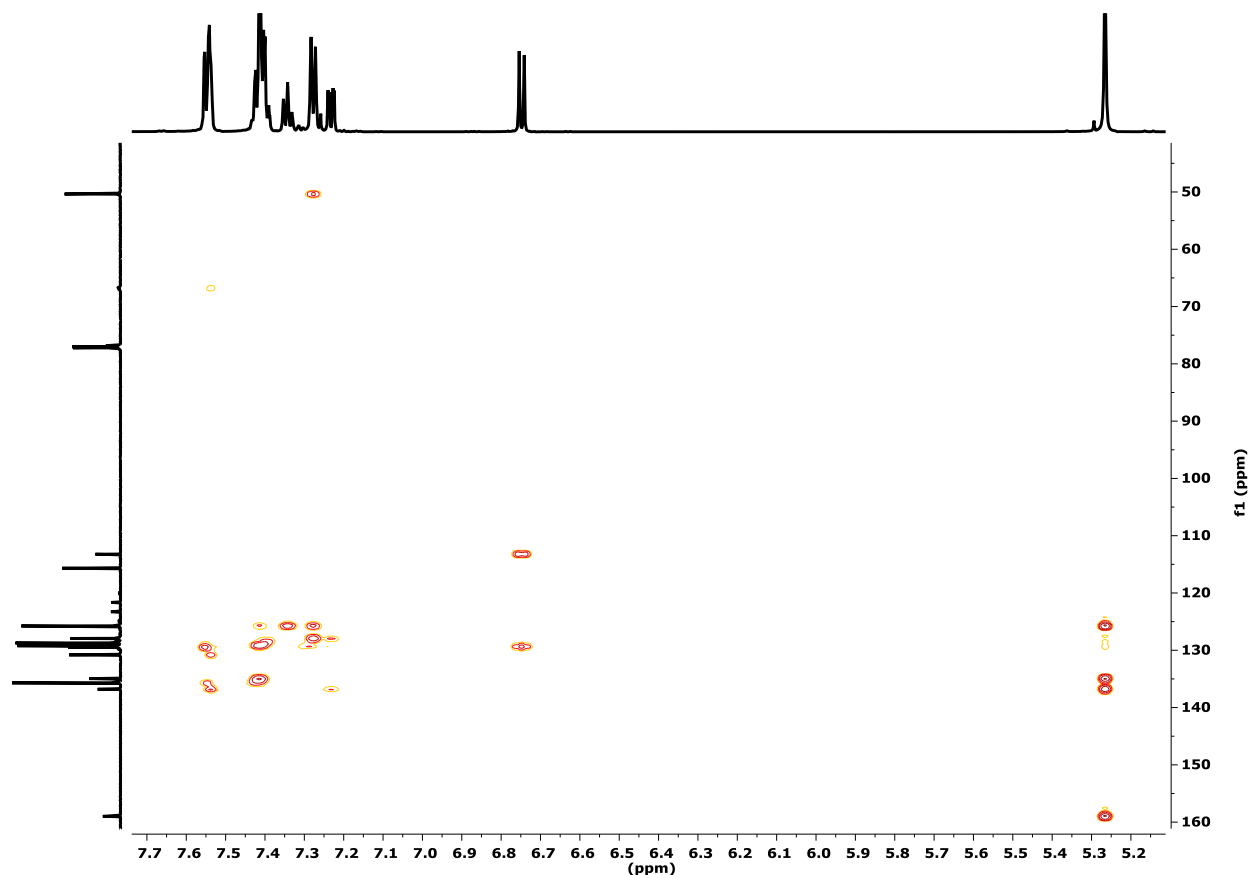
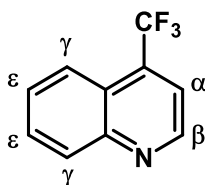


Fig. S141.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:



### Selective 2- or 4- C-H trifluoromethylation of Quinolines

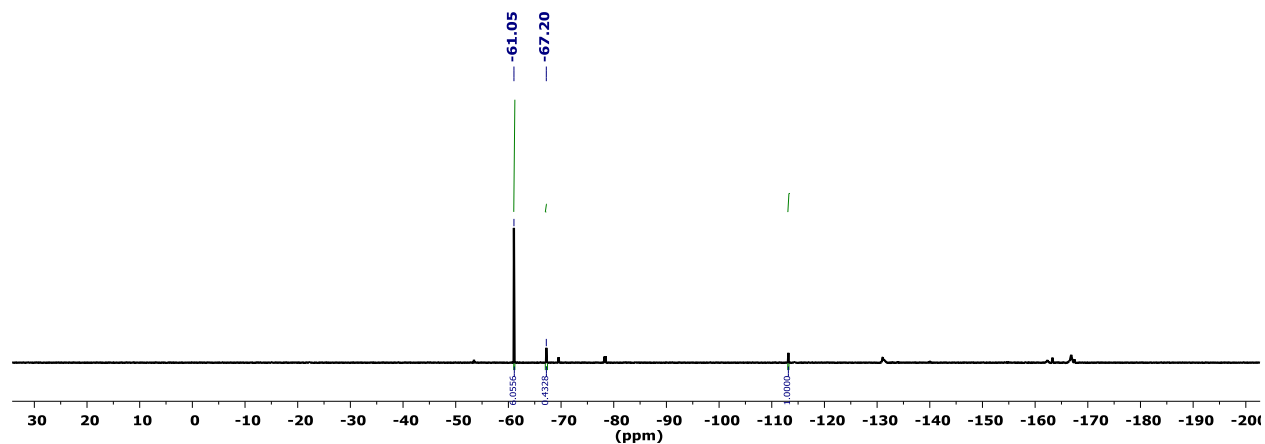


#### 4-Trifluoromethylquinoline:

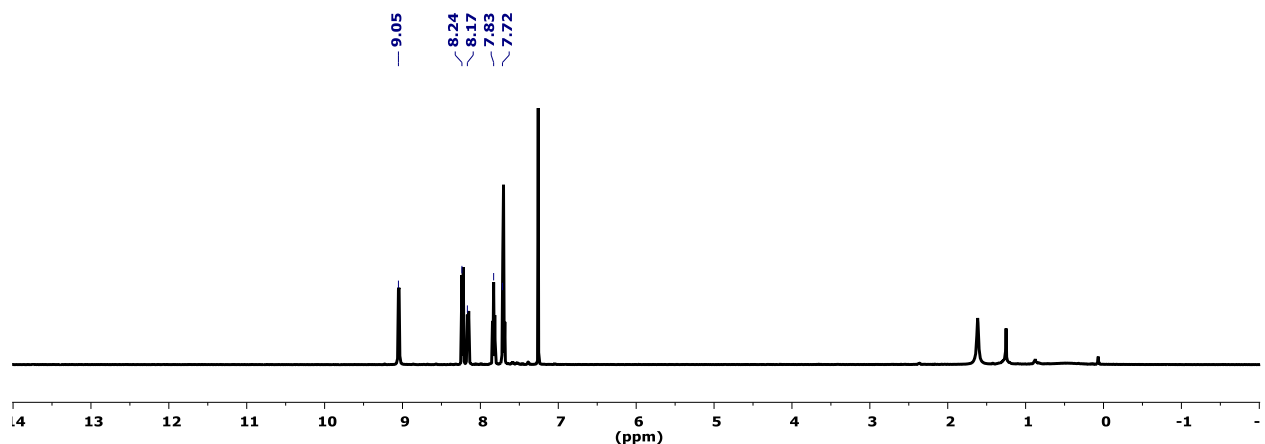
Experimental: Quinoline (51.6 mg, 0.400 mmol) was dissolved in 2 mL THF along with  $\text{B}(\text{C}_6\text{F}_5)_3$  (204 mg, 0.400 mmol). This was cooled to  $-30\text{ }^\circ\text{C}$ , and combined with  $\text{K}(18\text{-crown-}6)(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (2.00 mL, 0.2 M in THF, 0.400 mmol) with stirring. The reaction was allowed to warm to room temperature over 30 minutes, NMR spectra recorded, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (181 mg, 0.800 mmol) was added. *In-situ* NMR spectra showed conversion to the dearomatized *para*, rather than the *ortho*, intermediate in 93% selectivity. The reaction was stirred for 1 hour at room temperature, and the reaction mixture quenched with water. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL), the  $\text{CH}_2\text{Cl}_2$  extract was dried and concentrated, and the crude oil was purified by flash silica chromatography. Chromatography conditions: 0-80% Hexane/Ethyl acetate, 16 column volumes, 50 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 50.2 mg colorless oil, 65%.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 9.05 ( $\beta$ , 1H, (d,

$J_{\text{H-H}}=4.2$ ), 8.24 ( $\gamma$ , 1H, (d,  $J_{\text{H-H}}=8.5$ )), 8.17 ( $\gamma$ , 1H, (d,  $J_{\text{H-H}}=8.5$ )), 7.83 ( $\epsilon$ , 1H, (t,  $J_{\text{H-H}}=7.2$ )), 7.72 ( $\epsilon$ ,  $\alpha$ , 2H, m (overlap)).  $^{13}\text{C-NMR}$ : 149.53, 148.94, 134.28 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=31.8$ ), 130.41, 130.21, 128.32, 124.03 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=2.2$ ), 123.40 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=274.7$ ), 122.95, 117.93 (q,  $J_{^{13}\text{C}-^{19}\text{F}}=5.3$ ).  $^{19}\text{F-NMR}$ : -61.46 (s). HRMS (ESI $^{+}$ ): 198.0523 (M+H: 198.0525).

**Fig. S142. *In-Situ*  $^{19}\text{F}$  NMR Spectrum of *Ortho* and *Para* Dearomatized Intermediates**



**Fig. S143.  $^1\text{H}$  NMR Spectrum:**



**Fig. S144.  $^{13}\text{C}$  NMR Spectrum:**

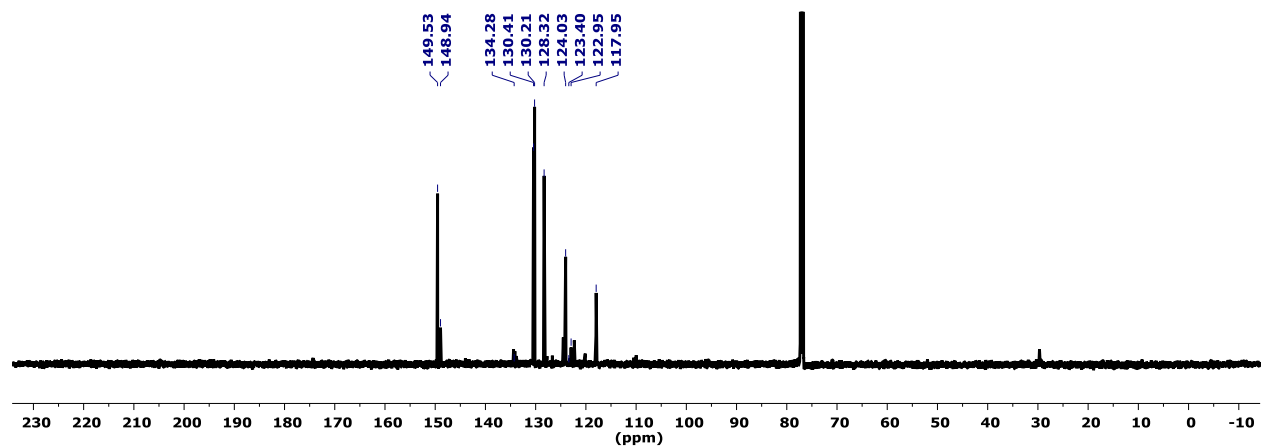
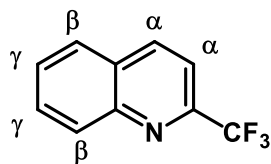
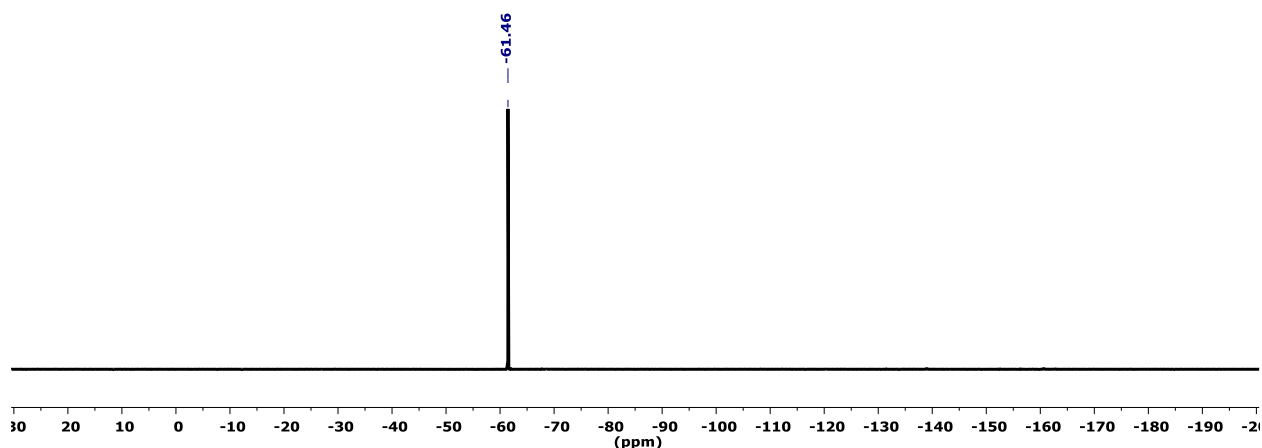


Fig. S145.  $^{19}\text{F}$  NMR Spectrum:



### 2-Trifluoromethylquinoline:

Experimental: Quinoline (51.6 mg, 0.400 mmol) was dissolved in 2 mL THF along with  $\text{BF}_3$  (204 mg, 0.400 mmol). This was cooled to  $-30\text{ }^\circ\text{C}$ , and combined with  $\text{K}(18\text{-crown-}6)(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (2.00 mL, 0.2 M in THF, 0.400 mmol) with stirring. The reaction was allowed to warm to room temperature over 30 minutes, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (181 mg, 0.800 mmol) was added. *In-situ* NMR spectra showed conversion to the dearomatized *ortho*, rather than the *para*, intermediate in 85% selectivity. The reaction was stirred for 1 hour at room temperature, and the reaction mixture was quenched with water. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL), the  $\text{CH}_2\text{Cl}_2$  extract dried and concentrated, and the crude oil purified by flash silica chromatography. Chromatography conditions: 0-80% Hexane/Ethyl acetate, 16 column volumes, 50 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 21.6 mg white solid, 27%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 8.36 ( $\alpha$ , 1H, (d,  $J_{\text{H-H}}=8.5$ )), 8.24 ( $\alpha$ , 1H, (d,  $J_{\text{H-H}}=8.5$ )), 7.91 ( $\beta$ , 1H, (d,  $J_{\text{H-H}}=8.2$ )), 7.82 ( $\gamma$ , 1H, (t,  $J_{\text{H-H}}=7.6$ )), 7.75 ( $\beta$ , 1H, (d,  $J_{\text{H-H}}=8.5$ )), 7.65 ( $\gamma$ , 1H, (t,  $J_{\text{H-H}}=7.6$ )).  $^{13}\text{C-NMR}$ : 147.89 (q,  $J_{13\text{C-}^{19}\text{F}}=34.6$ ), 147.14, 138.10, 130.79, 130.08, 128.83, 128.57, 127.66, 121.55 (q,  $J_{13\text{C-}^{19}\text{F}}=275$ ), 116.75.  $^{19}\text{F-NMR}$ : -67.13 (s). HRMS (ESI+): 198.0522 ( $\text{M}+\text{H}^+$ : 198.0525).



Fig. S146. *In-Situ*  $^{19}\text{F}$  NMR Spectrum of *Ortho* and *Para* Dearomatized Intermediates

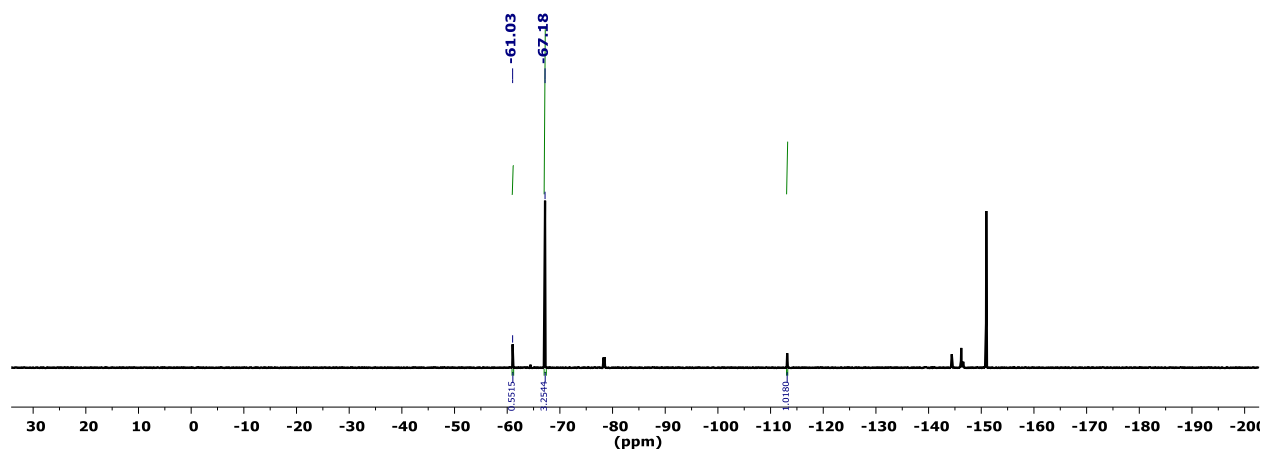


Fig. S147.  $^1\text{H}$  NMR Spectrum:

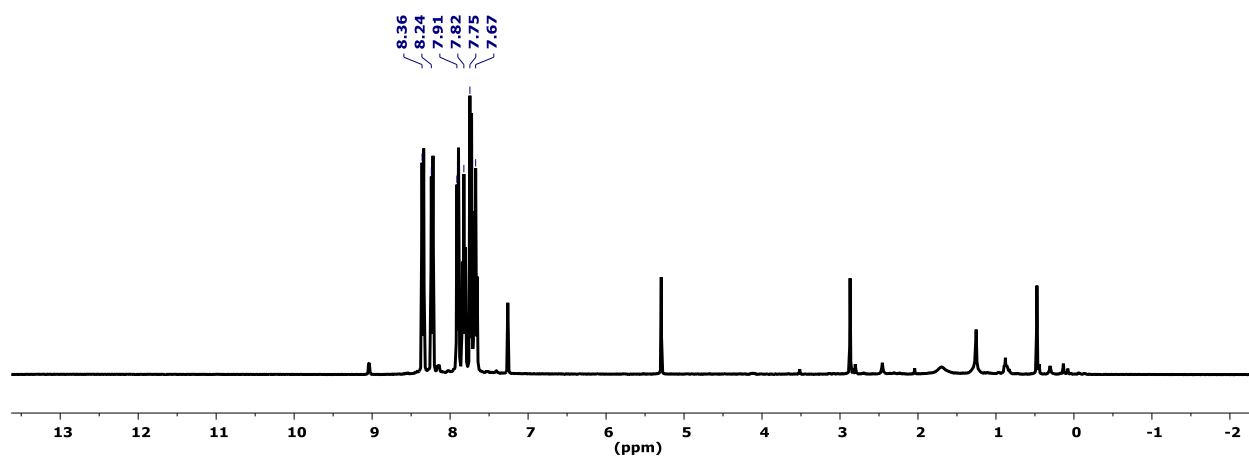


Fig. S148.  $^{13}\text{C}$  NMR Spectrum:

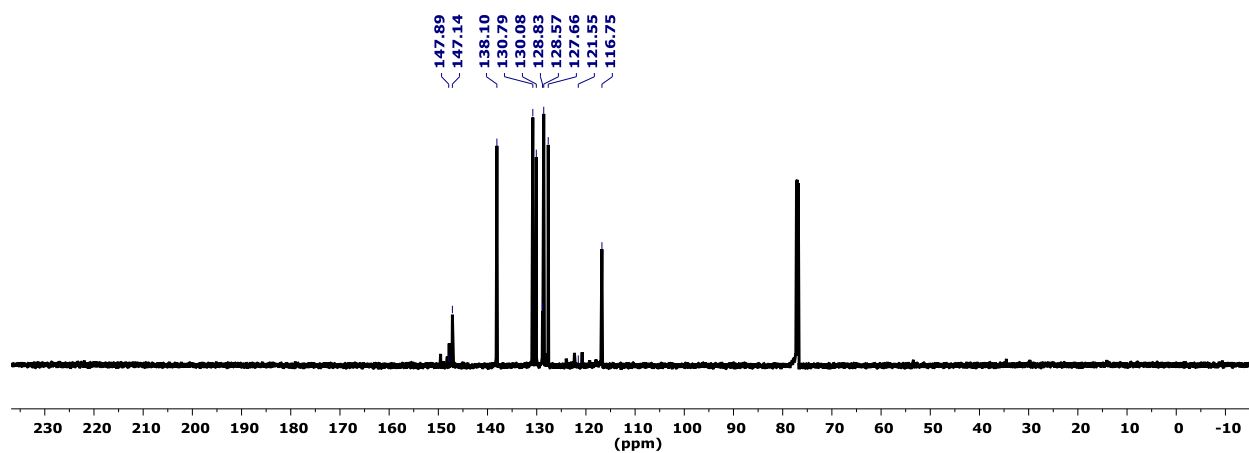
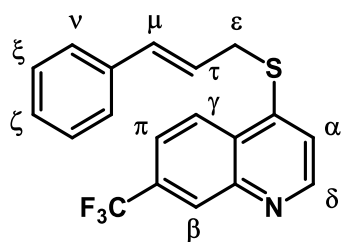
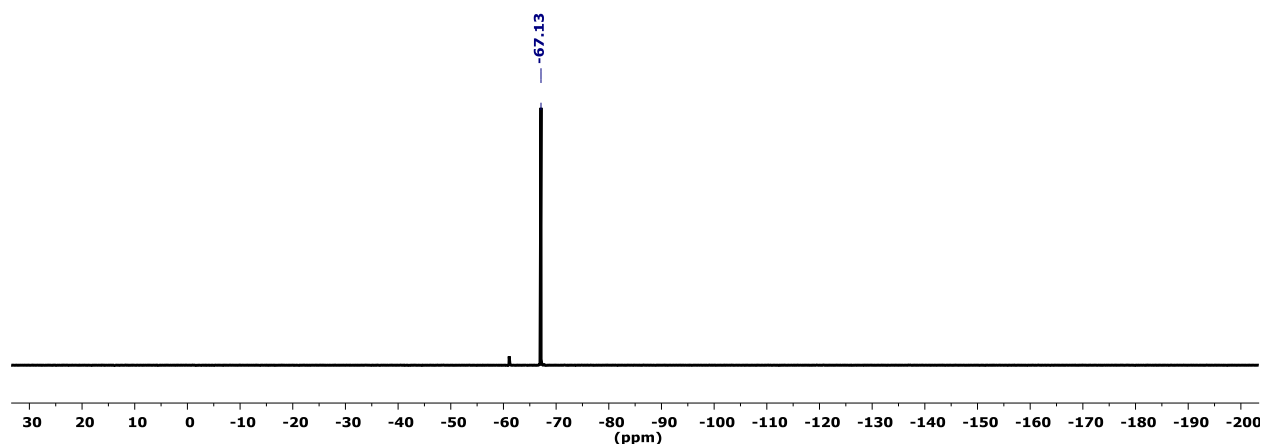


Fig. S149.  $^{19}\text{F}$  NMR Spectrum:



**4-(Cinnamylthio)-2,7-bis(trifluoromethyl)quinoline:**

Experimental: 4-(thio)-7-trifluoromethylquinoline (229 mg, 1.00 mmol) was dissolved in 10 mL THF and combined with K<sub>Ot</sub>Bu (112 mg, 1.00 mmol). After stirring for 5 minutes, cinnamyl bromide was added (197 mg, 1.00 mmol). After five additional minutes, the reaction solvent was evaporated, 10 mL water added, and the product extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL). The  $\text{CH}_2\text{Cl}_2$  extract was then dried and concentrated, and the crude oil purified by flash silica chromatography. Chromatography conditions: 5-40% Hexane/Ethyl Acetate, 16 column volumes, 100 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 280 mg white solid, 81%.  $^1\text{H}$ -NMR ( $\text{CD}_3\text{OD}$ ): 8.75 ( $\delta$ , 1H, (d,  $J_{\text{H-H}}=4.9$ )), 8.37 ( $\gamma$ , 1H, (d,  $J_{\text{H-H}}=8.8$ )), 8.27 ( $\beta$ , 1H, s), 7.81 ( $\pi$ , 1H, (d,  $J_{\text{H-H}}=8.8$ )), 7.63 ( $\alpha$ , 1H, (d,  $J_{\text{H-H}}=4.9$ )), 7.38 ( $\nu$ , 2H, (d,  $J_{\text{H-H}}=7.7$ )), 7.28 ( $\xi$ , 2H, (t,  $J_{\text{H-H}}=7.3$ )), 7.21 ( $\zeta$ , 1H, (t  $J_{\text{H-H}}=7.4$ )), 6.77 ( $\mu$ , 1H, (d,  $J_{\text{H-H}}=15.7$ )), 6.40 ( $\tau$ , 1H, (dt,  $J_{\text{H-H}}=15.7, 7.0$ )), 4.09 ( $\epsilon$ , 2H, (d,  $J_{\text{H-H}}=7.0$ )).  $^{19}\text{F}$ -NMR: -63.11 (2, s), -67.98 (1, s). HRMS (ESI<sup>+</sup>): 346.0872 ( $\text{M}+\text{H}^+$ : 346.0877).

Fig. S150.  $^1\text{H}$  NMR Spectrum:

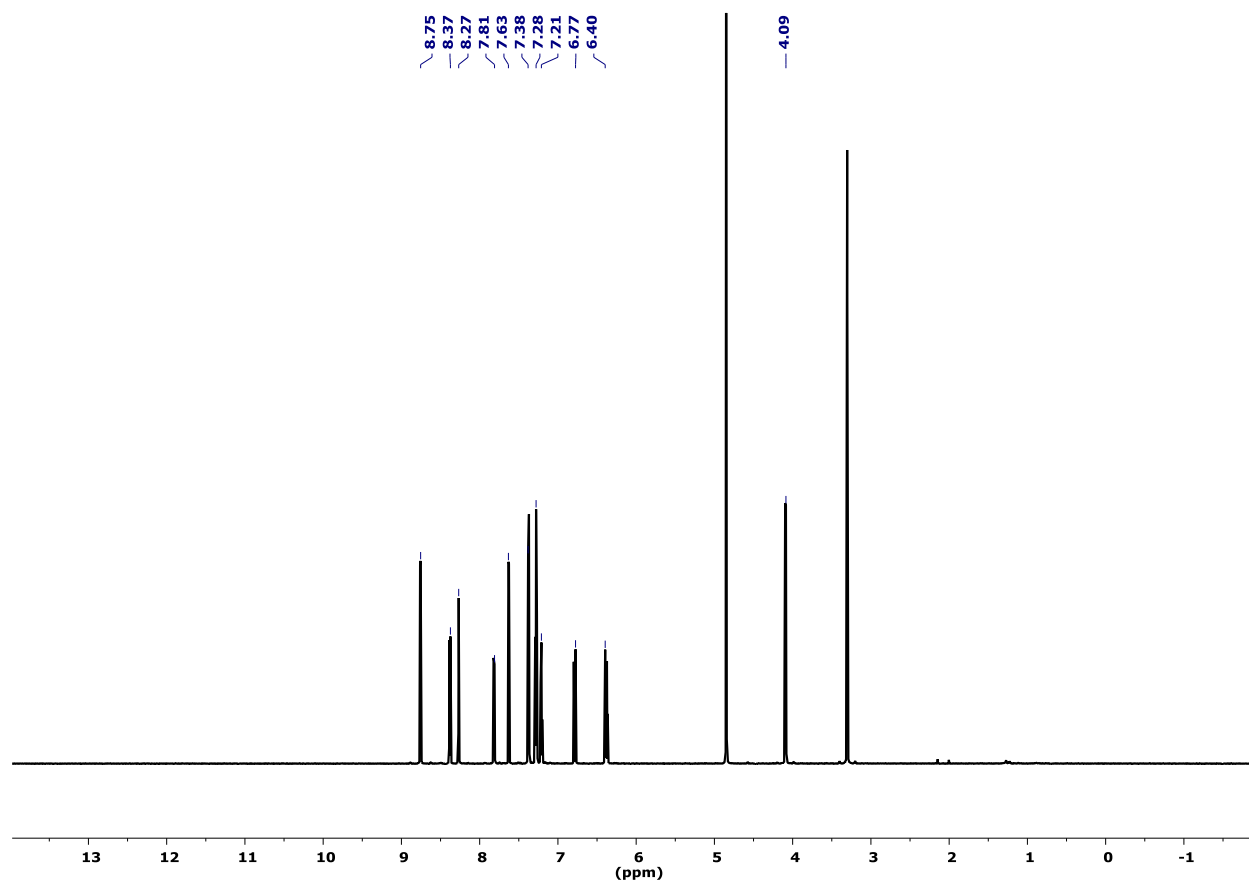


Fig. S151.  $^{13}\text{C}$  NMR Spectrum:

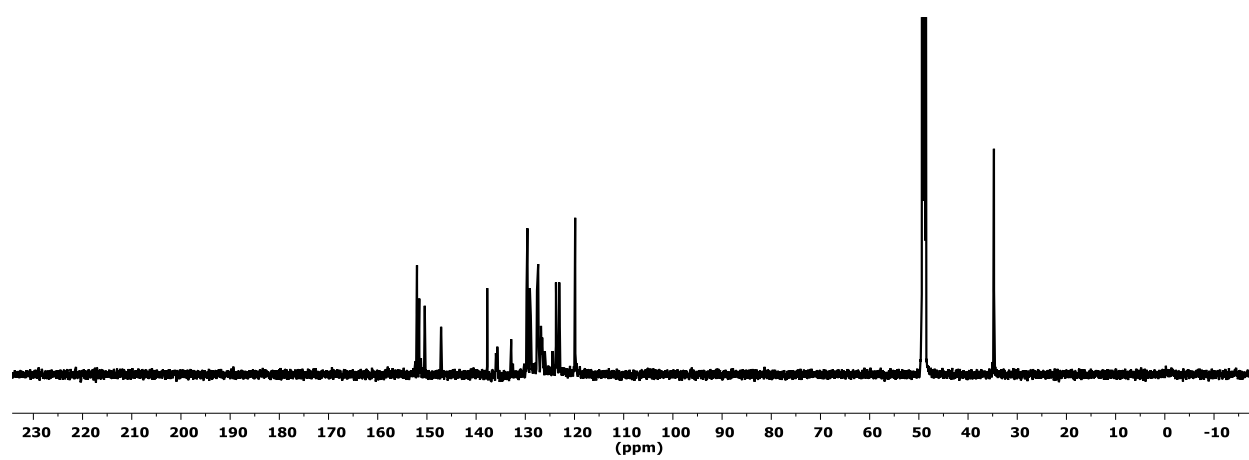


Fig. S152.  $^{19}\text{F}$  NMR Spectrum:

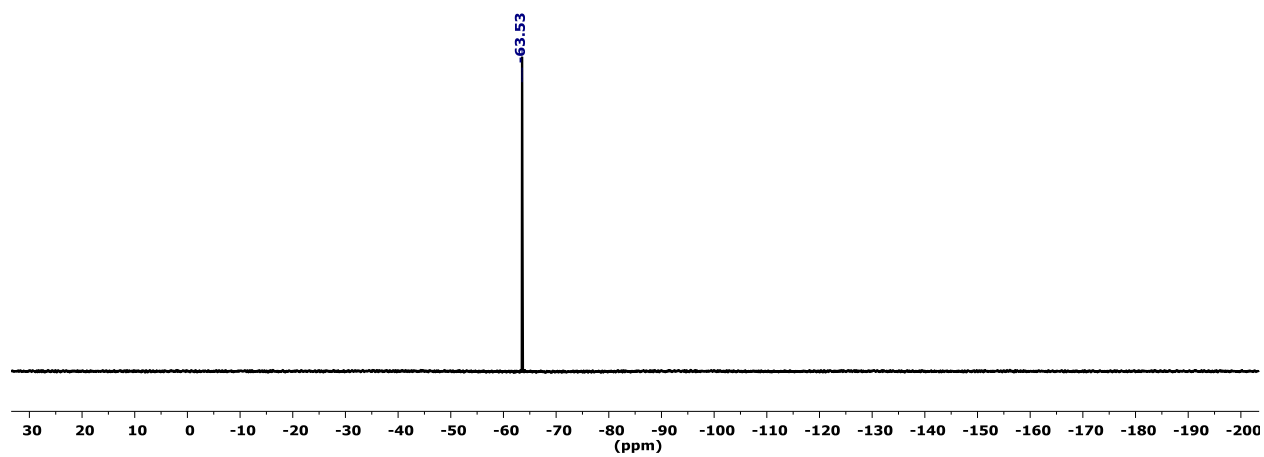


Fig. S153.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:

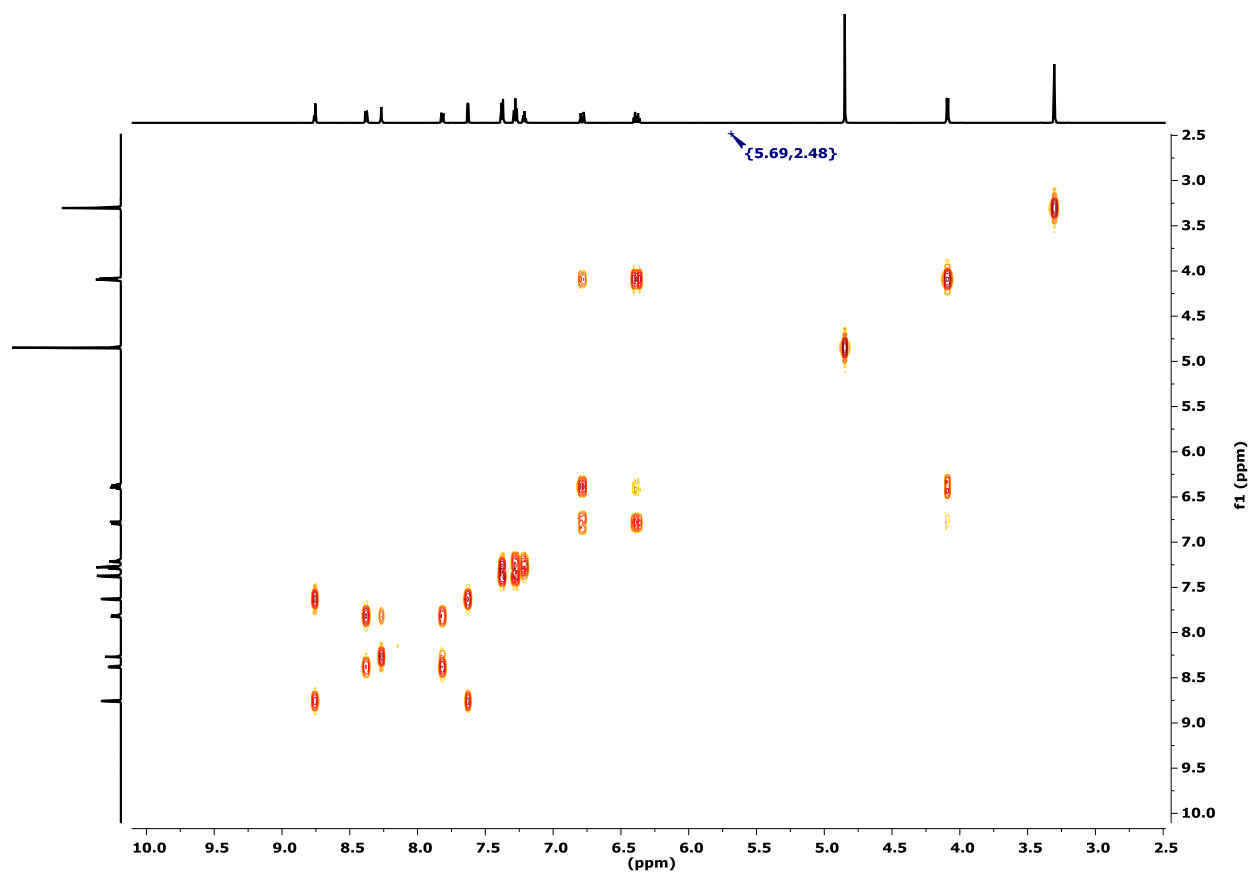


Fig. S154.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

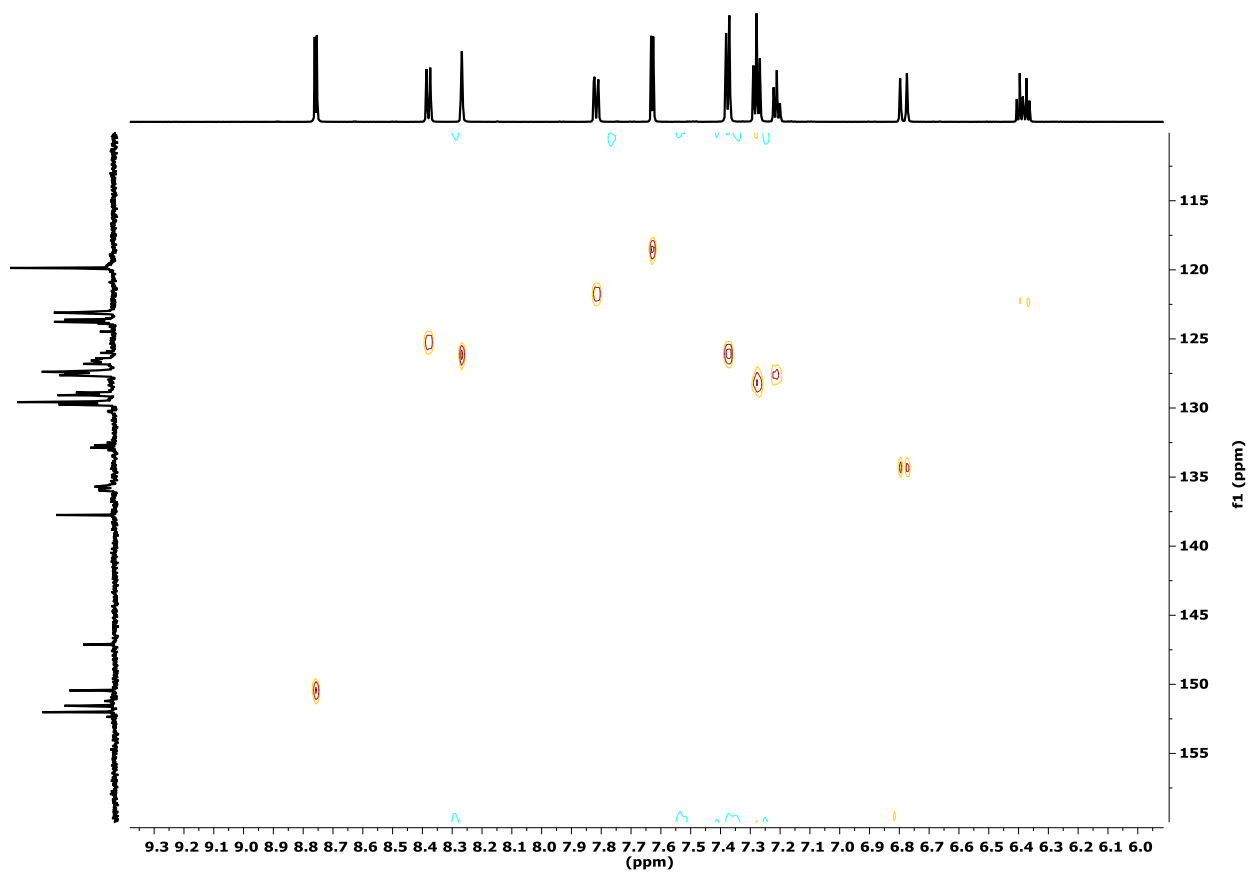
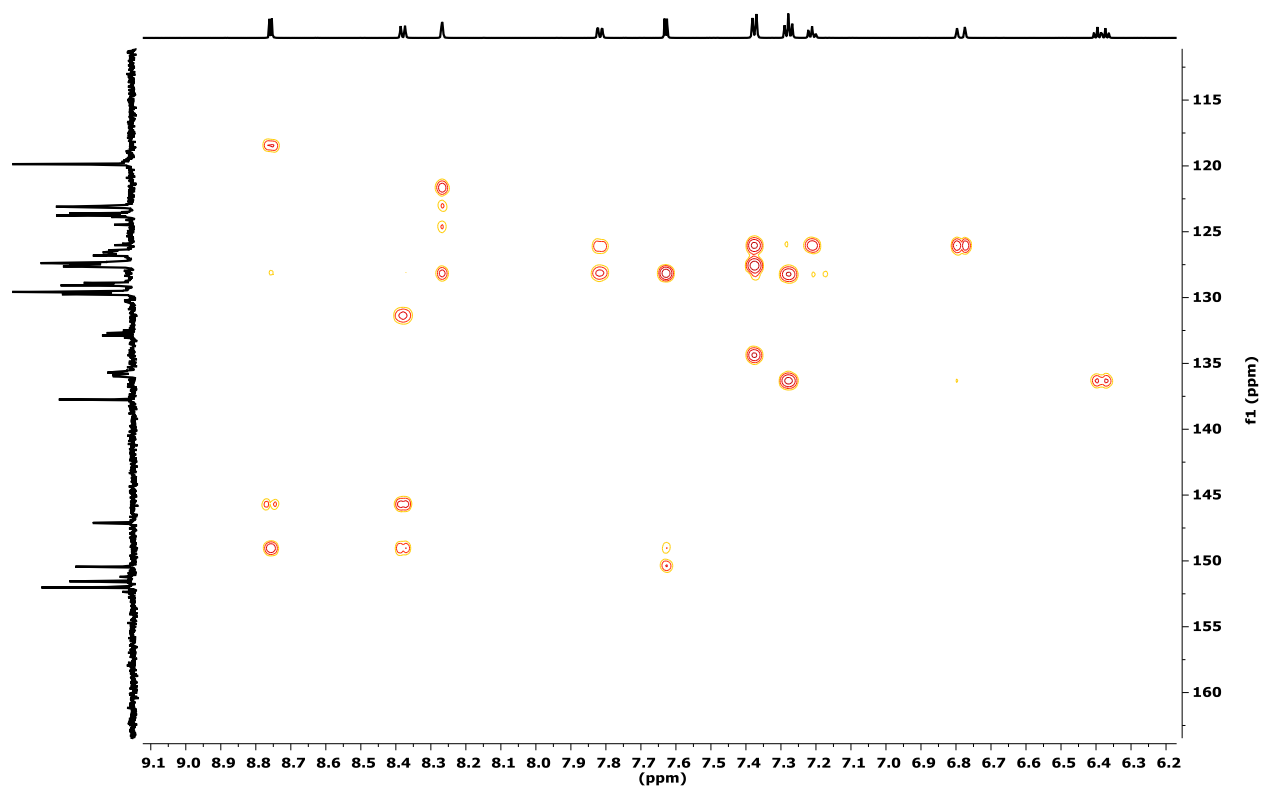
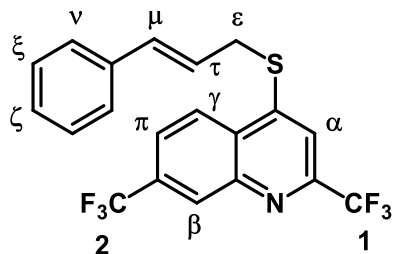


Fig. S155.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:





#### 4-(Cinnamylthio)-2,7-bis(trifluoromethyl)quinoline:

Experimental: 4-(Cinnamylthio)-2,7-bis(trifluoromethyl)quinoline (204 mg, 0.600 mmol) was dissolved in 0.75 mL THF along with  $\text{BF}_3$  (74  $\mu\text{L}$ , 0.600 mmol). This was cooled to  $-30\text{ }^\circ\text{C}$ , and combined with  $\text{K}(18\text{-crown-6})(\text{B}_3\text{N}_3\text{Me}_6\text{CF}_3)(\text{THF})$  (3.00 mL, 0.2 M in THF, 0.600 mmol) with stirring. The reaction was allowed to warm to room temperature over 10 minutes, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (181 mg, 0.800 mmol) was added. After 10 minutes, the solvent was evaporated and the reaction quenched with 5% NaOH solution in water. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 2 mL), the  $\text{CH}_2\text{Cl}_2$  extract dried and concentrated, and the crude oil purified by flash silica chromatography. Chromatography conditions: 0-20% Hexane/DCM, 12 column volumes, 25 g  $\text{SiO}_2$ , flow rate 1 column volume per minute. 91.9 mg white solid, 37%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 8.50 ( $\beta$ , 1H, s), 8.29 ( $\gamma$ , 1H, (d,  $J_{\text{H-H}}=8.8$ )), 7.82 ( $\pi$ , 1H, (d,  $J_{\text{H-H}}=8.8$ )), 7.65 ( $\alpha$ , 1H, s), 7.36 ( $\nu$ , 2H, (d,  $J_{\text{H-H}}=7.5$ )), 7.32 ( $\xi$ , 2H, (t,  $J_{\text{H-H}}=7.6$ )), 7.27 ( $\zeta$ , 1H, (t  $J_{\text{H-H}}=7.6$ )), 6.79 ( $\mu$ , 1H, (d,  $J_{\text{H-H}}=15.7$ )), 6.28 ( $\tau$ , 1H, (dt,  $J_{\text{H-H}}=15.5, 7.1$ )), 4.04 ( $\epsilon$ , 2H, (d,  $J_{\text{H-H}}=7.0$ )).  $^{13}\text{C-NMR}$ : 150.86, 148.22 (q,  $J_{13\text{C}-19\text{F}}=34.7$ ), 145.49, 135.77, 135.59, 132.79 (q,  $J_{13\text{C}-19\text{F}}=33.1$ ), 128.63 (m), 128.61 (m), 128.53 (m), 128.46 (m), 126.62, 124.92 (d,  $J_{13\text{C}-19\text{F}}=24.9$ ), 123.85 (d,  $J_{13\text{C}-19\text{F}}=22$ ), 123.43 (q,  $J_{13\text{C}-19\text{F}}=273$ ), 121.40, 121.23 (q,  $J_{13\text{C}-19\text{F}}=276$ ), 113.18 (q,  $J_{13\text{C}-19\text{F}}=35.2$ ), 34.36.  $^{19}\text{F-NMR}$ : -63.11 (2, s), -67.98 (1, s). HRMS (ESI $^+$ ): 414.0742 ( $\text{M}+\text{H}^+$ : 414.0751).

Fig. S156.  $^1\text{H}$  NMR Spectrum:

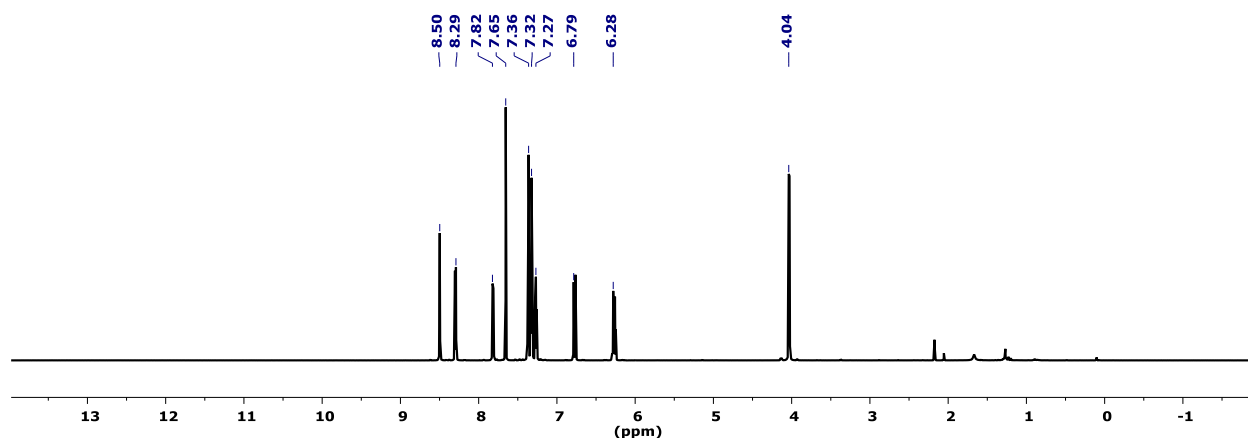


Fig. S157.  $^{13}\text{C}$  NMR Spectrum:

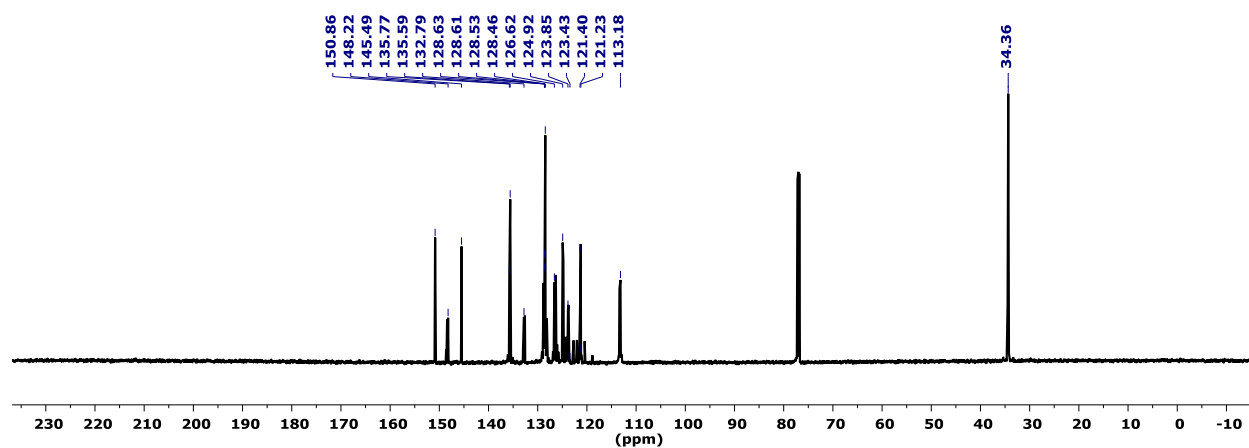


Fig. S158.  $^{19}\text{F}$  NMR Spectrum:

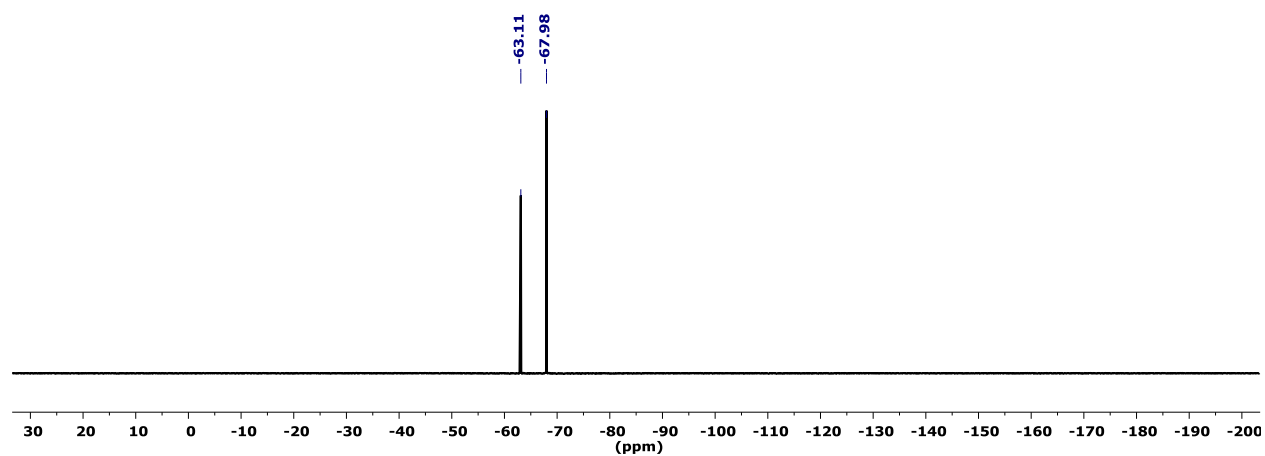




Fig. S159.  $^1\text{H}$ - $^1\text{H}$  gCOSY Spectrum:

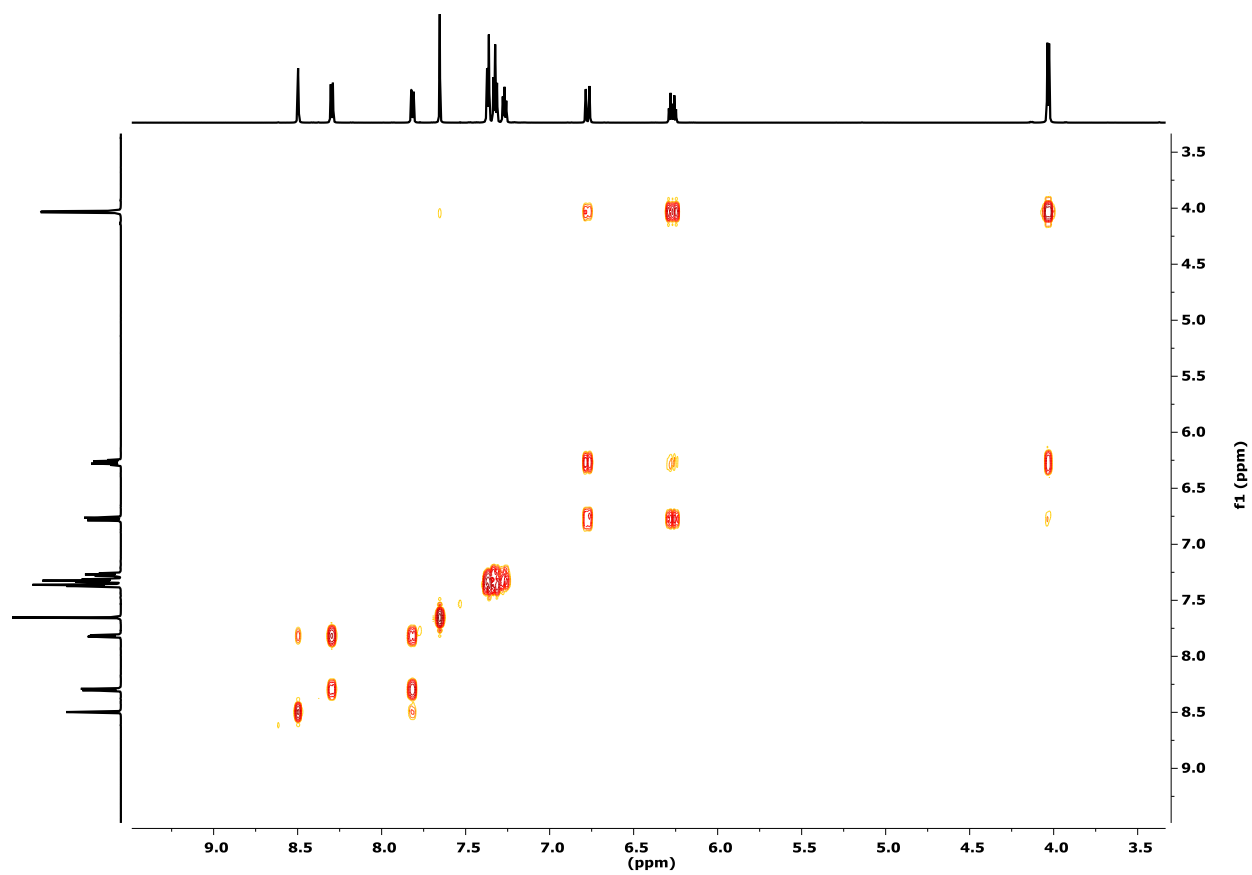


Fig. S160.  $^1\text{H}$ - $^{13}\text{C}$  gHSQCAD Spectrum:

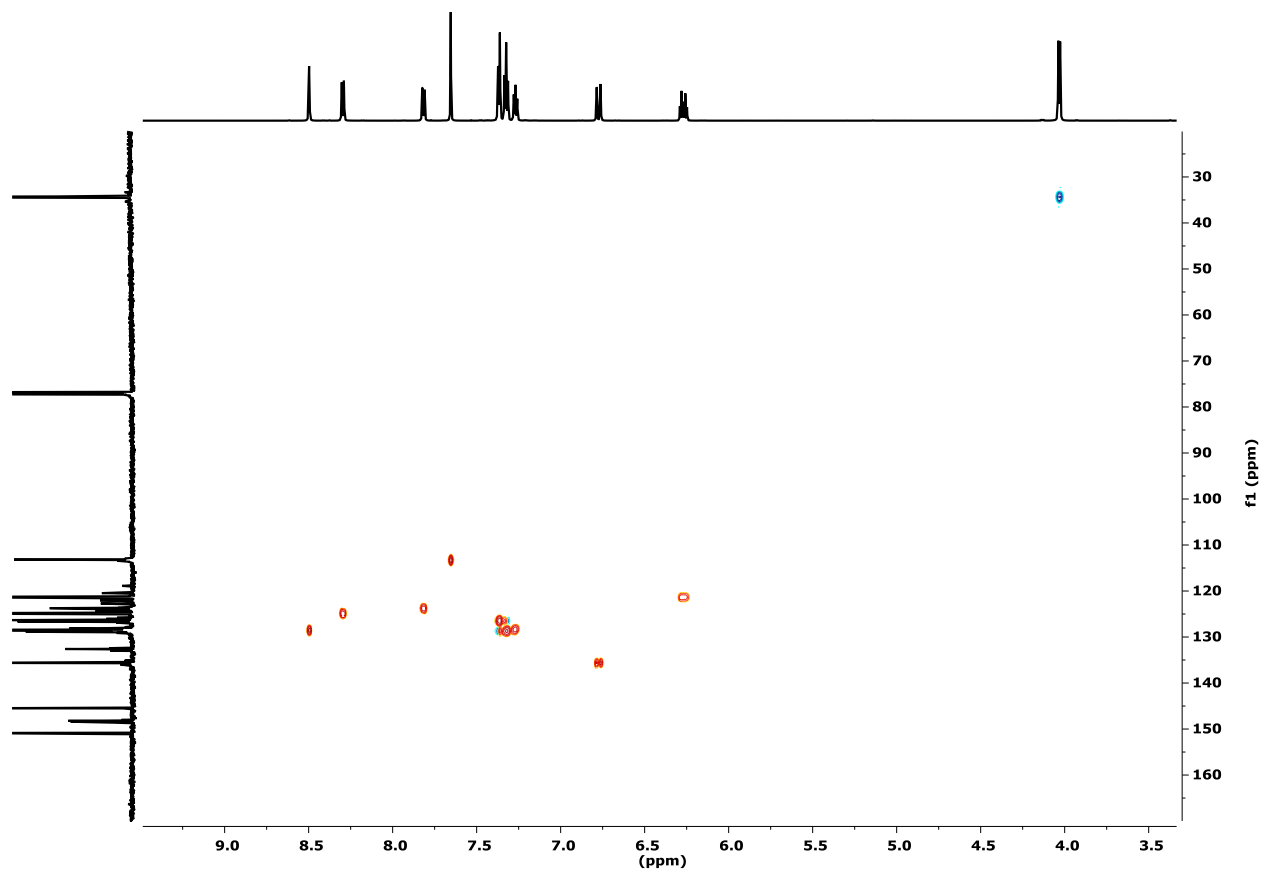
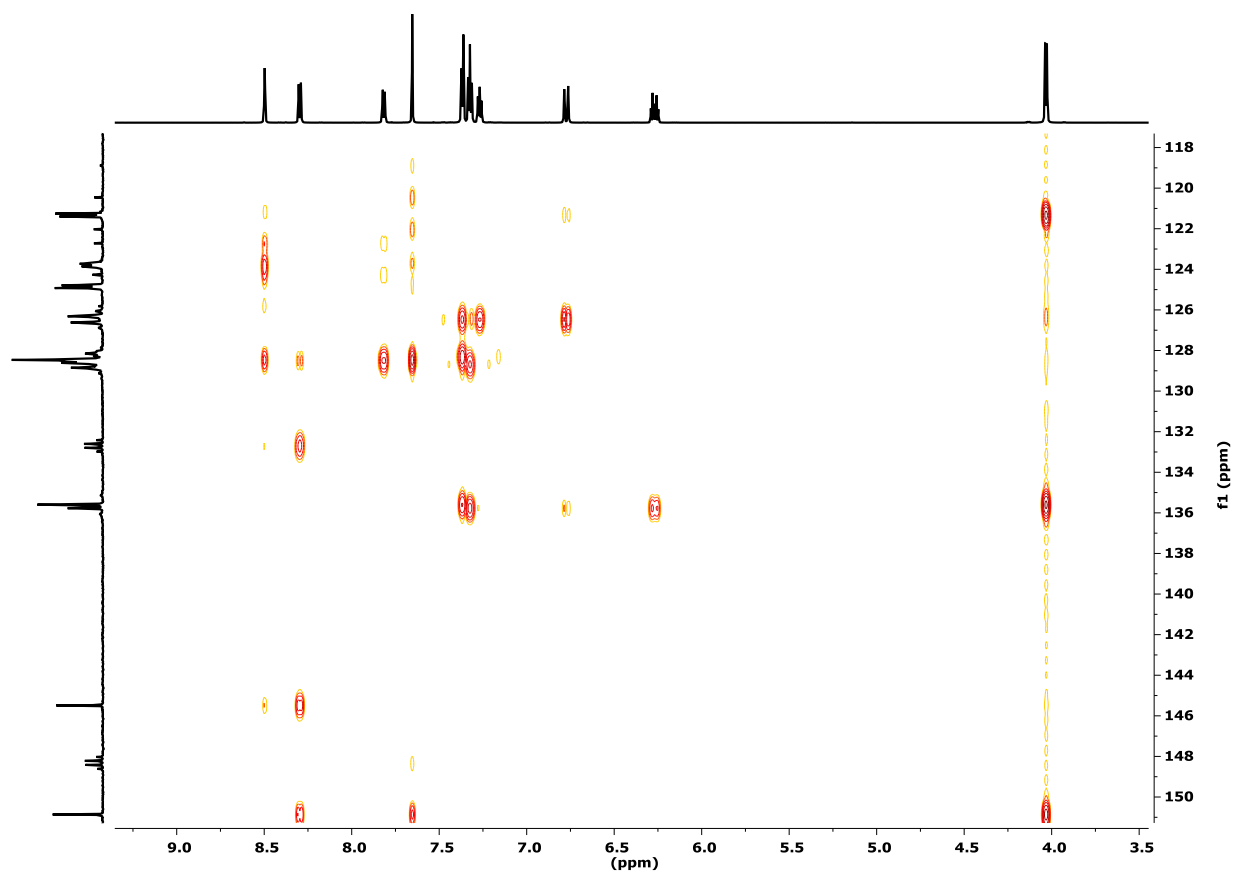
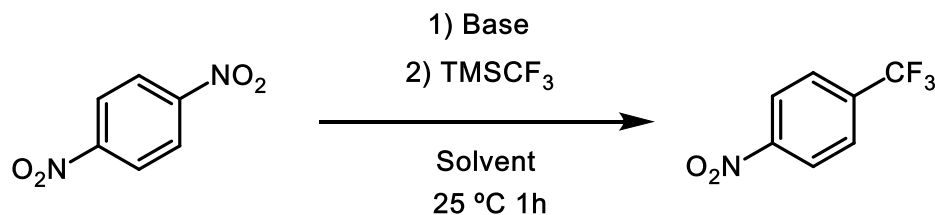


Fig. S161.  $^1\text{H}$ - $^{13}\text{C}$  gHMBCAD Spectrum:



## Comparison Between **2** and SiMe<sub>3</sub>CF<sub>3</sub> in Aromatic Trifluoromethylation

### Optimization of Activator and Solvent for **1a**

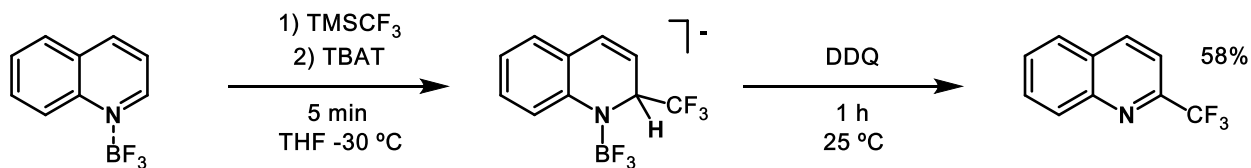


	(NMe <sub>4</sub> )(F)	(NBu <sub>4</sub> )(SiPh <sub>3</sub> F <sub>2</sub> )	KOAc	Cs <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	KO <sup>t</sup> Bu	none
Tol	6.6%	38%	0%	0%	0%	0.8%	0%
THF	19%	53%	0.4%	1.2%	0.4%	1.0%	0%
DMF	20%	60%	55%	30%	32%	6.8%	0.6%
DCM	0.3%	3.2%	0%	0%	0%	0.3%	0%

A stock solution of 1,4-dinitrobenzene (1.0 M) containing (0.1 M) hexamethylbenzene as internal standard were prepared. This was used to prepare 1 mL (0.1 M) reaction mixtures, which were charged with 0.1 mmol of activator and stirred in a 8 mL scintillation vial. SiMe<sub>3</sub>CF<sub>3</sub> (17.72 μL, 0.120 mmol) was added, and the mixture stirred for 1 hour. Yield was determined by GC (FID). A reaction with **2** in place of SiMe<sub>3</sub>CF<sub>3</sub>/activator in THF afforded 58% chemical yield.

### Control Reactions for **1b**

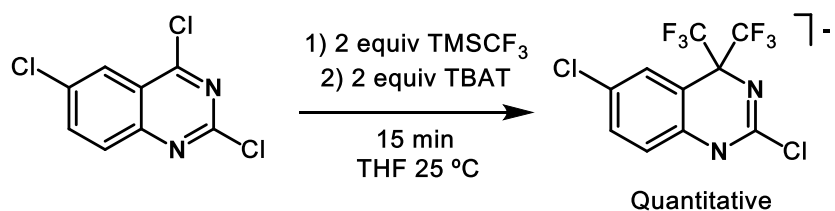
#### **2** Trifluoromethylation of Quinoline Using **1b**



Quinoline (11.82 μL, 0.10 mmol) was dissolved in 1.0 mL of THF and BF<sub>3</sub>•OEt<sub>2</sub> (12.34 μL, 0.10 mmol) added in an 20 mL scintillation vial charged with a small magnetic stirbar and chilled to -30 °C. One equiv. SiMe<sub>3</sub>CF<sub>3</sub> was added as a -30 °C solution (0.12 mL, 1.0 M THF) to the reaction mixture. Solid (NBu<sub>4</sub>)(SiPh<sub>3</sub>F<sub>2</sub>) (53.5 mg, 0.10 mmol) was added and the vial was shaken and kept at -30 °C for 5 minutes. The vial was then warmed to 25 °C and stirred with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (22.7 mg, 0.10 mmol) for 1 hour. Chemical yield (58%) was determined by integration of the product peak against fluorobenzene as internal standard in the <sup>19</sup>F

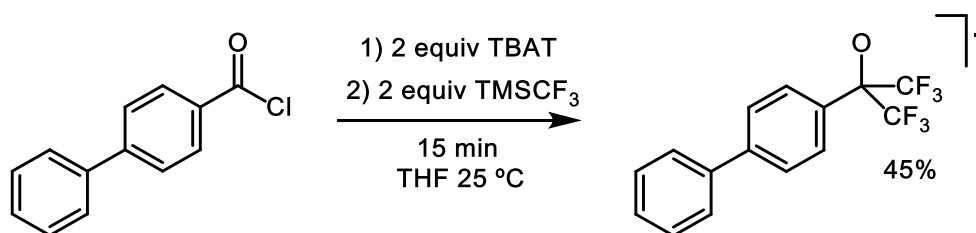
NMR spectrum. When  $(\text{NBu}_4)(\text{SiPh}_3\text{F}_2)$  was added before  $\text{SiMe}_3\text{CF}_3$ , 1% chemical yield was observed. A reaction with **2** in place of  $\text{SiMe}_3\text{CF}_3$  afforded 32% chemical yield.

## 2 Trifluoromethylation of 2,4,6 Trichloro Quinalozine Using 1b



2,4,6 trichloroquinazoline (11.5 mg, 0.05 mmol) was dissolved in 1 mL of THF along with (14.78  $\mu\text{L}$ , 0.10 mmol) of  $\text{SiMe}_3\text{CF}_3$ .  $(\text{NBu}_4)(\text{SiPh}_3\text{F}_2)$  (54.1 mg, 0.10 mmol) was added to the reaction mixture, which was vigorously shaken until homogeneous. Fluorobenzene internal standard was then added and the reaction mixture transferred to an NMR tube for  $^{19}\text{F}$  NMR analysis. The product was formed in quantitative chemical yield. When  $\text{SiMe}_3\text{CF}_3$  was added last, the reaction provided 84% chemical yield. A reaction with **2** in place of  $\text{SiMe}_3\text{CF}_3$  also affords quantitative chemical yield.

## 2 Trifluoromethylation of 4-Phenyl Benzoyl Chloride Using 1b



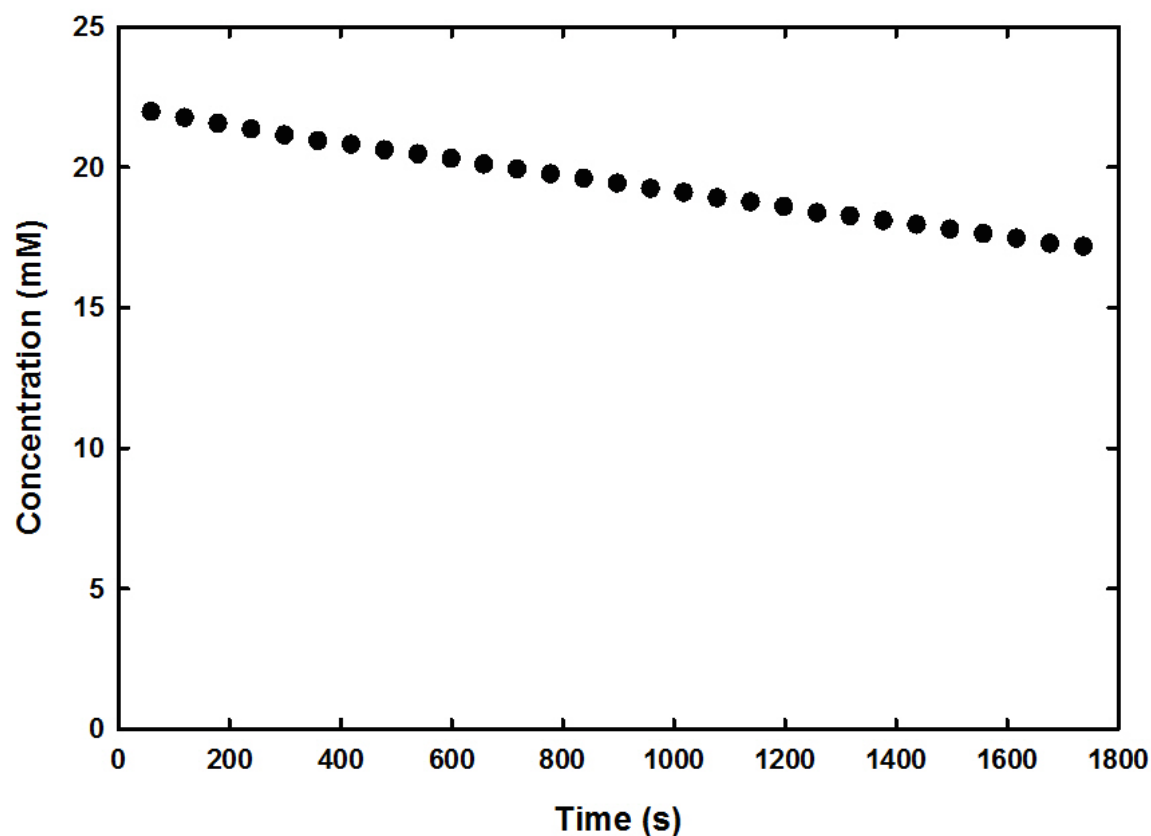
4-Phenyl benzoyl chloride (9.1 mg, 0.05 mmol) was dissolved in 1 mL of THF along with  $(\text{NBu}_4)(\text{SiPh}_3\text{F}_2)$  (53.7 mg, 0.10 mmol) at 25 °C in an 8 mL scintillation vial.  $\text{SiMe}_3\text{CF}_3$  (14.78  $\mu\text{L}$ , 0.10 mmol) was added. The reaction mixture was shaken until homogeneous, charged with fluorobenzene as internal standard and transferred to an NMR tube for  $^{19}\text{F}$  NMR analysis. 45% chemical yield. Adding  $(\text{NBu}_4)(\text{SiPh}_3\text{F}_2)$  last provided 40% chemical yield. Using reagent **2**, the *isolated* yield was 84% (see above).

## Kinetic Measurements of CF<sub>3</sub> Transfer and Decomposition:

### General Protocol:

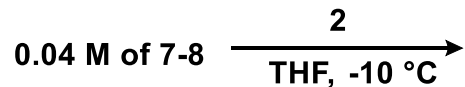
**2** (dispensed as a -78 °C 0.2 M stock solution in THF) was added to a solution of electrophile at -78 °C in a glovebox cold well to give desired concentrations of **2** and electrophile. A 0.7 mL sample of this reaction mixture was then transferred into a -78 °C NMR tube, and the tube rapidly (<30 s) transferred to a -78 °C dry ice acetone bath outside the glovebox. The NMR samples were then inserted into an NMR spectrometer probe held at the desired reaction temperature, and the reaction progress monitored by <sup>19</sup>F NMR spectroscopy (spectra were taken at the rate of 1 spectrum per minute to provide kinetic traces. d1 = 2.5 s, pw = 2.958 μs, aq = 602.931 ms; interpulse delay: 3.1 s). For determination of reactant order, initial rates were measured through a linear fit of the first 30 minutes of the reaction, or of data encompassing the first 15% of reaction progress, whichever was shorter. In all other cases, reaction profiles were obtained through at least 75% reaction progress. Concentrations were calculated by integration against a known concentration of fluorobenzene internal standard.

### Example Linear Fit



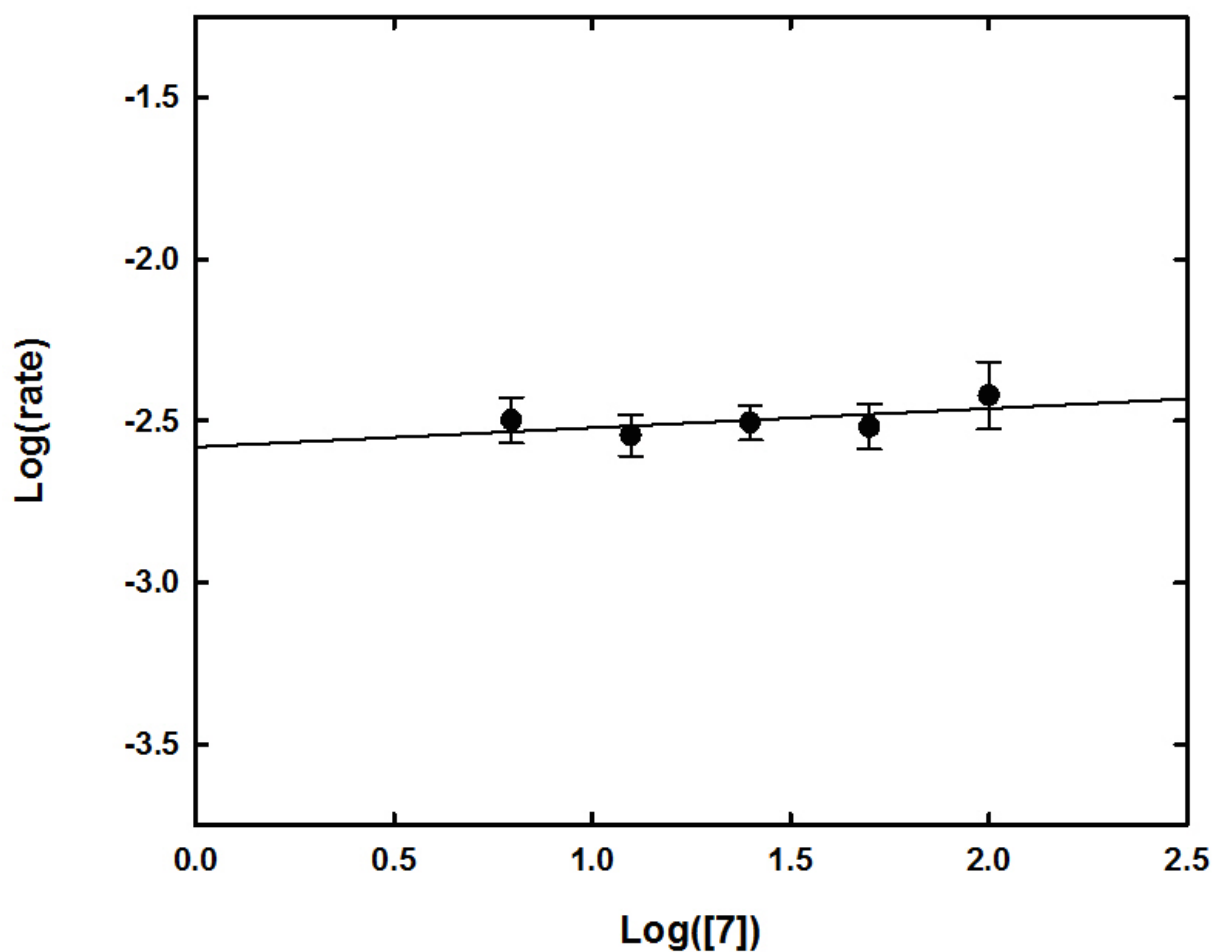
0.025 M **2** with 0.025 M **7** at -10 °C in THF. Rate: -0.00283 mM/s for consumption of **2**; R<sup>2</sup> = 0.999.

Order in 2 for CF<sub>3</sub><sup>-</sup> transfer to 7-8

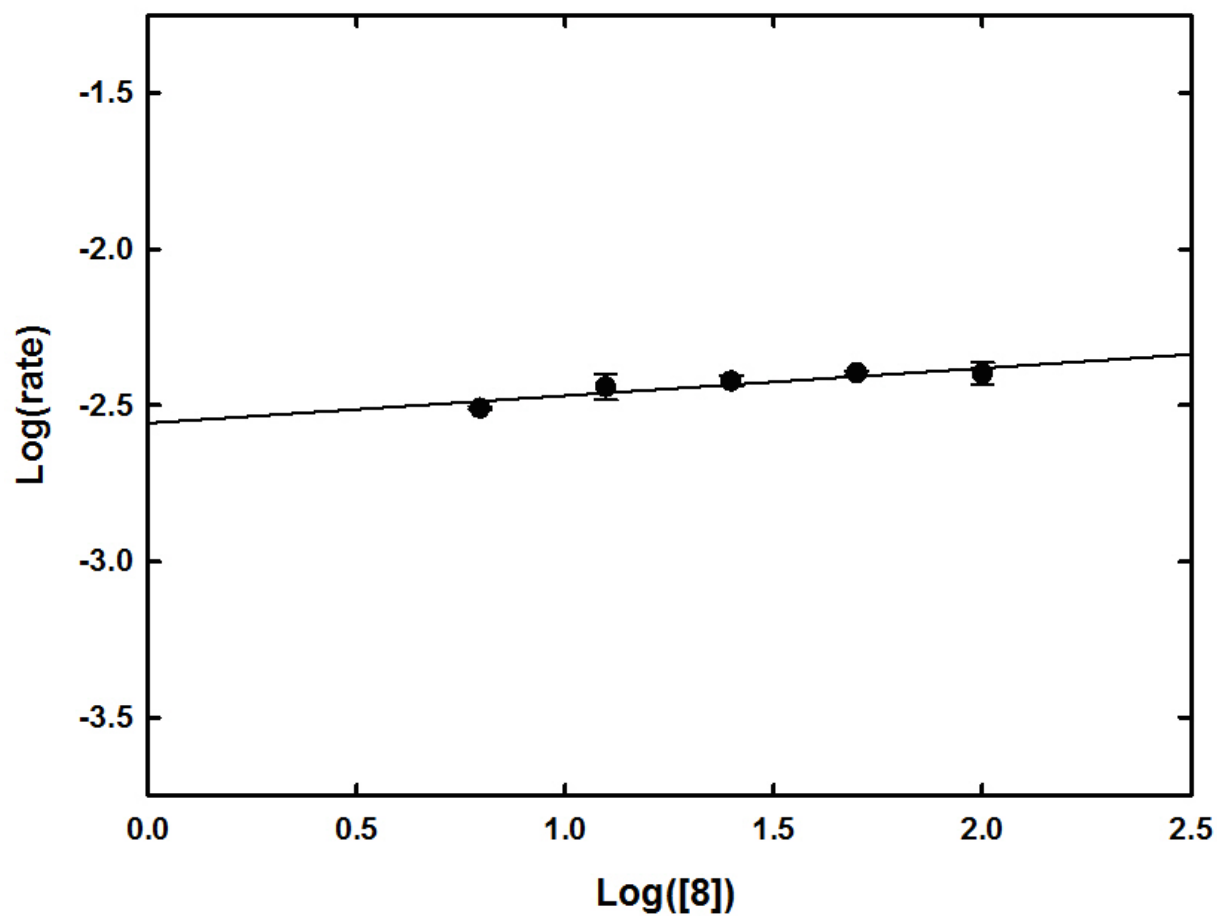


2 (M)	0.16 M	0.08 M	0.04 M	0.02 M	0.01 M
7 (rate)	1.8(3)*10 <sup>-2</sup>	1.0(1)*10 <sup>-2</sup>	5.2(7)*10 <sup>-3</sup>	3.0(3)*10 <sup>-3</sup>	1.5(2)*10 <sup>-3</sup>
8 (rate)	1.9(3)*10 <sup>-2</sup>	1.0(2)*10 <sup>-2</sup>	5.8(1)*10 <sup>-3</sup>	3.5(6)*10 <sup>-3</sup>	1.8(1)*10 <sup>-3</sup>

Reaction rates with uncertainty in mM/s for 0.04 M of electrophile with varying equivalents of 2

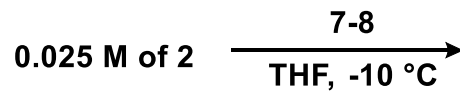


0.025 M 2 (0.00625 M, 0.0125 M, 0.025 M, 0.05 M, 1 M) 7, slope 0.06 following 2 decomposition



0.025 M **2** (0.00625 M, 0.0125 M, 0.025 M, 0.05 M, 1 M) **8** slope 0.09 following **8** consumption

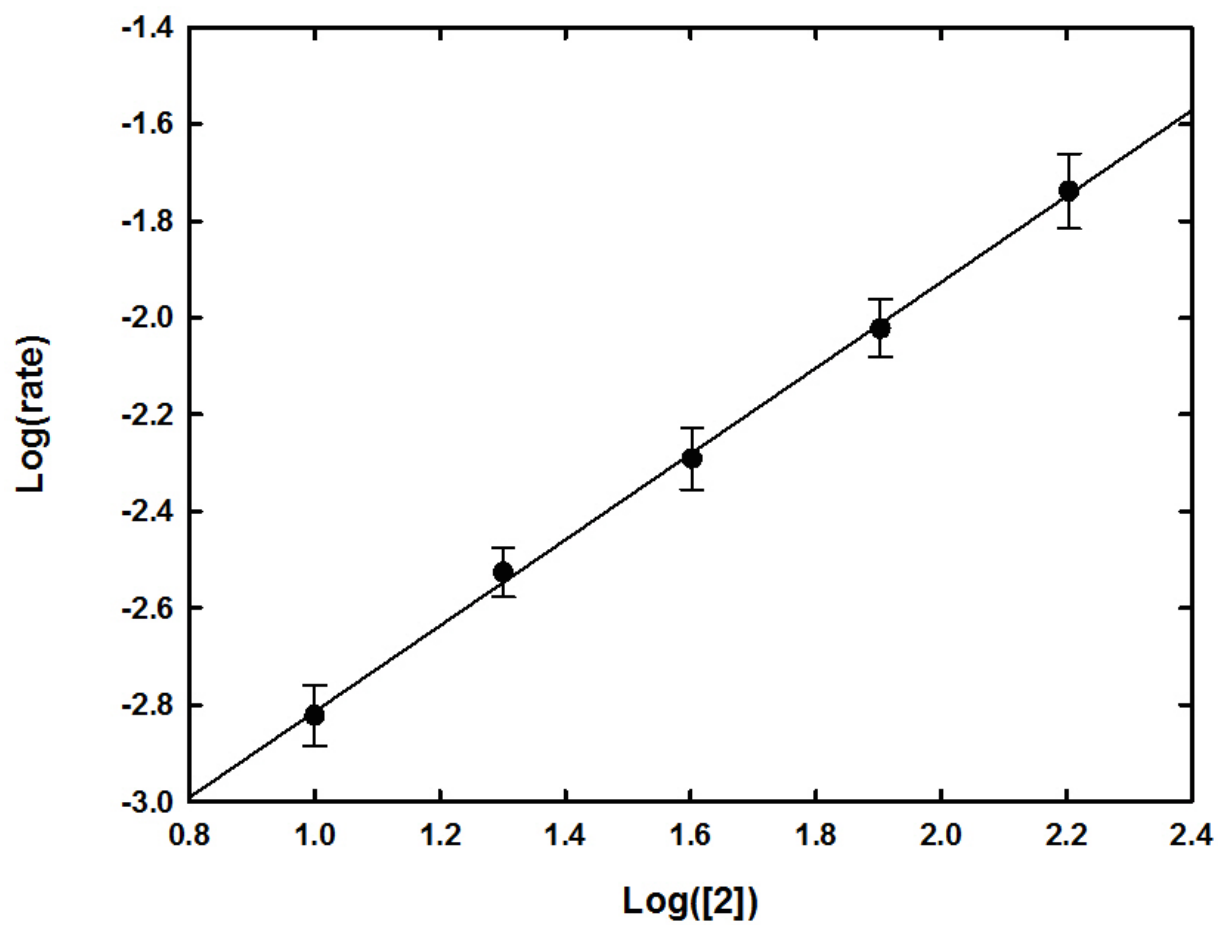
Order in 7-8 for CF<sub>3</sub><sup>-</sup> transfer from **2**



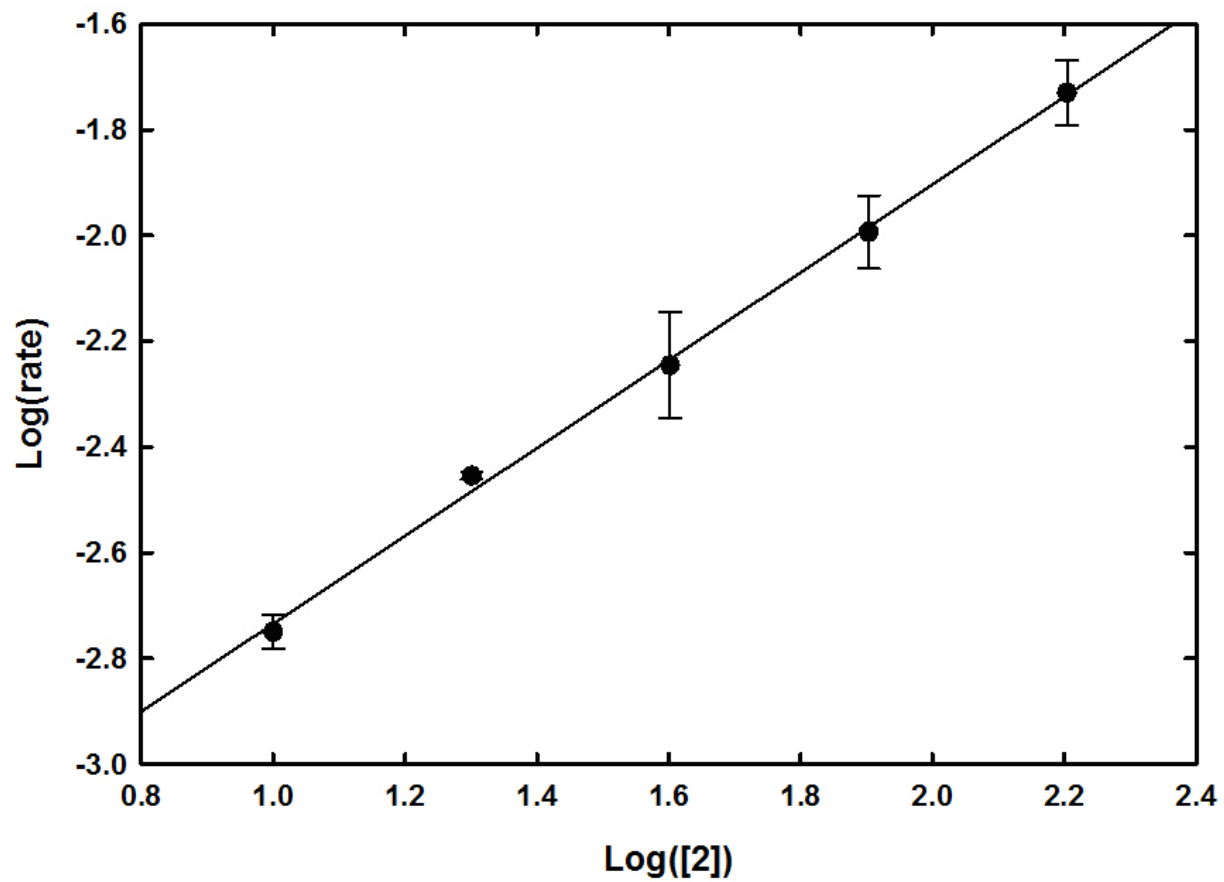
E (M)	0.1 M	0.05 M	0.025 M	0.0125 M	0.00625 M
7 (rate)	4(1)*10 <sup>-3</sup>	3.1(5)*10 <sup>-3</sup>	3.1(4)*10 <sup>-3</sup>	2.9(4)*10 <sup>-3</sup>	3.2(5)*10 <sup>-3</sup>
8 (rate)	4.0(3)*10 <sup>-3</sup>	4.01(7)*10 <sup>-3</sup>	3.8(1)*10 <sup>-3</sup>	3.6(4)*10 <sup>-3</sup>	3.10(3)*10 <sup>-3</sup>

Reaction rates with uncertainty in mM/s for 0.025 M of **2** with varying equivalents of electrophile (electrophile=E)



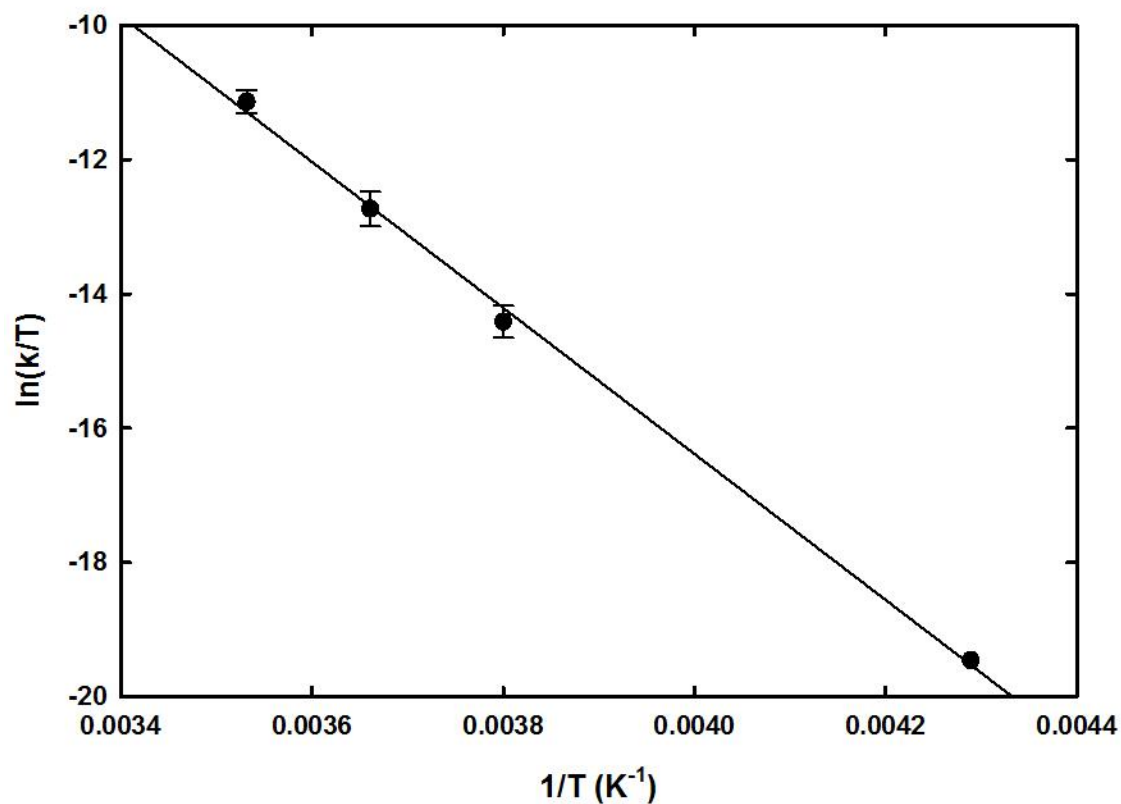


0.04 M **7** (0.01 M, 0.02 M, 0.04M, 0.08 M, 0.16 M) **2**, slope 0.89 following **2** decomposition



0.04 M **8** (0.01 M, 0.02 M, 0.04M, 0.08 M, 0.16 M) **2** slope 0.83 following **8** consumption

### Eyring Plot for 7



**Table of k Values ( $\text{s}^{-1}$ ) for Eyring Analysis**

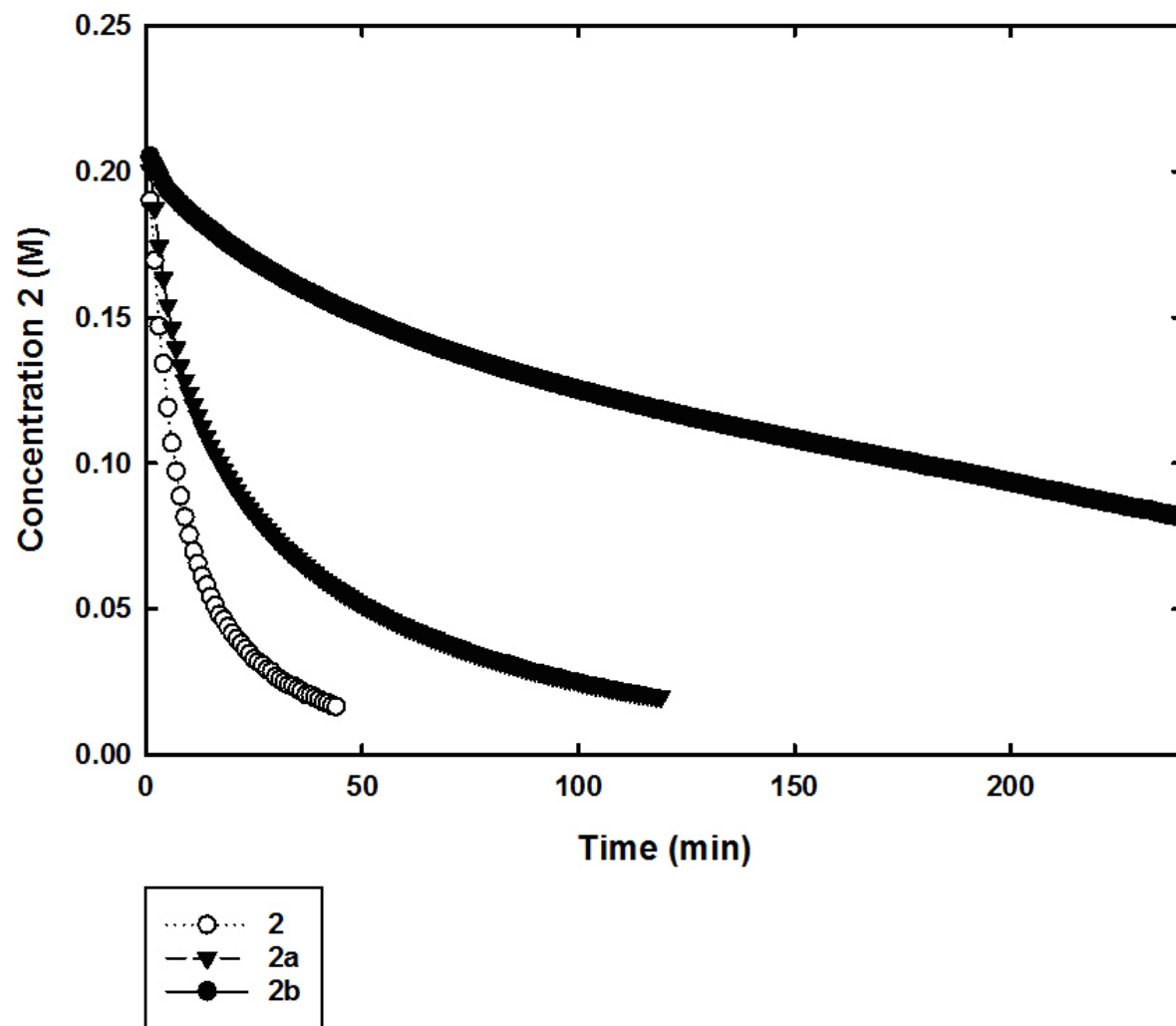
Temperature	-40 °C	-10 °C	0 °C	10 °C
k ( $\text{s}^{-1}$ )	$8.3 \cdot 10^{-7}$	$1.5(3) \cdot 10^{-4}$	$8(2) \cdot 10^{-4}$	$4.2(7) \cdot 10^{-3}$

Linear fit parameters:

Slope: -11700(479); Intercept: 30(1)

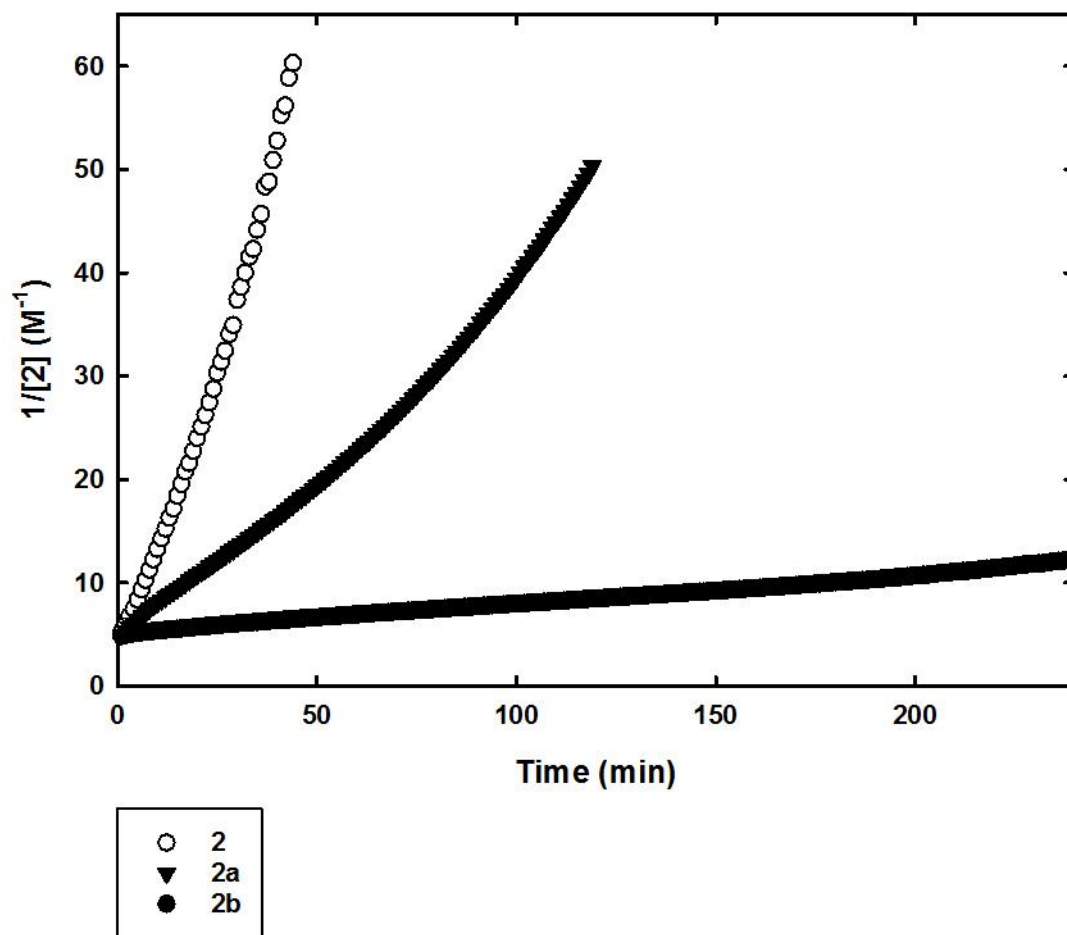
Enthalpy of activation: 23.3(9) kCal/mol; Entropy of activation: 12(3) eu.

Kinetic Traces for Thermal Decomposition of **2**, **2a**, and **2b** at 60 °C



**2a** was prepared in-situ by addition of one equiv. 18-crown-6 to solutions of **2**.

### Kinetic Traces for Thermal Decomposition of 2, 2a, and 2b at 60 °C

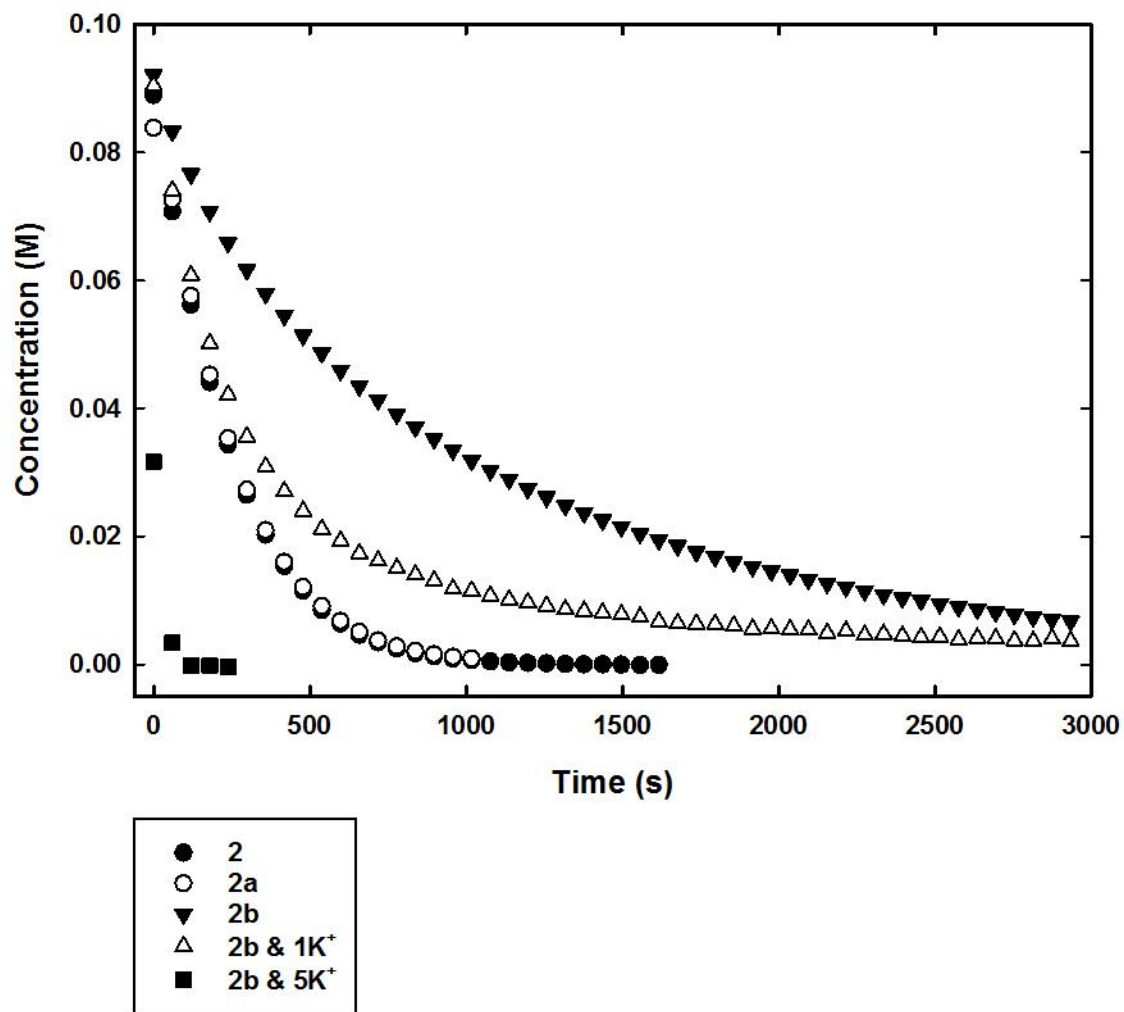


**2:**  $k=1.25 \text{ M}^{-1}\text{s}^{-1}$ , linear fit  $R^2=0.986$ .

**2a:**  $k=0.364 \text{ M}^{-1}\text{s}^{-1}$ , linear fit  $R^2=0.983$ .

**2b:**  $k=0.0280 \text{ M}^{-1}\text{s}^{-1}$ , linear fit  $R^2=0.996$ .

$\text{CF}_3^-$  transfer to **7** from **2**, **2b**, and **2b** activated with  $\text{K}^+$  at  $10^\circ\text{C}$



0.1 M **2** and 0.1 M **7**,  $10^\circ\text{C}$ . One equiv.  $\text{KB}(\text{C}_6\text{F}_5)_4$  ( $\text{K}^+$ ) was added last as a THF solution at  $-78^\circ\text{C}$  to activate **2b** prior to kinetic measurements at  $10^\circ\text{C}$  in **2b &  $1\text{K}^+$**  and 5 equiv. added in **2b &  $5\text{K}^+$** .

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