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A Broadly Applicable Crosslinker for Aliphatic Polymers Containing C–H Bonds

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Abstract:

Addition of molecular crosslinks to polymers increases mechanical strength and improves corrosion resistance. However, it remains challenging to install crosslinks in low-functionality macromolecules in a well-controlled manner. Typically, high-energy processes are required to generate highly reactive radicals in situ, allowing only a limited control over the degree and type of crosslink. We rationally designed a bis-diazirine molecule whose decomposition into carbenes under mild and controllable conditions enables the crosslinking of essentially any organic polymer via double C–H activation. The utility of this molecule as a crosslinker was demonstrated for several diverse polymer substrates (including polypropylene, a low-functionality polymer of long-standing challenge to the field) and in applications including adhesion of low-surface energy materials and the strengthening of polyethylene fabric.

One Sentence Summary:

A rationally designed bis-diazirine can crosslink any alkyl polymer.

Addition of crosslinks to polymeric materials confers several important advantages to the final product. By converting a thermoplastic into a thermoset, a polymer's impact resistance, tensile strength and high temperature performance are greatly enhanced, while material creep and unwanted thermal expansion are reduced (*1*). Crosslinked polymers also have increased resistance to solvents and electrical discharge, as well as to chemical and biological effects. While crosslinking can present challenges from the perspective of recyclability, it is advantageous in applications where chemical, biological or electrical degradation are concerns (*2, 3*). Crosslinked polyethylene, for example, is used for medical devices (*4*), insulation for electrical wires (*5, 6*), and containers for corrosive liquids (*7*). The principal disadvantage to crosslinking lies with an increase in brittleness, because the polymer chains are no longer free to slip across each other. Since these properties are highly correlated to the crosslink density, the control of the crosslinking process is key to the production of high-performance materials.

Crosslinks can be established in polymers through various strategies. The most common method in the academic literature involves the use of copolymers wherein one of the monomer constituents incorporates a linkable fragment (*1, 8*). Alternatively, a monomer that has two functional groups may give rise to a linear prepolymer that can be thermally or photochemically cured (*9*). Unfortunately, neither of the above strategies is appropriate when one needs to crosslink a polymer material that lacks functionality within its chemical structure. This includes important commodity plastics like polyethylene and polypropylene. Similarly, biomass-derived polymers (e.g., polylactic acid) and important biodegradable polymers (e.g., polycaprolactone) often lack any crosslinkable functional groups, even though they contain some functionality within their linear chains.

For these reasons, high-energy radical processes involving peroxides, electron- or γ-irradiation are used industrially to produce crosslinked polyethylene (PEX) (*2, 3*). However, the conditions required to initiate crosslinking via hydrogen abstraction are a limitation, and such methods are ineffective for polypropylene (*1*). The need to break a strong C–H bond (390–400 kJ/mol) in the vicinity of comparatively weaker C–C bonds (~350 kJ/mol) sets the stage for competing fragmentation and branching processes that can compromise the integrity of the material (Fig. S1). Moreover, these methods do not allow for control over the type of molecular

crosslink established, meaning that one cannot easily tune the mechanical properties of the final material.

We hypothesized that a superior crosslinking strategy could emerge from the use of low-barrier C–H insertions. Singlet carbenes are known to add directly to C–H, O–H and N–H bonds through a concerted process that does not involve the generation of any new high-energy species (*10*). Carbene-generating reagents have been used for decades in the field of chemical biology to link small molecules to their protein targets, with the 3-trifluoromethyl-3*H*-diazirine motif (Fig. 1A) established as a particularly effective carbene precursor (*11*). Although a few records of multivalent diazirines exist, their occasional application to polymer crosslinking has remained limited to substrates with weak C–H bonds such as polyethylene glycol and highly functionalized materials in organic electronics (*12-15*). The corresponding bis-azides (which function through nitrene insertion) have been somewhat better developed (*16*), but nitrenes are generally less reactive toward C–H insertion than carbenes, and are more prone to undesirable rearrangement reactions (*11*). We envisioned that an optimally designed bis-diazirine could permit the crosslinking of unfunctionalized alkane polymers under mild conditions and without unwanted branching or fragmentation (Fig. 1B).

Fig. 1. A bis-diazirine strategy for polymer crosslinking. (**A**) Mechanism of carbene formation from the light- or heat-promoted decomposition of diazirines, followed by C–H insertion. (**B**) Crosslinking of non-functionalized polymers via double C–H insertion of bis-diazirines.

We began our search for an effective bis-diazirine crosslinker by preparing the known compound **1** (*12-15*) and the pyridyl analogue **2** (Fig. 2A). Both of these molecules were surprisingly volatile (Fig. S2), and subsequent thermal analysis according to Yoshida's correlations (*17, 18*) (Fig. 2B and Eq. S2–3) suggested that each possessed a significant explosion risk. Although preliminary crosslinking trials demonstrated their ability to crosslink model substrates, both the volatility and the explosion risk negated the utility of these molecules for practical applications.

Stimulated by these observations, we designed and synthesized improved crosslinker **3** (Fig. 2A). Design features for **3** included: (a) an increased molecular weight relative to **1** and **2**, for reduced volatility and explosion risk; (b) the absence of any labile C–O or C–N bonds (*12-15*), which would limit the robustness of crosslinked products; (c) the use of an electron-deficient linker para to the diazirine motif, for improved handling under ambient conditions (*19*); and (d) the absence of any aliphatic C–H bonds, to reduce the risk of self-reaction.

Crosslinker **3** was found to have many desirable properties. It showed good solubility in a wide range of solvents (facilitating its dispersal into polymer matrices) and had a melting point conveniently just above room temperature (Table 2F) – meaning that it could be handled either as a liquid or crystalline solid. Thermogravimetric analysis (TGA) revealed that it cleanly lost 2 equivalents of N_2 upon gentle heating (Fig. 2C and Eq. S1), while differential scanning calorimetry (DSC) and application of Yoshida's correlations confirmed that **3** was not a likely explosive (Fig. 2B). Subsequent mechanical tests (*20*) revealed no propensity for explosion with **3**, at which point its synthesis was safely scaled up to afford multigram quantities.

Fig. 2. Survey of crosslinkers 1–3. (**A**) Compound structures and illustration of cyclohexane crosslinking. (**B**) Yoshida correlations showing that **1** and **2**, but not **3**, are potential explosion hazards. (**C**) TGA/DSC analysis of **3**, showing that the crosslinker is activated above 100 °C, and loses mass corresponding exactly to two equivalents of N_2. (**D**) UV spectra collected during the photochemical and thermal crosslinking of cyclohexane with **3**, showing that thermal initiation is faster and produces less diazoisomer. Asterisks indicate bands associated with each chromophore. (**E**) ^{1}H and ^{19}F NMR data for purified adduct **6**, produced from crosslinking of cyclohexane with **3**. $^{19}F\{^{1}H\}$ indicates a proton-decoupled experiment. (**F**) Physical properties for **1**–**3**, and yields for purified cyclohexane adducts.

Crosslinkers that are capable of inserting into the strong 2° C–H bonds of polyethylene should have equal or greater effectiveness against most other polymer substrates, since virtually every other aliphatic polymer (aside from perhalogenated materials like Teflon) has C–H bonds of equal or lower strength (e.g., polypropylene or polystyrene) or contains O–H or N–H bonds that react more quickly with carbenes (e.g., polyalcohols or polyamides) (*11*). We therefore elected to

first test **1**–**3** in models of polyethylene crosslinking, with the expectation that any successful crosslinkers identified in these trials would be broadly applicable to other systems. Seeking an initial substrate that would permit full spectroscopic characterization of crosslinked products, we first employed cyclohexane as a molecular model for polyethylene, since it similarly contains only 2° C–H bonds.

The crosslinking of cyclohexane with **1**–**3** was studied under both thermal and photochemical activation conditions (Fig. 2A). Both long-wave UV irradiation (350 nm) or heating (110–140°C) were effective in activating all three bis-diazirines. A difference in the rate of photochemical conversion was observed: while **3** was consumed within 1 h, **1** and **2** required ~2 h and ~4 h, respectively, for complete conversion. In all cases, a small amount of linear diazo isomer (resulting from the known rearrangement of the diazirine group) was detected under photochemical conditions (Fig. 2D and Fig. S5–11). These isomeric species persisted 2–3 times longer, but can also participate in crosslinking (*21*). Under thermal activation at 140°C, the reaction was much faster (< 20 min) and no linear diazo intermediate was observed.

Successful crosslinking was confirmed by careful isolation and characterization of products **4**–**6** (Table 2F). For all three adducts, ^{1}H NMR spectra showed a doublet of quartets at ~3.1 ppm, and ^{19}F NMR revealed a proton-coupled resonance at –63 ppm ($^{3}J_{H\text{-}F}$ = 10 Hz), both indicating the presence of a hydrogen atom α to a trifluoromethyl group and at the foot of a new C(H)–C(H) bond (Fig 2E). The modest isolated yields for **4**–**6**, independent from the method of activation, should not be taken as an absolute measure of crosslinking efficacy, since several alternative crosslink structures (e.g., those in which **1**–**3** oligomerize prior to crosslinking) would not be included within these yields. Indeed, observations of the spectroscopic signatures described above within the crude NMR spectra indicate that the overall C–H insertion efficacy in each case is >50% (*20*). Although the pyridine unit within **2** was added in the hopes of increasing crosslinking efficiency (*19*), this compound did not offer any advantages relative to **1** or **3**.

With crosslinking of the molecular model substrate established, we turned our attention to crosslinking of relevant polymers, beginning with soluble, low-molecular weight polyethylene (*i.e.* paraffin). Increasing amounts of bis-diazirine **3** (5–200wt%, Table S2) were easily dissolved in molten paraffin and activated at 110°C (Fig. S15–16). Analysis by gel permeation chromatography (GPC) revealed a continuous increase in molecular weight with the amount of

bis-diazirine added (Fig. 3A, blue arrow), providing evidence of crosslinking. Simultaneous UV detection confirmed that the chromophore from **3** was predominantly associated with higher weight fractions (red arrow) – again consistent with successful crosslinking. At 200wt% of **3**, crosslinking of paraffin afforded a tough gel with diminished solubility in THF (Fig. S16; hence the decreased intensity in the GPC data), which supports the creation of a 3-dimensional network. Subsequent studies also confirmed crosslinking in less-soluble, unbranched polyethylene (Fig. S29–30).

Fig. 3. Crosslinking of soluble and insoluble polymers. (**A**) Crosslinking of paraffin monitored by GPC. (**B**) Crosslinking of PDMS monitored by GPC. (**C**) Crosslinking of polypropylene increases the glass transition temperature (T_g) and decreases the fusion enthalpy (ΔH_{fus}). (**D**) Structure of molecular control **7**, used to validate mechanism. (**E**) Lap-shear data confirming adhesion for HDPE samples treated with **3**, but not those treated with **7**. Numbers indicate the total number of samples exhibiting sufficient adhesion for testing. (**F**) Drop-tower testing confirming reduced back-face signature and increased resistance to penetration upon crosslinking of UHMWPE fabric with **3**. (**G**) Tear testing data confirming increased mechanical strength for UHMWPE samples treated with **3**, but not those treated with **7**. Error bars correspond to standard deviations (N = 5 for panel E and N = 4 for panel F; sample replicates for panel G are indicated in Table S13). Statistical identifiers: n.s.: not statistically significant; *: $p<0.05$; **: $p<0.01$; ***: $p<0.001$.

Crosslinker **3** was then tested on other polymer substrates. Experiments with polydimethylsiloxane (PDMS) provided similar results to those for paraffin: low-viscosity PDMS exhibited an increased molecular weight upon thermal crosslinking with 5wt% **3** (Fig. 3B) while high-viscosity PDMS was transformed into a rubbery solid with negligible solubility in THF (Fig. S17). Photochemical crosslinking with **3** likewise converted the liquid PDMS substrate into a stable gel (*20*). Similar observations were made when crosslinking polycaprolactone (Fig. S19–20), polystyrene (Fig. S31–33), and polyisoprene (Fig S34–37). Polyvinyl alcohol crosslinked with increasing amounts of **3** progressively lost its aqueous solubility (Fig. S24–25). The use of low concentrations of **3** for polyvinyl alcohol gave a product

that floated atop the aqueous sample, while the use of higher concentrations gave a product that was heavier than water, demonstrating that crosslinker loading could control material density.

We next sought to demonstrate the efficacy of **3** for crosslinking commercial polypropylene samples. With increasing concentrations of crosslinker applied to low molecular weight polypropylene, we observed a monotonically increasing glass transition temperature (T_g) and decreased solubility (Fig. 3C and Fig. S26). We also observed a consistent decrease in the enthalpy associated with the melting transition, while the actual T_m temperature remained constant. This makes sense, in that crosslinked regions of the polymer structure will be non-melting (leading to a reduction in ΔH_{fus}) while residual non-crosslinked regions will possess a similar T_m to that of unmodified polypropylene. Even more profound effects were observed upon crosslinking of higher molecular weight polypropylene: the T_g was driven to a high of nearly room temperature, while the melting transition was almost completely lost at high crosslinking density (Fig. S27).

In order to demonstrate the utility of **3** for industrial processes, we were particularly interested to explore its effectiveness as an adhesive for high density polyethylene (HDPE), and as a strengthening agent for polyethylene fabric. Adhesion of low-surface energy materials like HDPE is a significant problem in manufacturing (*22*). Bis-diazirine **3** can in principle connect two polymer surfaces together through strong C–C bonds. We applied bis-diazirine **3** between bars of high-density polyethylene (HDPE), crosslinked the assemblies at 110°C and then challenged them on a lap-shear experiment, along with appropriate controls (Fig. 3E). The crosslinked bars required far more load to be pulled apart than any of the controls, and analysis of separated samples by optical profilometry (Fig. S40–41) indicated that residue derived from **3** was present on both faces – consistent with a cohesive rather than adhesive failure mechanism (*23*). Control samples prepared with no additives or with an equivalent weight (10 mg) of commercial SuperGlue® could not be measured since they did not adhere. A set of samples coated with an equivalent weight of molecular control **7** (Fig 3D) only barely adhered, proving that most of the adhesive force was due to crosslinking rather than simple surface modification. The use of a larger amount of **3** (25 mg) did not increase bonding strength.

To explore the effect of crosslinking ultrahigh molecular weight polyethylene (UHMWPE) fabric, we dissolved **3** in pentane and applied this solution to two different deniers of fabric (75

or 90 g/m²) from two different suppliers. The pentane was evaporated, and impregnated samples (or vehicle controls, treated with pentane but not **3**) were crosslinked at 110°C. Samples treated with as low as 1wt% **3** exhibited increased performance in both drop-tower and tear testing (Fig. 3F–G). Increasing the crosslinker density to 10wt% further improved material strength, but by a less dramatic increment. Evidently surface sites on the UHMWPE fibers become saturated, providing diminishing returns upon addition of more crosslinker. Fabric treated with molecular control **7** did not exhibit improved strength, once again confirming that the above results are due to authentic crosslinking and not surface modification. Crosslinking of aramid fabric likewise improved impact resistance, although the substantially increased rigidity in this case made the treated material easier to tear (Fig. S43–46).

Bis-diazirine **3** is remarkably stable (it can be recovered unchanged after dispersion in concentrated sulfuric acid at 70°C), but is easily activated by two complementary modes of activation: heating to >100°C or irradiation with ~350 nm light. Once activated, **3** is able to crosslink any aliphatic polymer containing C–H bonds, resulting in increased molecular weight, decreased solubility, increased T_g, and increased material strength: all well-known hallmarks of molecular crosslinking.

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Supplementary Materials:

Materials and Methods

NMR spectra (^{1}H, ^{19}F and ^{13}C) for Characterized Compounds

Supplementary Text

Figures S1 to S46

Tables S1 to S13

Movies S1 to S3

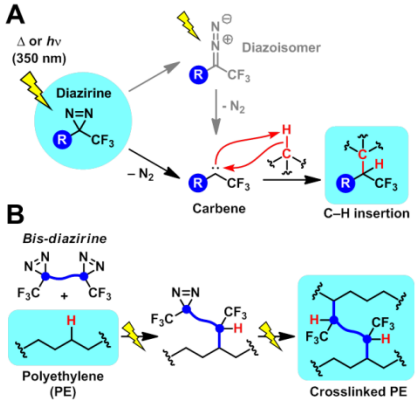
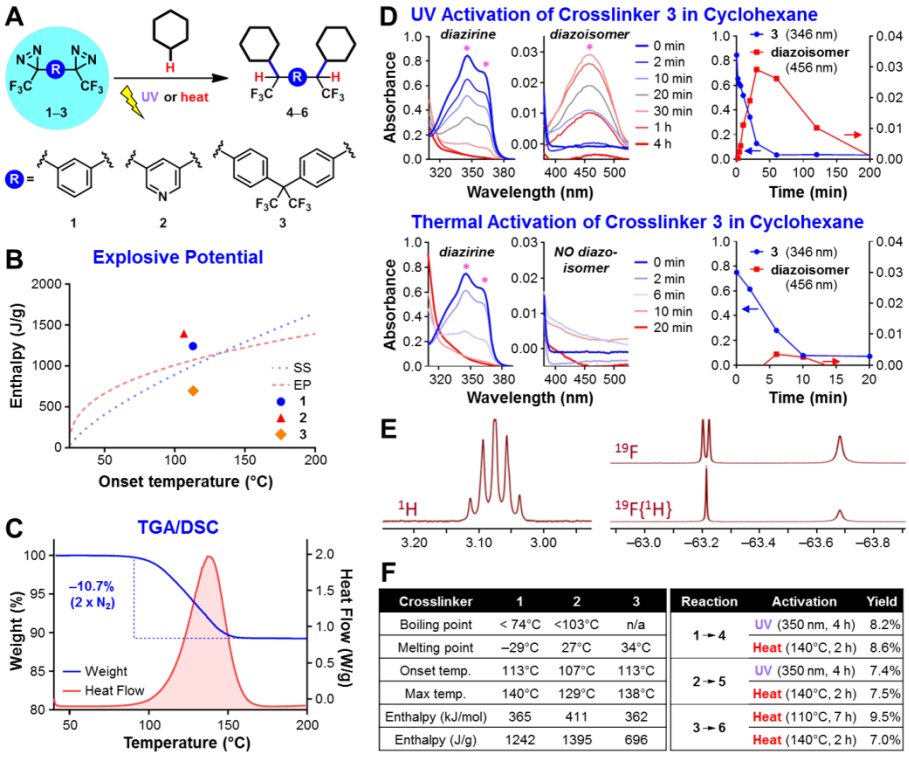


Figure 1



F

Crosslinker	1	2	3
Boiling point	< 74°C	<103°C	n/a
Melting point	–29°C	27°C	34°C
Onset temp.	113°C	107°C	113°C
Max temp.	140°C	129°C	138°C
Enthalpy (kJ/mol)	365	411	362
Enthalpy (J/g)	1242	1395	696

Reaction	Activation	Yield
1 → 4	UV (350 nm, 4 h)	8.2%
	Heat (140°C, 2 h)	8.6%
2 → 5	UV (350 nm, 4 h)	7.4%
	Heat (140°C, 2 h)	7.5%
3 → 6	Heat (110°C, 7 h)	9.5%
	Heat (140°C, 2 h)	7.0%

Figure 2

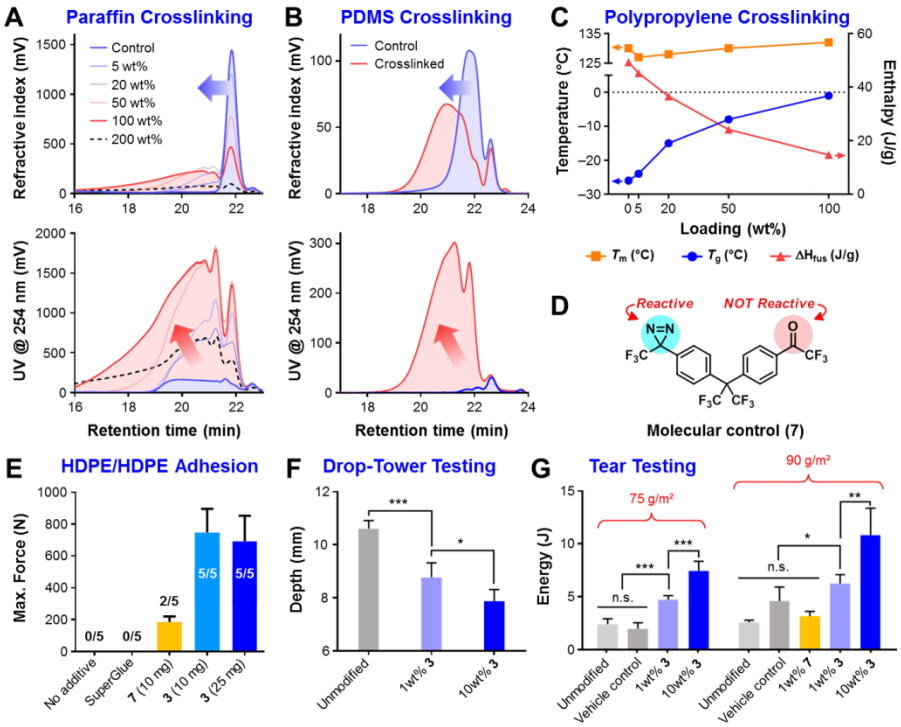

A
Paraffin Crosslinking
Refractive index (mV)
Control
5 wt%
20 wt%
50 wt%
100 wt%
200 wt%
UV @ 254 nm (mV)
Retention time (min)
B
PDMS Crosslinking
Refractive index (mV)
Control
Crosslinked
UV @ 254 nm (mV)
Retention time (min)
C
Polypropylene Crosslinking
Temperature (°C)
Enthalpy (J/g)
Loading (wt%)
T_m (°C)
T_g (°C)
ΔH_{fus} (J/g)
D
Reactive
NOT Reactive
Molecular control (7)
E
HDPE/HDPE Adhesion
Max. Force (N)
0/5
0/5
2/5
5/5
5/5
No additive
SuperGlue
7 (10 mg)
3 (10 mg)
3 (25 mg)
F
Drop-Tower Testing
Depth (mm)
***
*
Unmodified
1wt% 3
10wt% 3
G
Tear Testing
75 g/m²
90 g/m²
Energy (J)
n.s.
***
***
n.s.
*
**
Unmodified
Vehicle control
1wt% 3
10wt% 3
Unmodified
Vehicle control
1wt% 7
1wt% 3
10wt% 3

Figure 3

Science
AAAS

Supplementary Materials for

A Broadly Applicable Crosslinker for Aliphatic Polymers Containing C–H Bonds.

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This PDF file includes:

Supplementary files:

Movies S1, S2 and S3, the descriptions of which are provided at the end of this document.

Materials and Methods

General considerations

All commercial materials were used as received. Reagents used in the synthesis of the target compounds were purchased from Millipore Sigma except trimethyl(trifluoromethyl)silane (TMS-CF_3) which was purchased from ChemImpex.

All reactions were conducted in oven-dried glassware. THF was freshly dried over Na/benzophenone. Dichloromethane (DCM) was freshly dried over $CaCl_2$ or by passage over alumina in a commercial solvent purification system. Anhydrous cyclohexane was used in crosslinking experiments. Spectranalyzed™ pentane/hexane was used for purification of bisdiazirines and crosslinked products.

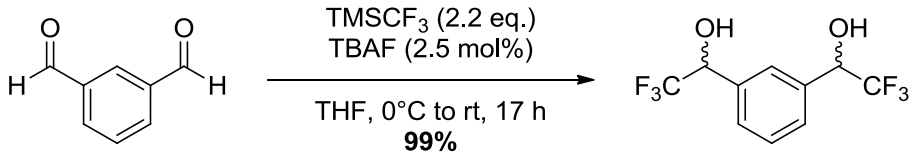
^{1}H, ^{13}C NMR, and ^{19}F spectra were recorded at ambient temperature using either a Bruker AVANCE 300 spectrometer or a Bruker AVANCE Neo 500 spectrometer. Chemical shifts in ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) and were referenced to residual protons of NMR solvents relative to tetramethylsilane. ^{1}H NMR data is presented in the format: chemical shift, (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet p = pentet, qd = quartet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, ddt = doublet of doublet of triplet, m = multiplet, br s = broad singlet), coupling constant *J* in Hertz, integration).^{13}C NMR data is presented in the same format as ^{1}H NMR data with the observed coupling pattern. Chemical shifts in ^{19}F spectra are reported in ppm and reported as obtained. Unless otherwise stated ^{19}F spectra are ^{1}H decoupled.

IR spectra were recorded using a Perkin-Elmer ATR spectrometer. IR wave numbers (v) are reported in cm^{-1}. High resolution electrospray ionization mass spectrometry (HRMS) data were acquired using a Thermo Scientific Orbitrap Exactive Plus spectrometer.

Syntheses

Synthesis of compound **1** was adapted from Blencowe *et al., React. Funct. Polymers* **68**, 868-875 (2008).

Synthesis of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-ol)

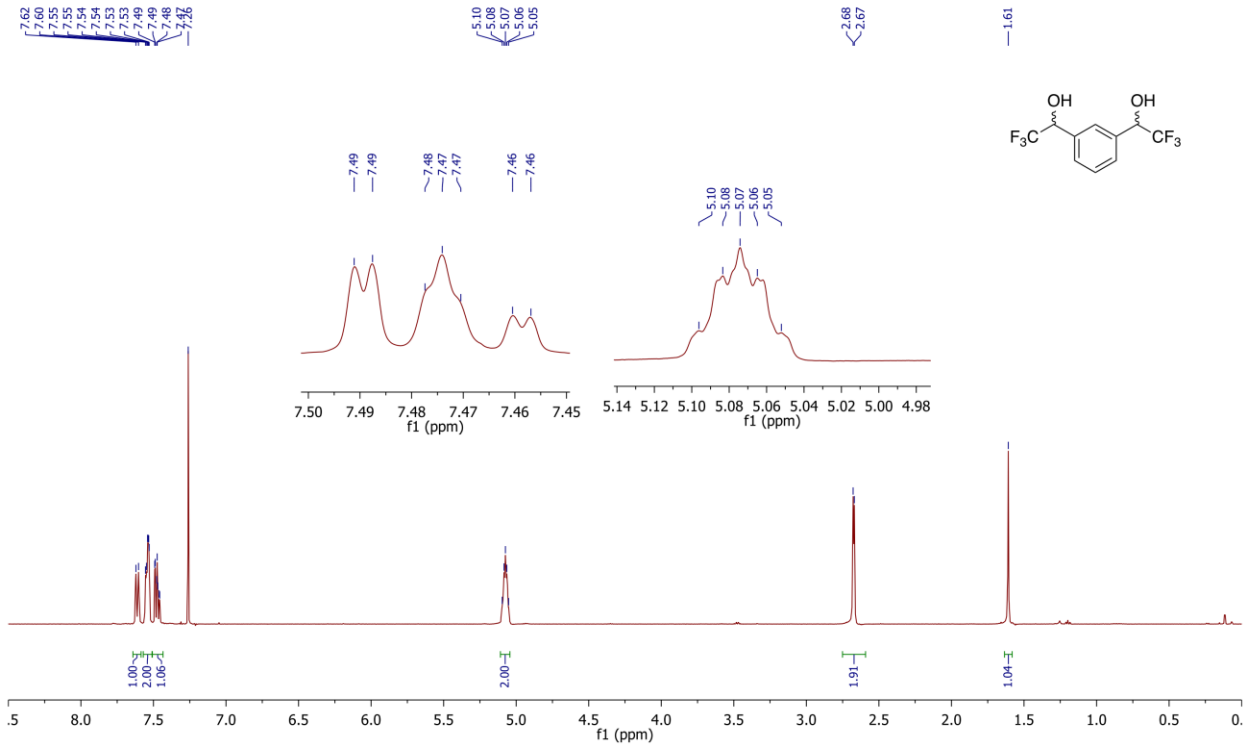


Chemical Formula: $C_8H_6O_2$
Exact Mass: 134.03678
Molecular Weight: 134.13204

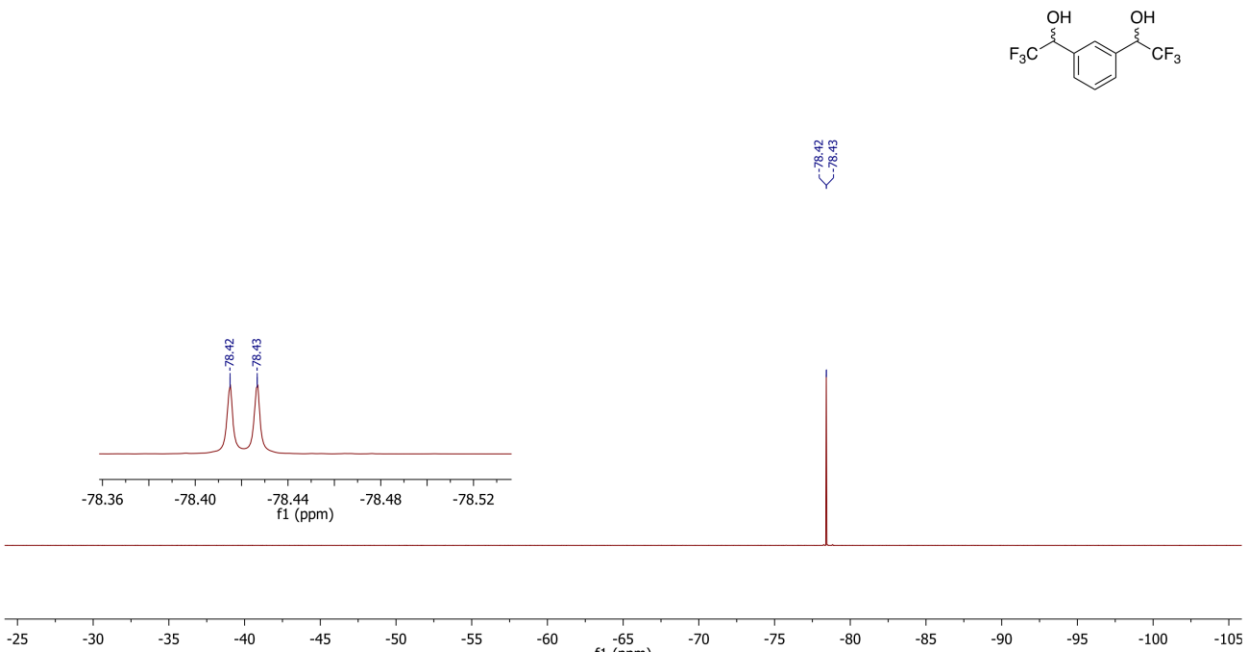
Chemical Formula: $C_{10}H_8F_6O_2$
Exact Mass: 274.04285
Molecular Weight: 274.15974

To a stirred solution of isophthalaldehyde (10.00 g, 74.55 mmol) in dry THF (150 mL) at 0 °C under argon, TMS-CF_3 (24.2 mL, 164.0 mmol) was added dropwise over 10 min. After stirring the reaction mixture for 5 minutes, 1.0 M tetrabutylammonium fluoride in THF (1.86 mL, 1.86 mmol) was added dropwise, and the reaction mixture was gradually warmed to room temperature. Stirring was continued for 17 h. The reaction mixture was then poured into 3 M HCl (400 mL) and stirred vigorously for 24 h. The resultant solution was extracted with DCM (3 x 250 mL). The organic layers were combined, subsequently washed with water (1 x 30 mL) and brine (1 x 30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a light yellow solid. The product (20.2 g, 99%) was obtained as a diastereomeric mixture. ^{1}H NMR (500.27 MHz, chloroform-*d*) δ 7.61 (d, *J* = 9.0 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.47 (ddd, *J* = 8.6, 6.8, 1.8 Hz, 1H), 5.07 (app. p, *J* = 6.4 Hz, 2H), 2.67 (d, *J* = 4.2 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 135.3, 128.4 and 128.4, 128.3 and 128.2, 126.7, 124.5 (q, *J* = 282.3 Hz), 71.9 (q, *J* = 31.4 Hz), 71.9 (q, *J* = 31.7 Hz). ^{19}F NMR (282.54 MHz, chloroform-*d*) δ -78.44, -78.45. IR (diamond-ATR) ν: 3355, 1437, 1258, 1164, 1118, 1060, 706. HRMS (ESI+) *m/z* [M+Na] calculated for $C_{10}H_8F_6O_2Na$: 297.03206, found: 297.03211.

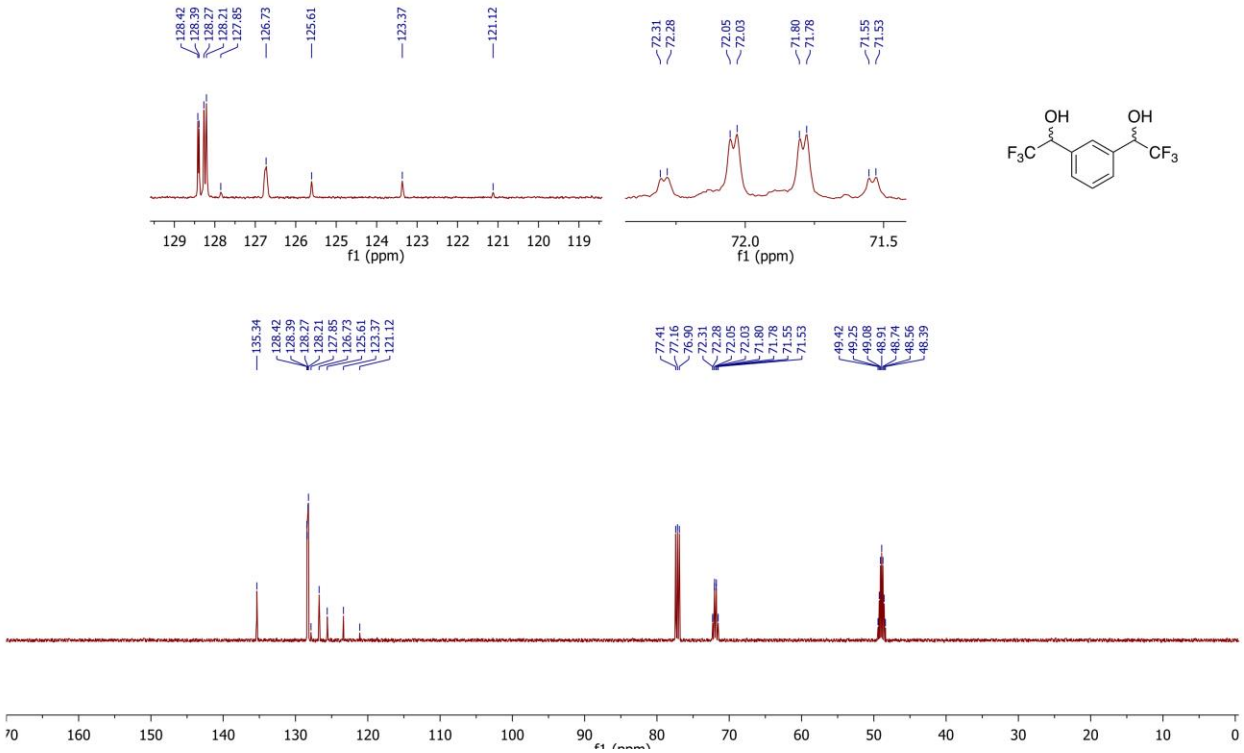
^{1}H NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-ol) in $CDCl_3$:



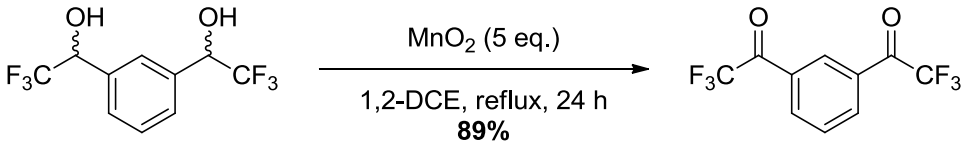
^{19}F NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-ol) in $CDCl_3$:



^{13}C NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-ol) in $CDCl_3$:



Synthesis of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one)

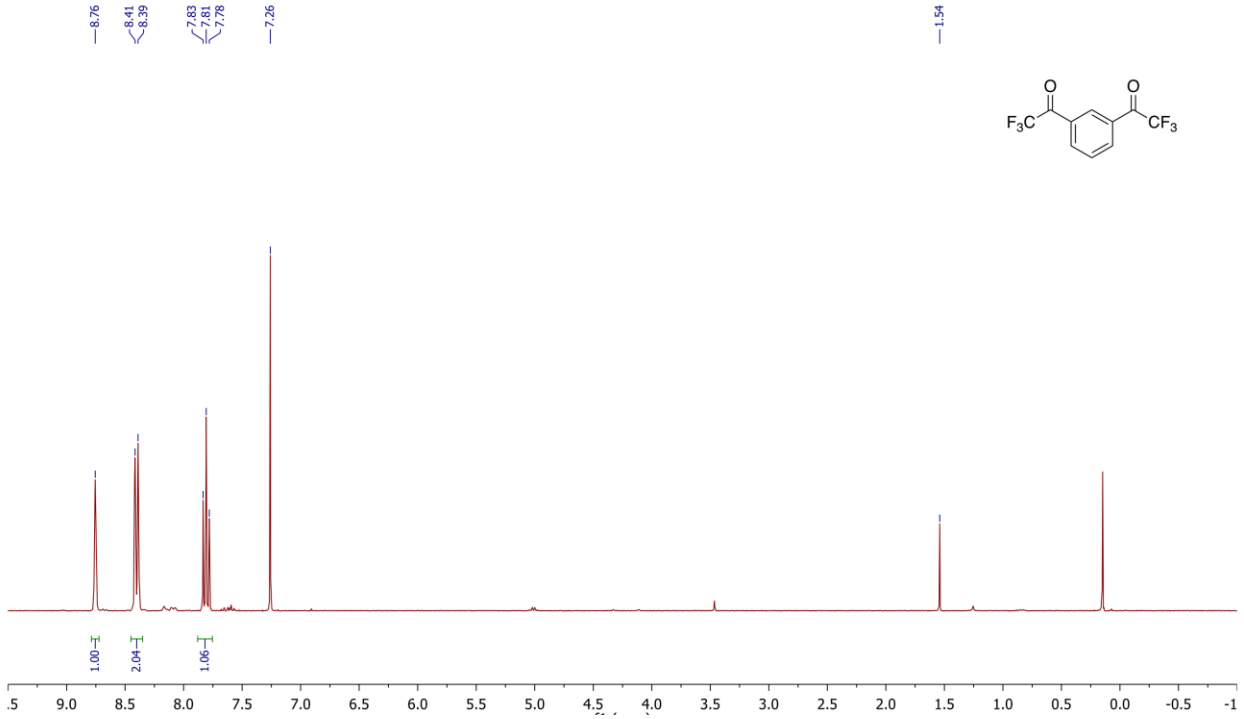


Chemical Formula: $C_{10}H_8F_6O_2$
Exact Mass: 274,0428
Molecular Weight: 274,1624

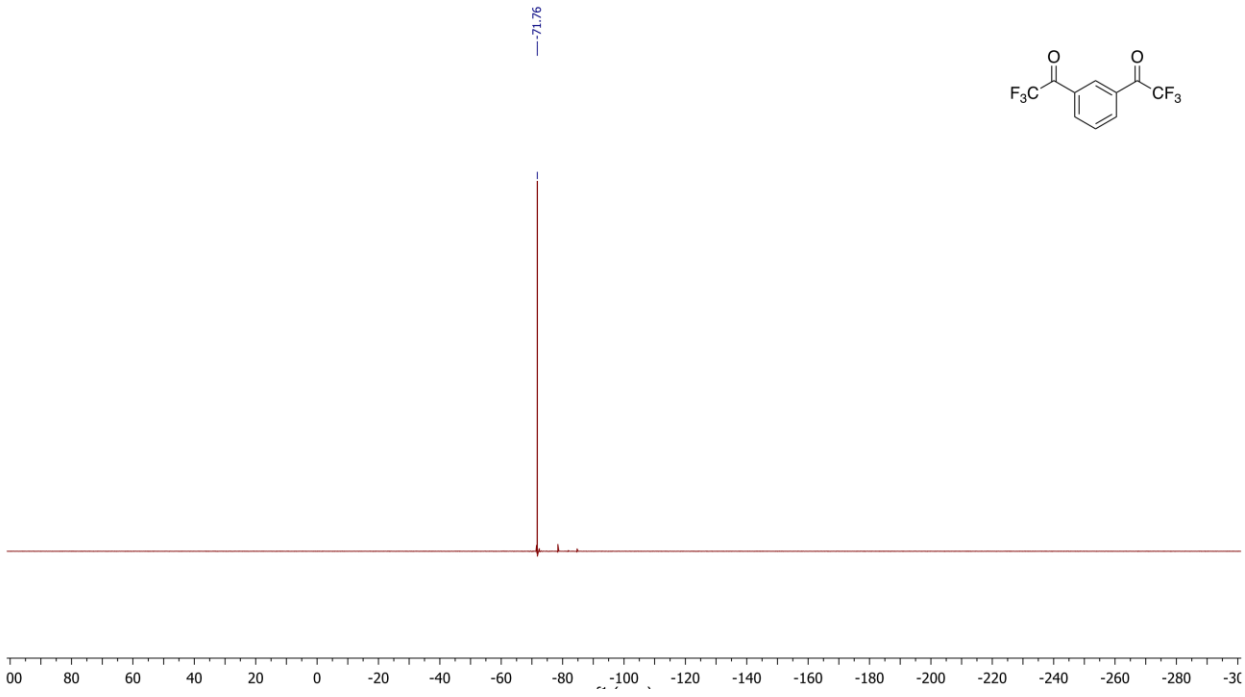
Chemical Formula: $C_{10}H_4F_6O_2$
Exact Mass: 270.01155
Molecular Weight: 270.12798

To a stirred solution of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-ol) (20.14 g, 74.56 mmol) in 1,2-dichloroethane (200 mL), MnO_2 (32.40 g, 372.8 mmol) was added at room temperature under argon. The reaction mixture was then heated to reflux for 24 h. Upon completion of the reaction, the reaction mixture was filtered through a celite pad and the residue washed with DCM (2 x 50 mL). The filtrate was concentrated in vacuo to afford a light yellow oil which was directly loaded onto silica gel and eluted with diethyl ether. The product (18.01 g, 89%) was isolated as clear colorless oil. ^{1}H NMR (300.27 MHz, chloroform-d) δ 8.76 (s, 1H), 8.40 (d, *J* = 7.6 Hz, 2H), 7.81 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (76 MHz, chloroform-d) δ 179.5 (q, *J* = 36 Hz), 136.3–136.1 (m), 131.7–131.5 (m), 131.0, 130.4, 116.5 (q, *J* = 291 Hz). ^{19}F NMR (282.54 MHz, chloroform-d) δ -71.76. IR (diamond-ATR) ν: 1725, 1600, 1438, 1199, 1134, 730, 684.

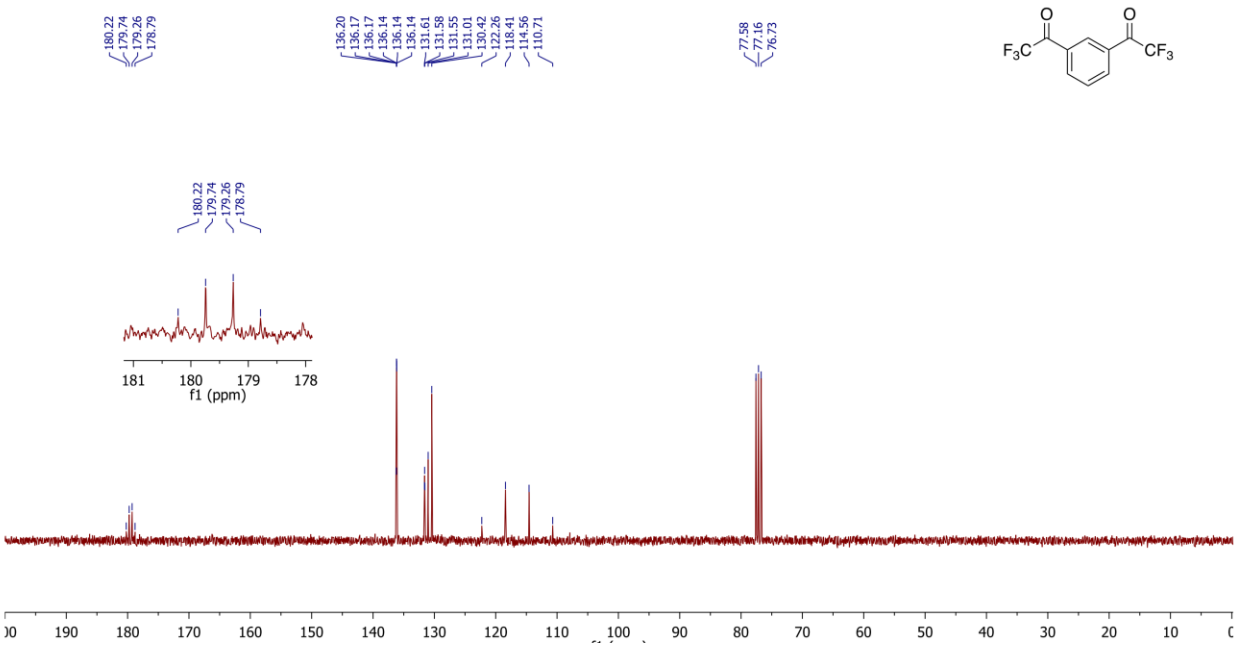
^{1}H NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) in $CDCl_3$:



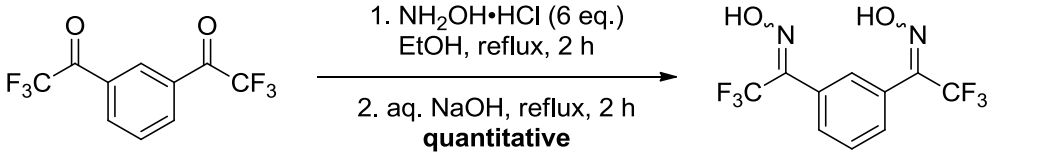
^{19}F NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) in $CDCl_3$:



^{13}C NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) in $CDCl_3$:



Synthesis of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) dioxime

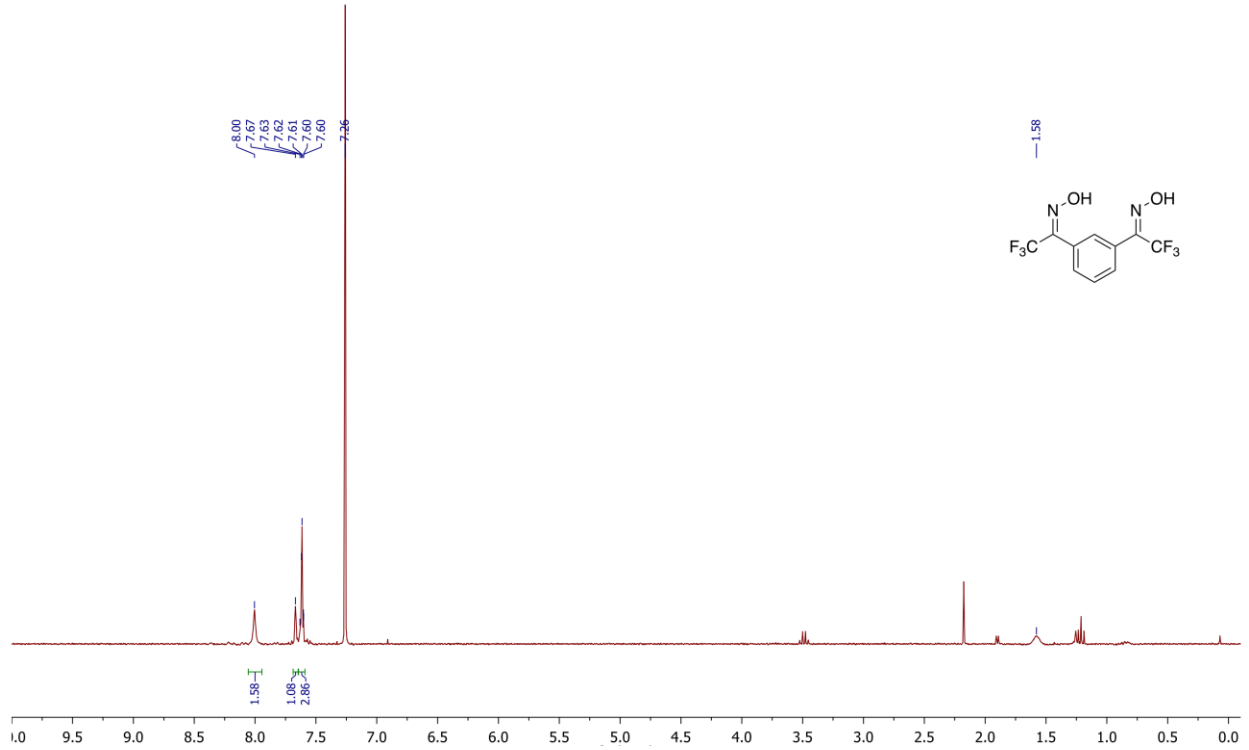


Chemical Formula: $C_{10}H_4F_6O_2$
Exact Mass: 270,0115
Molecular Weight: 270,1304

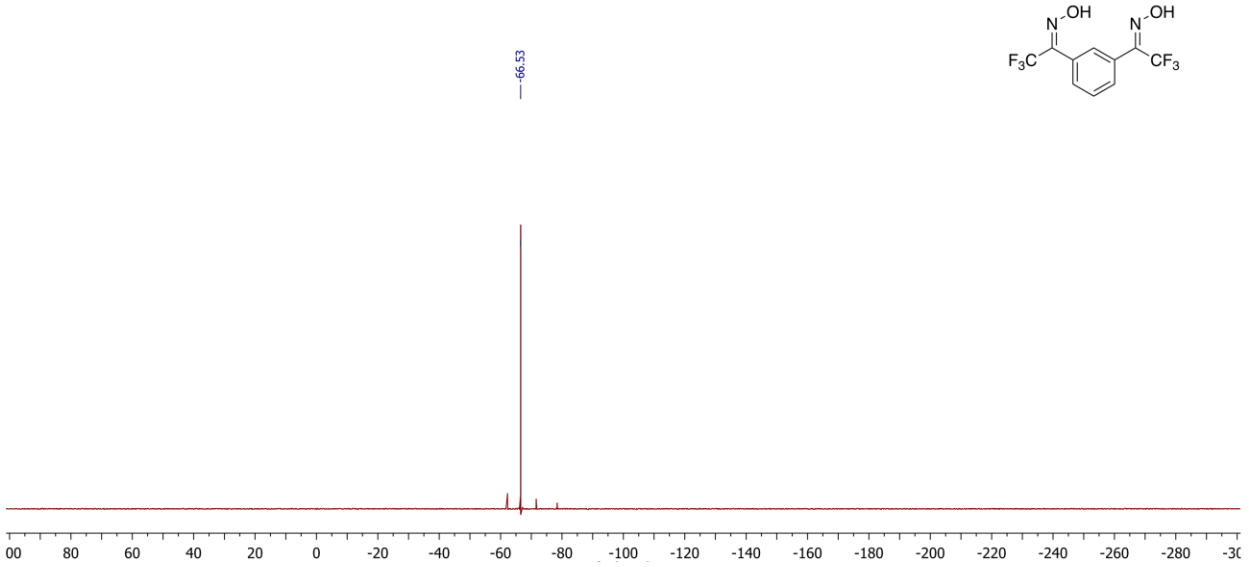
Chemical Formula: $C_{10}H_6F_6N_2O_2$
Exact Mass: 300.03335
Molecular Weight: 300.15726

To a stirred solution of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) (18.00 g, 66.63 mmol) in ethanol, hydroxylamine hydrochloride (27.80 g, 399.8 mmol) was added and the reaction mixture was heated to reflux for 2 h. The mixture was then cooled to room temperature and adjusted to pH ~7 with aqueous 8 M NaOH solution, then heated to reflux for another 2 h. After cooling the reaction mixture to room temperature, it was concentrated in vacuo. The resultant residue was partitioned between water and diethyl ether. Layers were separated, and the aqueous layer further extracted with diethyl ether (4 x 200 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in vacuo to give the product (20 g, 100%) as a colourless solid which was predominately one of the three possible geometric isomers. ^{1}H NMR (300.27 MHz, chloroform-d) δ 8.00 (br s, 2H), 7.67(s, 1H), 7.65-7.54 (m, 3H). ^{13}C NMR (75.50 MHz, chloroform-d +methanol-d_4) δ 145.5 (p, J = 32 Hz), 130.4, 129.2, 128.5, 127.2, 120.9 (q, *J* = 274 Hz). ^{19}F NMR (282.54 MHz, chloroform-d) δ -66.53. IR (diamond-ATR) ν: 3279, 1456, 1191, 1129, 960, 727. HRMS (ESI-) m/z [M-H] calculated for $C_{10}H_5F_6N_2O_2$: 299.02552, found: 299.02584.

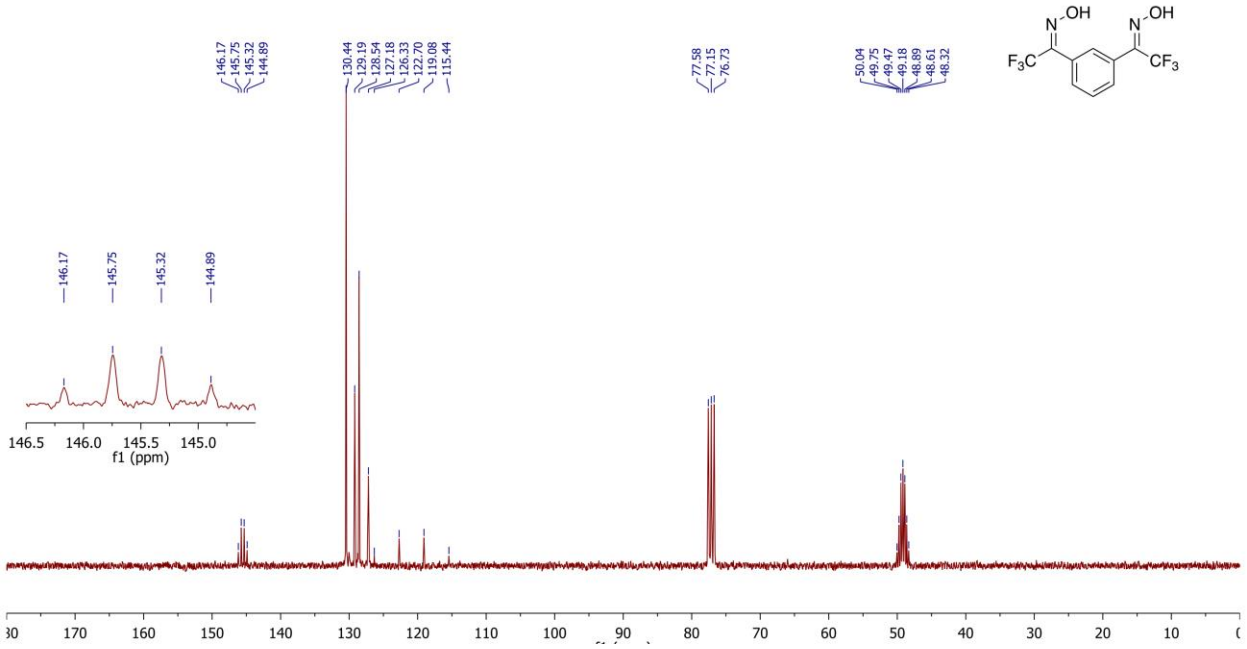
^{1}H NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) dioxime in $CDCl_3$:



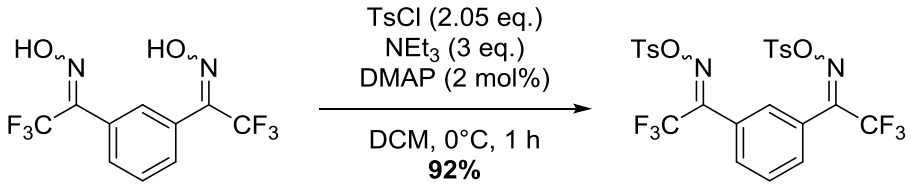
^{19}F NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) dioxime in $CDCl_3$:



^{13}C NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) dioxime in a mixture of $CDCl_3$ and CD_3OD:



Synthesis of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime

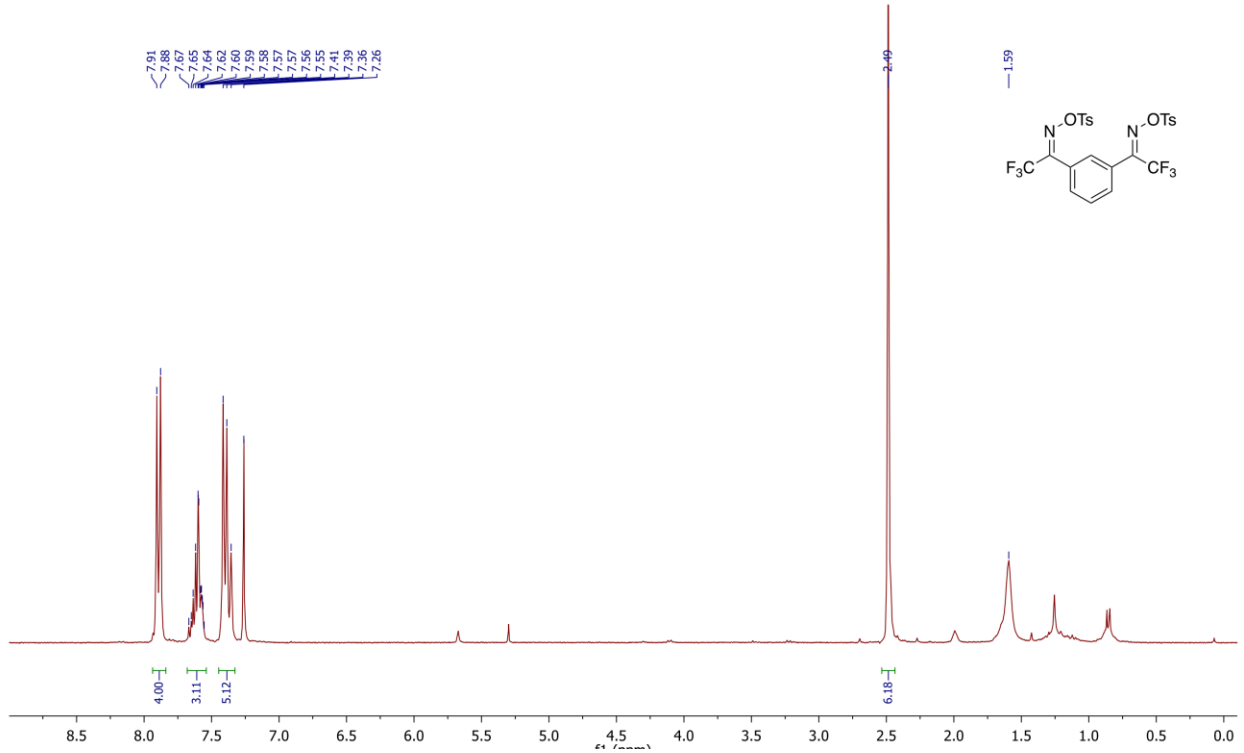


Chemical Formula: $C_{10}H_6F_6N_2O_2$
Exact Mass: 300,0333
Molecular Weight: 300,1604

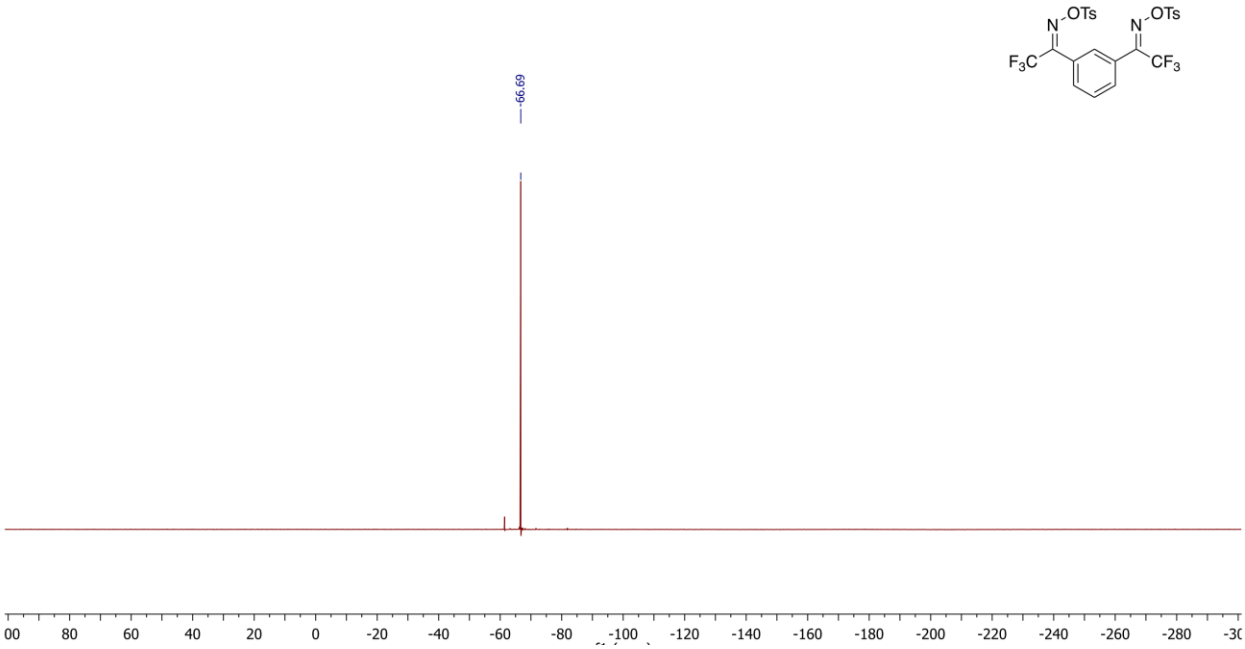
Chemical Formula: $C_{24}H_{18}F_6N_2O_6S_2$
Exact Mass: 608,0510
Molecular Weight: 608,5264

To a stirred solution of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) dioxime (20.00 g, 66.63 mmol) in dry DCM (200 mL) at 0 °C under argon, triethylamine (27.9 mL, 200 mmol), p-toluenesulfonyl chloride (26.04 g, 136.59 mmol) and DMAP (0.16 g, 1.33 mmol) were added sequentially. The reaction was gradually warmed to room temperature and stirred for 1 h. The reaction mixture was then diluted with DCM (200 mL) and washed sequentially with 1 M HCl (2 x 20 mL), water (1 x 20 mL), and brine (1 x 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to give the product (37.33 g, 92% yield) as a colourless solid which was predominately one of the three possible geometric isomers. ^{1}H NMR (300.27 MHz, chloroform-d) δ 7.89 (d, J = 8.4 Hz, 4H), 7.68–7.53 (m, 3H), 7.40 (d, *J* = 8.1 Hz, 4H), 7.36 (s, 1H), 2.49 (s, 6H). ^{13}C NMR (126 MHz, chloroform-d) δ 152.4 (p, *J* = 34 Hz), 146.6, 131.8, 131.0, 130.2, 129.8, 129.5, 128.2, 125.6, 119.5 (q, *J* = 278 Hz), 22.0. ^{19}F NMR (282.54 MHz, chloroform-d) δ -66.69. IR (diamond-ATR) v: 1596, 1456, 1394, 1193, 1179, 1145, 1090, 1034, 904, 814, 756, 674, 544. HRMS (ESI+) m/z [M+Na] calculated for $C_{24}H_{18}F_6N_2O_6S_2Na$: 631.04027, found: 631.03997.

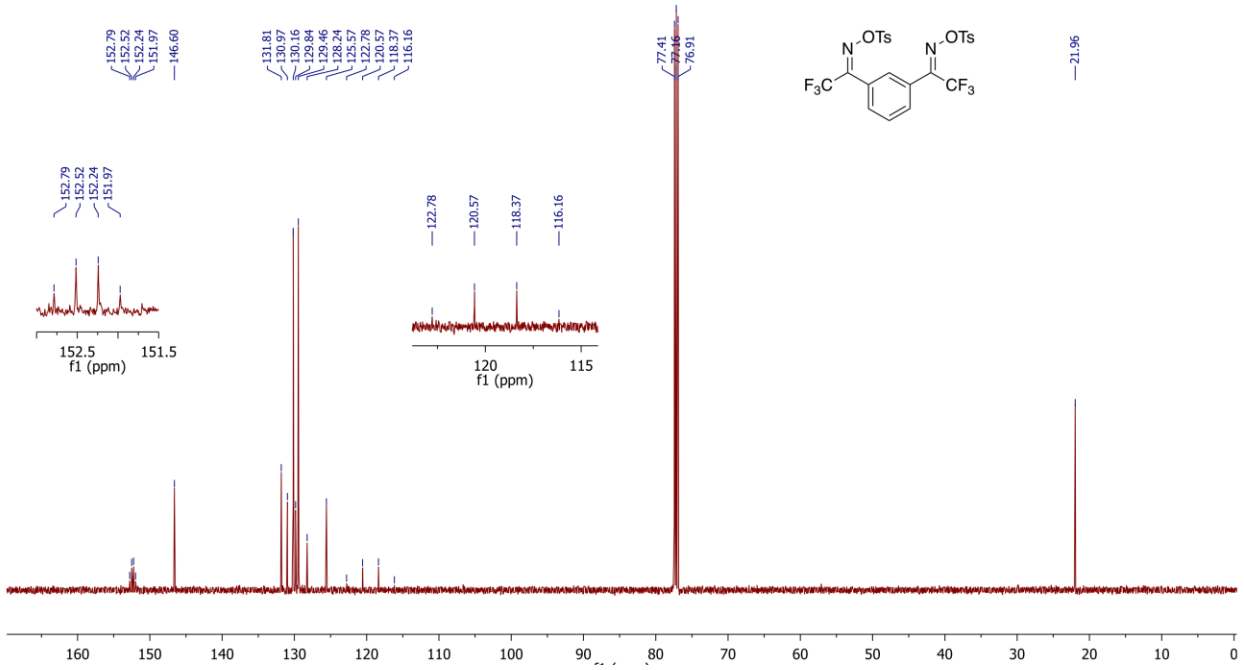
^{1}H NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$:



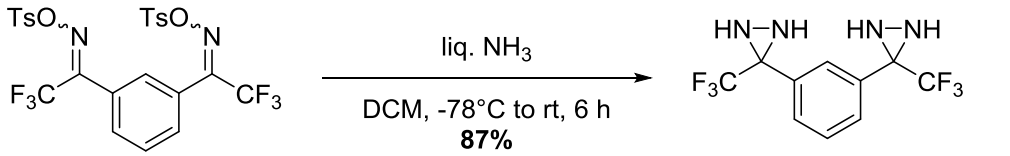
^{19}F NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$:



^{13}C NMR spectrum of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$:



Synthesis of 1,3-bis(3-(trifluoromethyl)diaziridin-3-yl)benzene



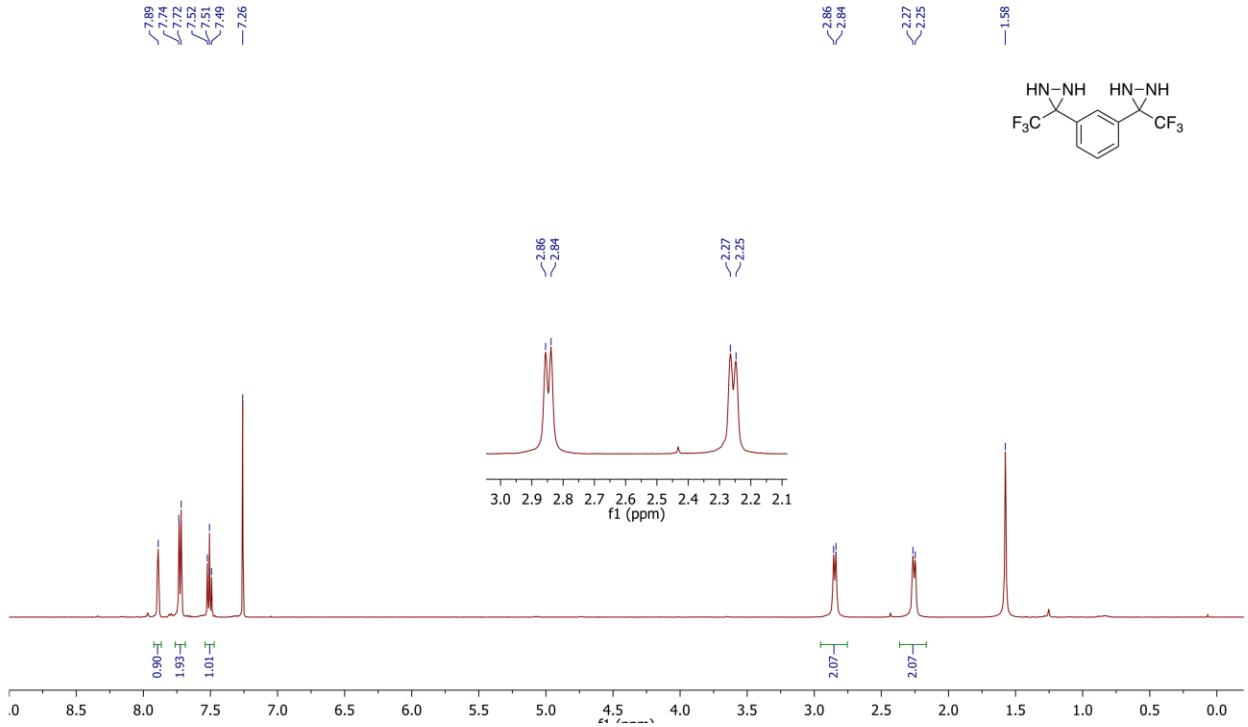
Chemical Formula: $C_{24}H_{18}F_6N_2O_6S_2$
Exact Mass: 608,0510
Molecular Weight: 608,5264

Chemical Formula: $C_{10}H_8F_6N_4$
Exact Mass: 298,0653
Molecular Weight: 298,1924

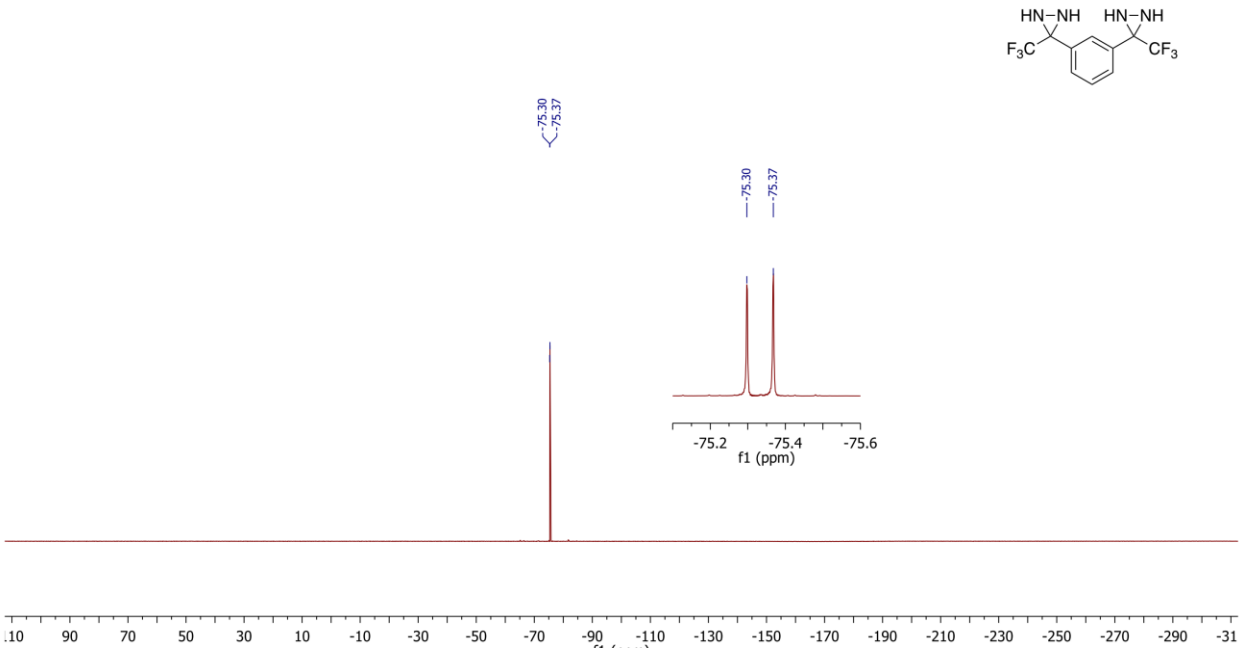
NH_3 gas (~80 mL) was condensed at −78 °C into a 500 mL three neck round bottom flask equipped with dewar, inlet and outlet for gas flow. In order to get dry NH_3 the gas was passed through tubing that contained layers of KOH pellets. To this liquid NH_3, a solution of 1,1'-(1,3-phenylene)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime (2.00 g, 3.29 mmol) in dry DCM (6 mL) was added dropwise over 10 min, using a cannula. The reaction was maintained at −78 °C for 6 h and then gradually allowed to warm to room temperature. After complete evaporation of excess NH_3, a white suspension was formed. To this, water (30 mL) and DCM (120 mL) were added. The organic layer was separated and washed subsequently with water (2 x 20 mL) and brine (1 x 20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude product which was purified by silica gel chromatography. The product (0.85 g, 87%) was isolated as white solid. ^{1}H NMR (500.27 MHz, chloroform-d) δ 7.89 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 2.85 (d, *J* = 8.9 Hz, 2H), 2.26 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-d) δ 132.7 and 132.7, 130.2 and 130.1, 129.5, 128.1 and 128.0, 123.4 (q, *J* = 274 Hz), 123.5 (q, *J* = 274 Hz), 58.0 (q, *J* = 36 Hz) 57.9 (q, *J* = 36 Hz). ^{19}F NMR (470.72 MHz, chloroform-d)

δ -75.30, -75.37. IR (diamond-ATR) ν: 3253, 3206, 3182, 1395, 1225, 1136, 953, 724, 654. HRMS (ESI-) m/z [M-H] calculated for $C_{10}H_7F_6N_4$: 297.05802, found: 297.05795.

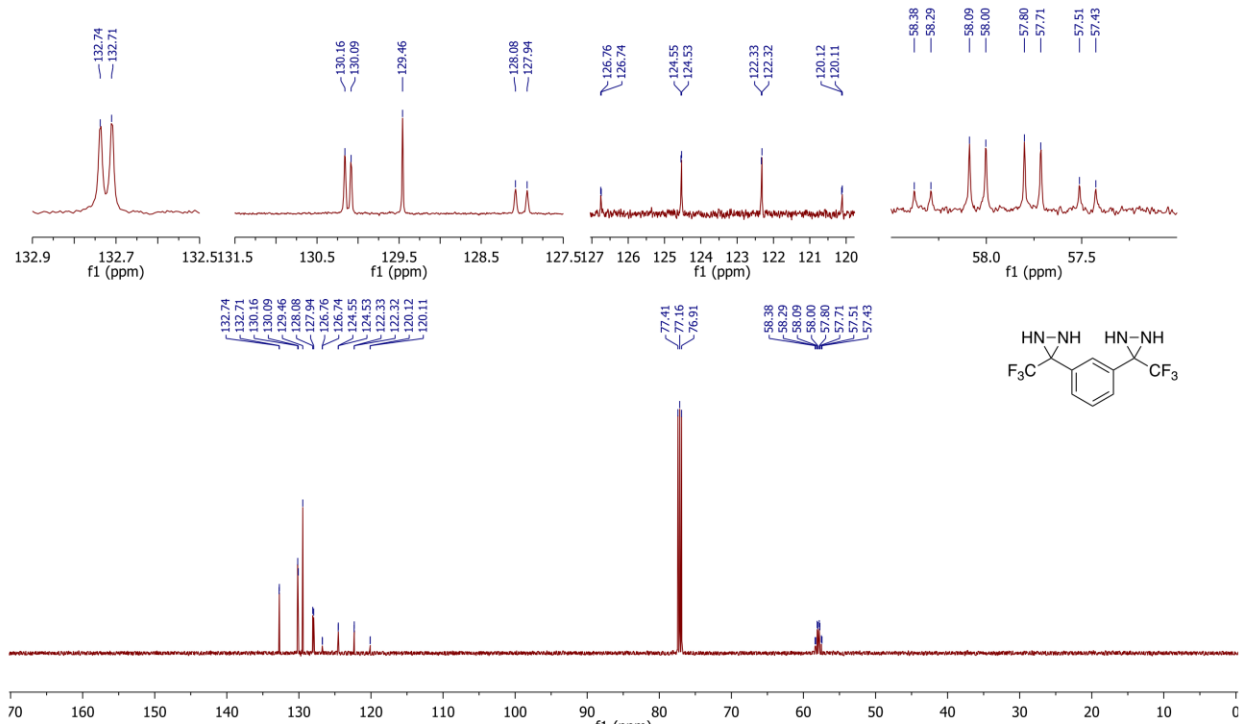
^{1}H NMR spectrum of 1,3-bis(3-(trifluoromethyl)diaziridin-3-yl)benzene in $CDCl_3$:



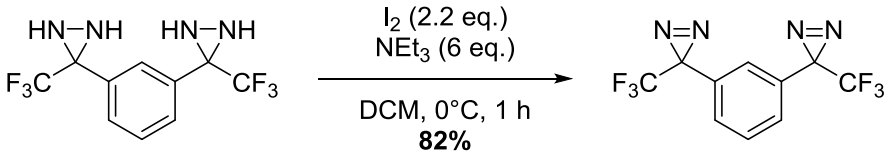
^{19}F NMR spectrum of 1,3-bis(3-(trifluoromethyl)diaziridin-3-yl)benzene in $CDCl_3$:



^{13}C NMR spectrum of 1,3-bis(3-(trifluoromethyl)diaziridin-3-yl)benzene in $CDCl_3$:



Synthesis of 1,3-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzene (**1**)



Chemical Formula: $C_{10}H_8F_6N_4$
Exact Mass: 298,0653
Molecular Weight: 298,1924

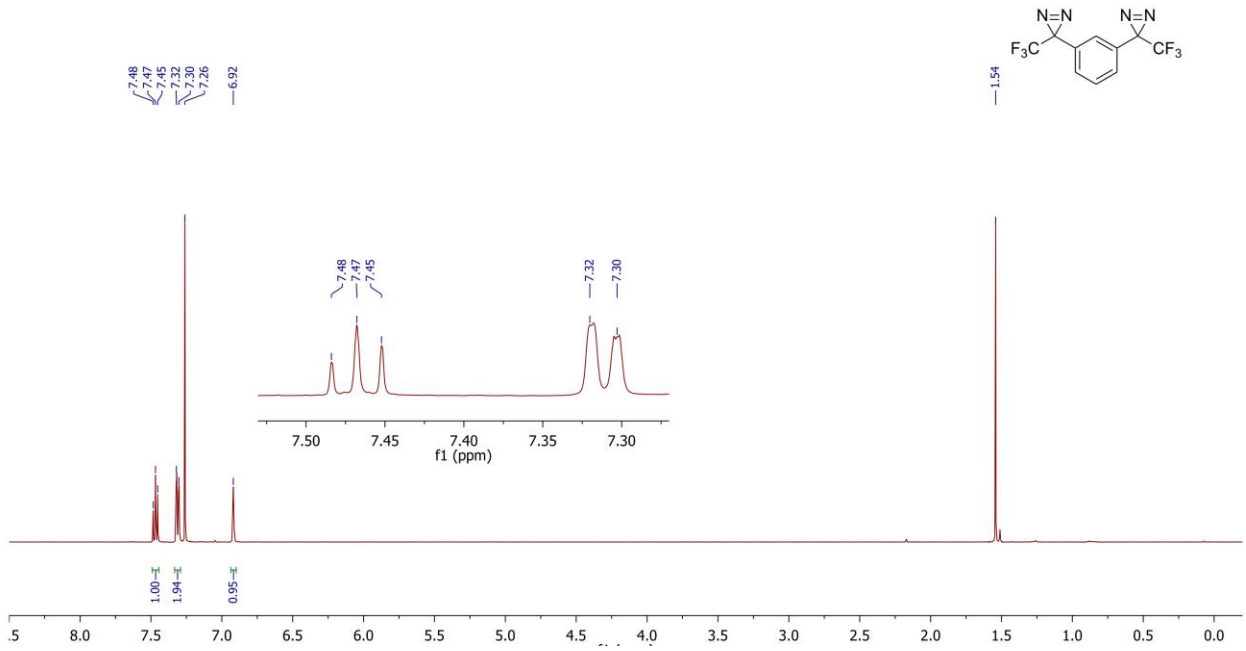
1

Chemical Formula: $C_{10}H_4F_6N_4$
Exact Mass: 294,0340
Molecular Weight: 294,1604

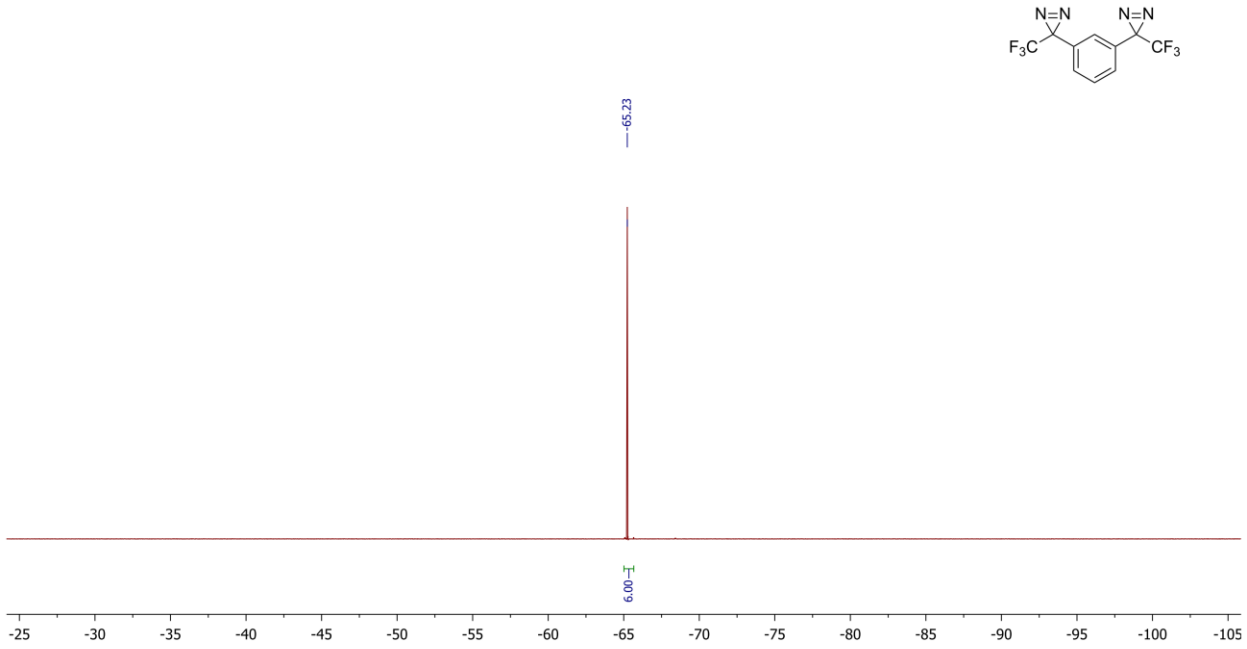
To a stirring solution of 1,3-bis(3-(trifluoromethyl)diaziridin-3-yl)benzene (1.00 g, 3.35 mmol) in DCM (20 mL) at 0 °C under argon, triethylamine (2.80 mL, 20.1 mmol) was added. To the resulting mixture, iodine (1.87 g, 7.37 mmol) was added in three portions and the reaction was stirred at 0 °C for 1 h. The reaction mixture was diluted with 20 mL DCM and washed with 1 M NaOH (1 x 20 mL), and water (2 x 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated carefully under low vacuum at < 10 °C (rotary evaporator water bath was filled with ice + water) to give a crude product which was purified through silica gel chromatography. The desired product was eluted with pentane and the compound-containing pentane fractions were concentrated under low vacuum at < 10 °C (0.80 g, 82% yield). Melting point = –29°C. ^{1}H NMR (500.27 MHz, chloroform-d) δ 7.47 (t, J = 7.9 Hz, 1H), 7.31 (d, J = 8.7 Hz, 2H), 6.92 (s, 1H). ^{13}C NMR (126 MHz, chloroform-d) δ 130.4, 129.7, 128.0, 125.3, 122.0 (q, J = 274 Hz), 28.4 (q, J = 41 Hz). ^{19}F NMR (470.72 MHz, chloroform-d) δ -65.23. IR (diamond-ATR) v: 1610, 1588, 1495,

1330, 1179, 1147, 792, 694. HRMS (ESI-) m/z [M-H] calculated for $C_{10}H_3F_6N_4$: 293.02672 found: 293.02684.

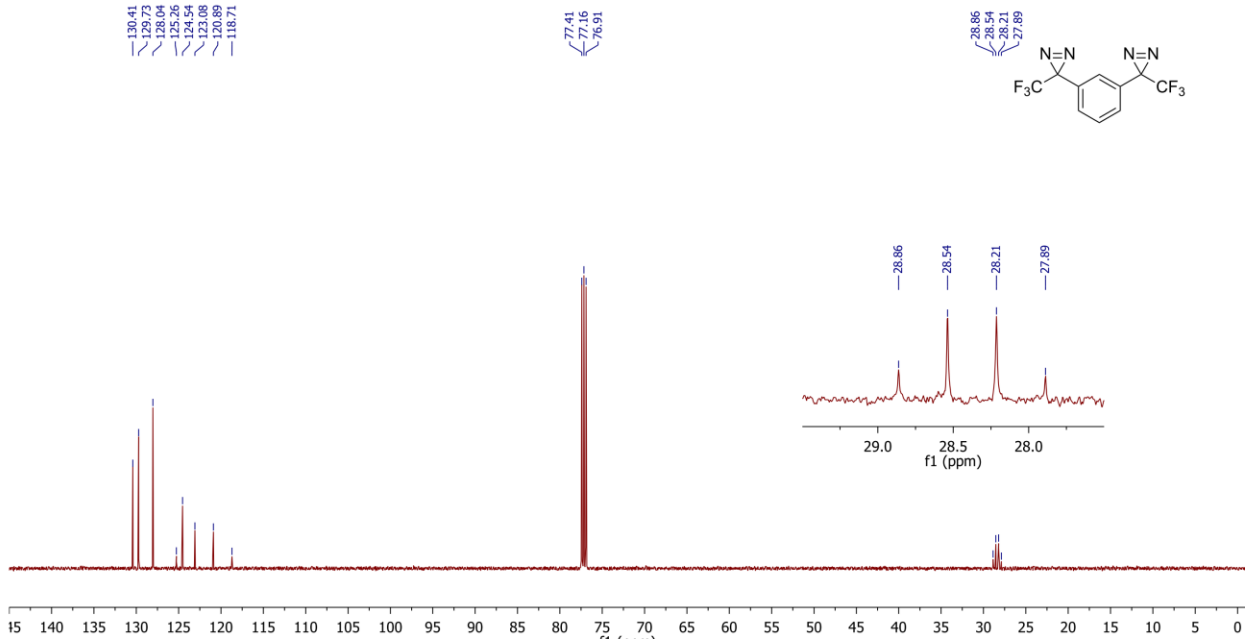
^{1}H NMR spectrum of 1,3-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzene (1) in $CDCl_3$:



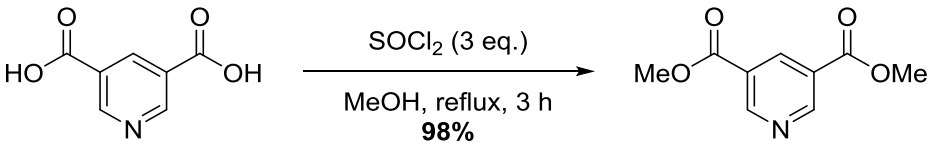
^{19}F NMR spectrum of 1,3-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzene (1) in $CDCl_3$:



^{13}C NMR spectrum of 1,3-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)benzene (1) in $CDCl_3$:



Synthesis of dimethyl pyridine-3,5-dicarboxylate

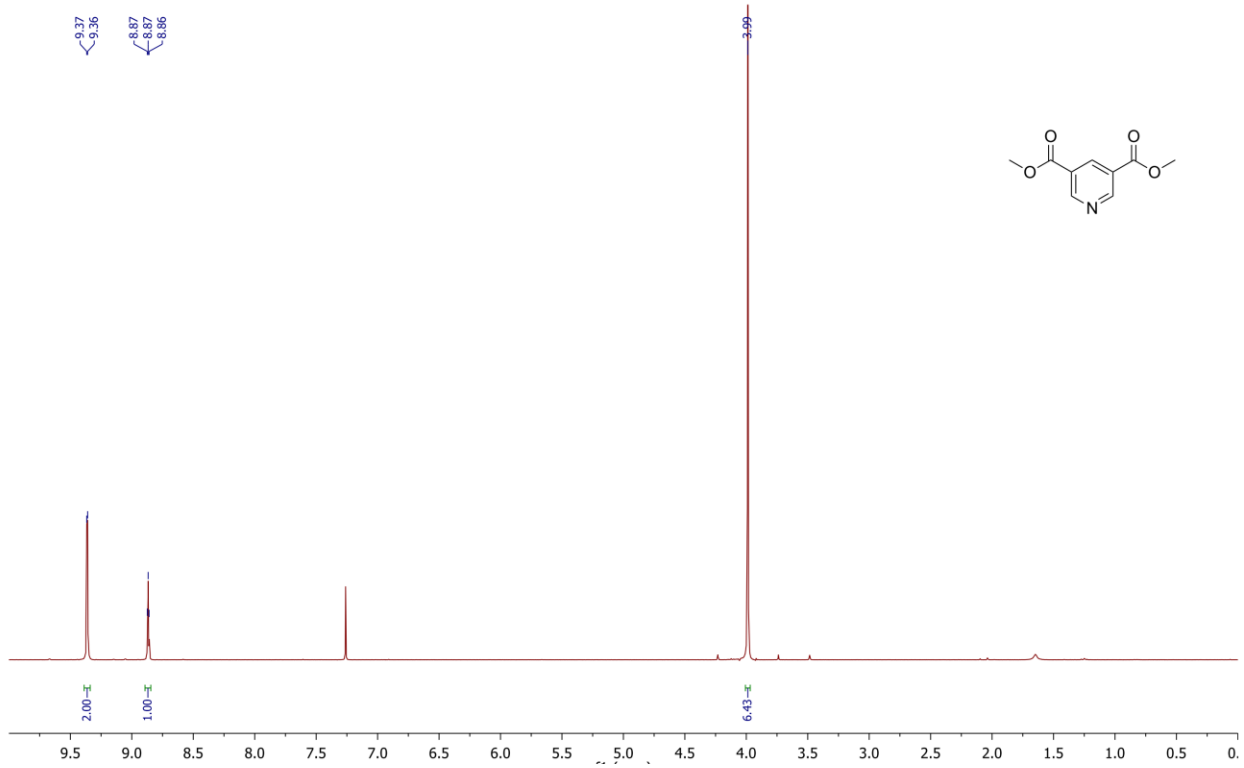


Chemical Formula: $C_7H_5NO_4$
Exact Mass: 167,0219
Molecular Weight: 167,1200

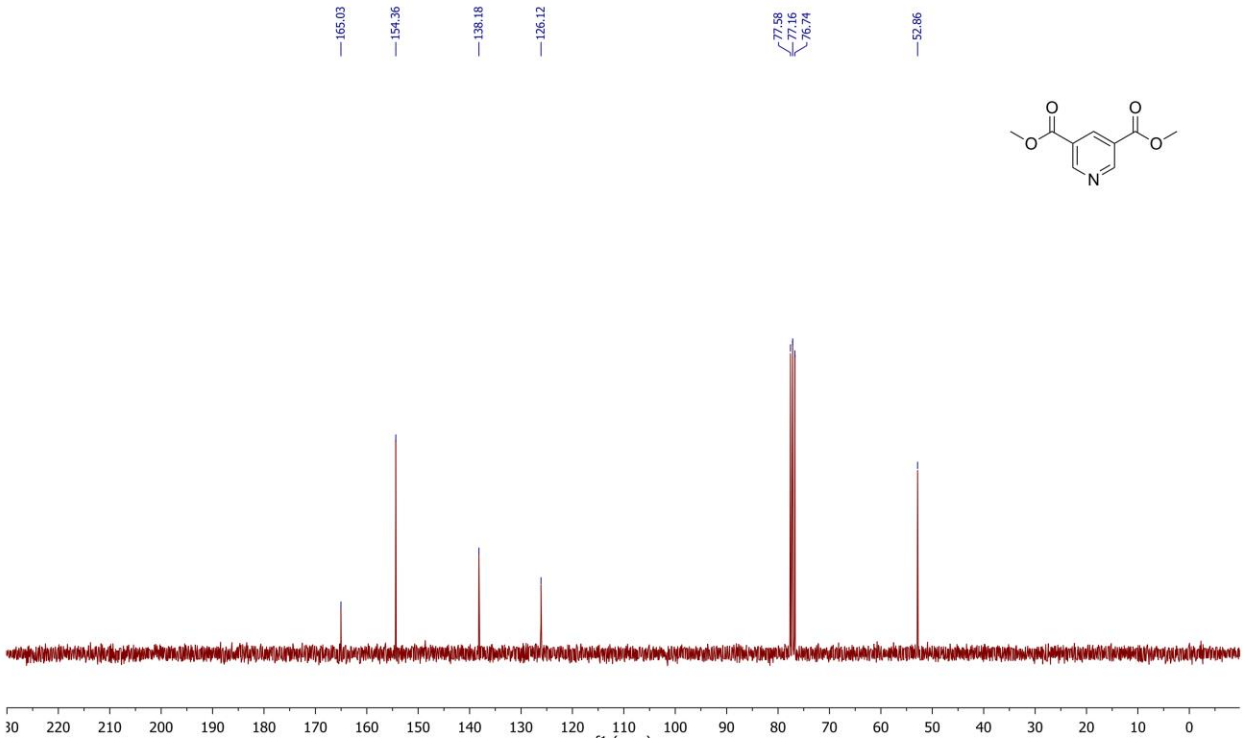
Chemical Formula: $C_9H_9NO_4$
Exact Mass: 195,0532
Molecular Weight: 195,1740

To a stirred suspension of 3,5-pyridinedicarboxylic acid (8.00 g, 47.90 mmol) in methanol (160 mL) at room temperature, $SOCl_2$ (10.42 mL, 143.7 mmol) was added dropwise. The mixture was heated to reflux. Within 30 minutes the suspension became a solution which was stirred under reflux for another 3 h. After cooling the reaction mixture to room temperature, the contents were concentrated in vacuo. To the resulting residue, water was added and adjusted pH ~7 with aqueous 8 M NaOH solution. The resulted suspension was extracted with EtOAc (3 x 100 mL). The organic layers were combined, washed subsequently with saturated $NaHCO_3$ (2 x 30 mL), water (1 x 30 mL) and brine (1 x 30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a white solid (9.2 g, 98%). ^{1}H NMR (300.27 MHz, chloroform-d) δ 9.36 (d, *J* = 2.1 Hz, 2H), 8.87 (t, *J* = 2.1 Hz, 1H), 3.99 (s, 6H). ^{13}C NMR (75.50 MHz, chloroform-d) δ 165.0, 154.4, 138.2, 126.1, 52.9. IR (diamond-ATR) v: 3087, 3012, 2962, 1716, 1602, 1264, 743, 691.

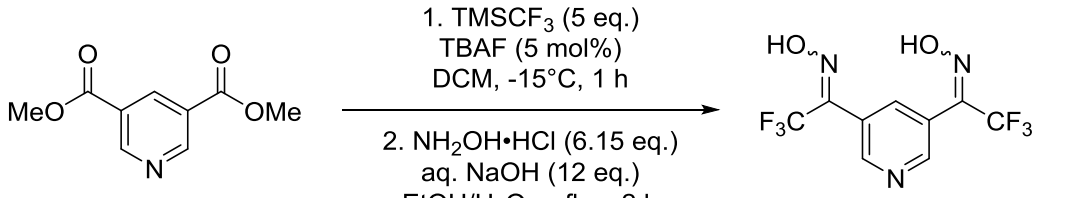
^{1}H NMR spectrum of dimethyl pyridine-3,5-dicarboxylate in $CDCl_3$:



^{13}C NMR spectrum of dimethyl pyridine-3,5-dicarboxylate in $CDCl_3$:



Synthesis of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) dioxime



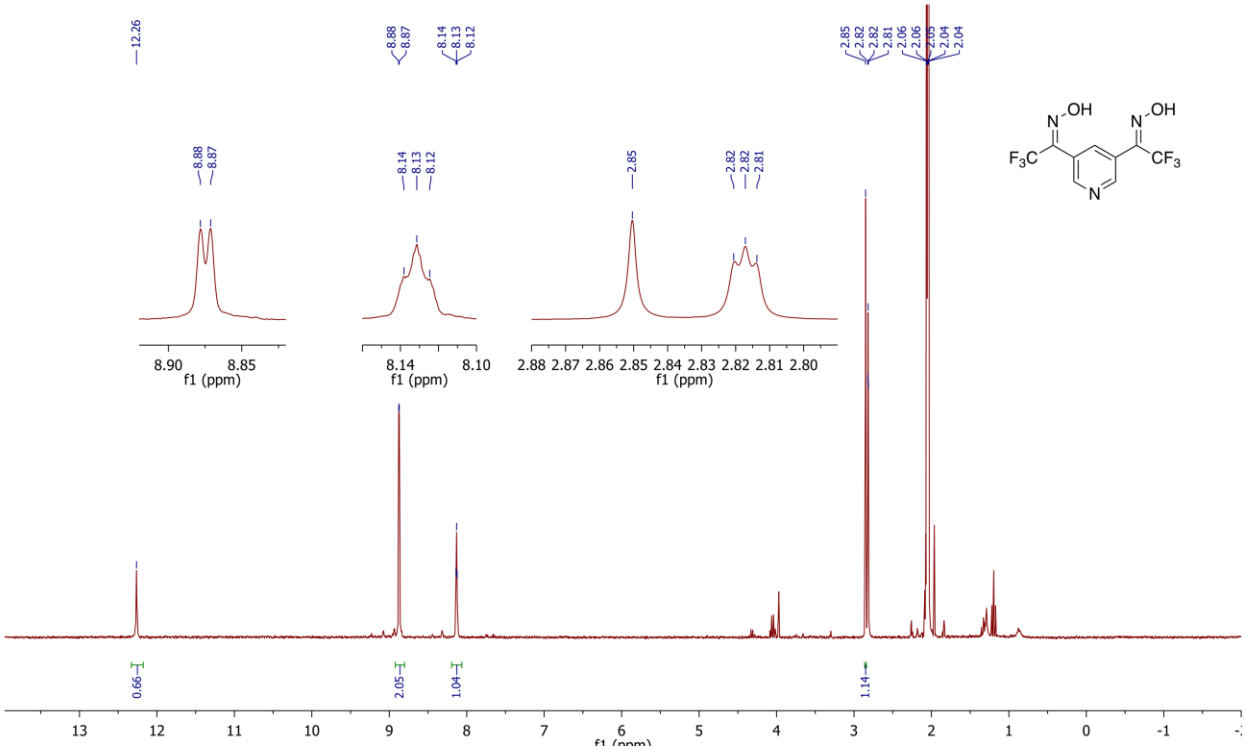
Chemical Formula: $C_9H_9NO_4$
Exact Mass: 195,0532
Molecular Weight: 195,1740

Chemical Formula: $C_9H_5F_6N_3O_2$
Exact Mass: 301,0286
Molecular Weight: 301,1484

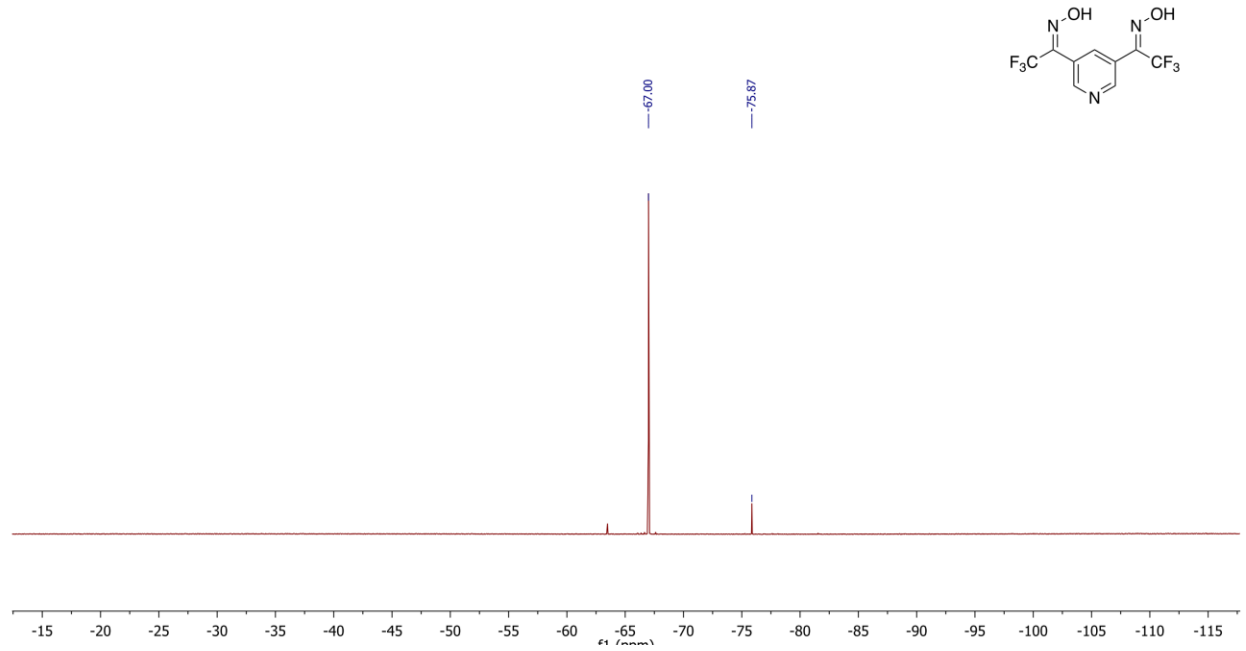
In a flame-dried flask under argon, to a solution of dimethyl pyridine-3,5-dicarboxylate (1 eq., 1.00 g, 5.12 mmol) and $TMSCF_3$ (5.0 eq., 3.79 mL, 25.6 mmol) in dry DCM (4 mL, distilled) at –15°C (ice/ethanol bath) was added dropwise a 1M solution of TBAF in THF (5 mol%, 256 µL, 256 µmol). The mixture was stirred for 1 h, giving a clear, dark reaction mixture. At 30 min, TLC and NMR analysis showed that the reaction was complete.

The reaction was quenched at –15°C by the addition of ethanol (25 mL), followed by hydroxylamine hydrochloride (6.15 eq., 2.19 g, 31.5 mmol). The mixture was brought to pH 11 with 2 M aq. NaOH (12 eq., 30 mL, 61.5 mmol), heated to reflux for 2 h and then left at room temperature overnight (12 h). The mixture was then neutralized (pH = 7–8) by the addition of small portions of 4 M HCl, and concentrated to remove most of the ethanol. The aqueous mixture was then treated with sat. aq. ammonium chloride (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried with sodium sulfate, filtered and concentrated. The residue was purified by silica gel column chromatography (gradient of AcOEt/hexanes from 5 % to 50%) to afford the desired bis-oxime (1.22 g, 4.03 mmol) in 79% yield over 2 steps. ^{1}H NMR (300.27 MHz, acetone-d_6) δ 12.26 (s, 1H), 8.87 (d, *J* = 2.0 Hz, 2H), 8.13 (t, *J* = 2.0 Hz, 1H), 2.85 (s, 1H). ^{13}C NMR (126 MHz, acetone-d_6) δ 151.4, 143.8 (q, *J* = 32.9 Hz), 137.5, 124.2, 121.8 (q, *J* = 273.0 Hz). ^{19}F NMR (282.54 MHz, acetone-d_6) δ -67.00. IR (diamond-ATR) ν: 3184, 3054, 2853, 1693, 1584, 1343, 1249, 1195, 1121, 969, 732. HRMS (ESI+) m/z [M+H] calculated for $C_9H_6F_6N_3O_2$: 302.03587; found: 302.0359.

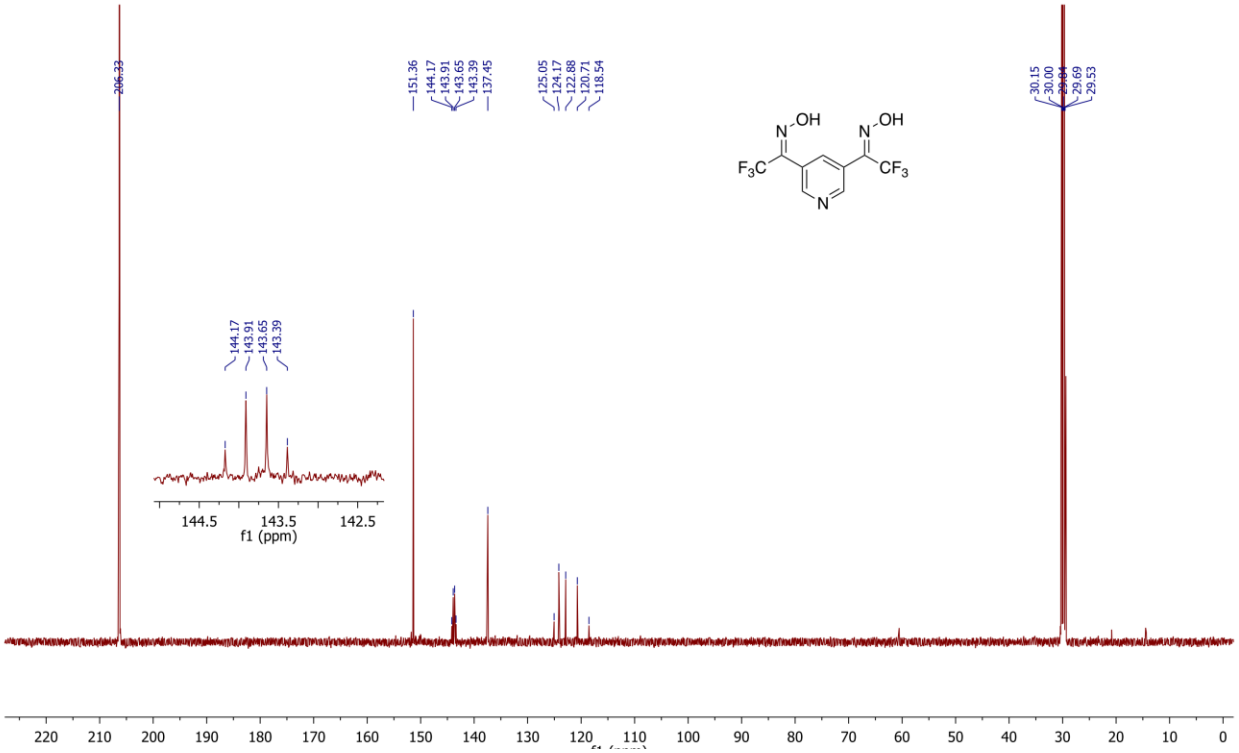
^{1}H NMR spectrum of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) dioxime in acetone-d_6:



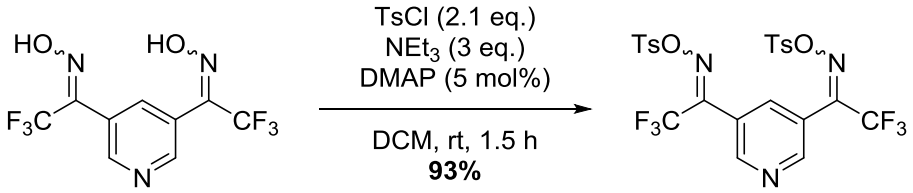
^{19}F NMR spectrum of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) dioxime in acetone-d_6:



^{13}C NMR spectrum of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) dioxime in acetone-d_6:



Synthesis of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime



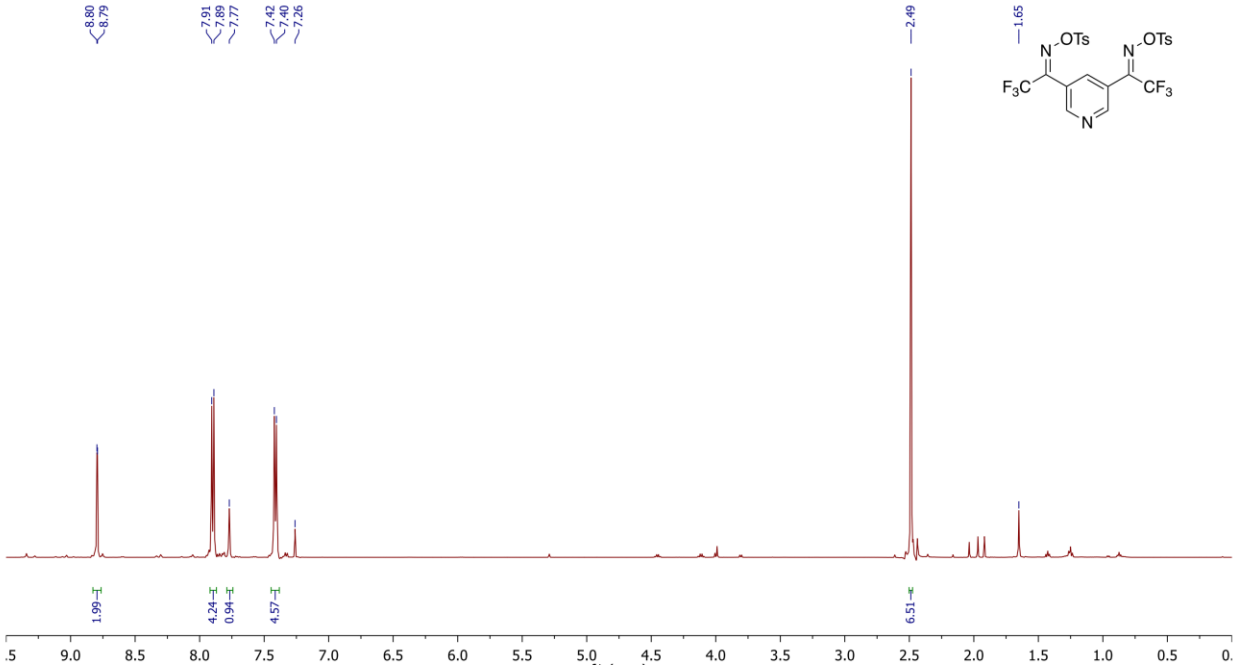
Chemical Formula: $C_9H_5F_6N_3O_2$
Exact Mass: 301,0286
Molecular Weight: 301,1484

Chemical Formula: $C_{23}H_{17}F_6N_3O_6S_2$
Exact Mass: 609,0463
Molecular Weight: 609,5144

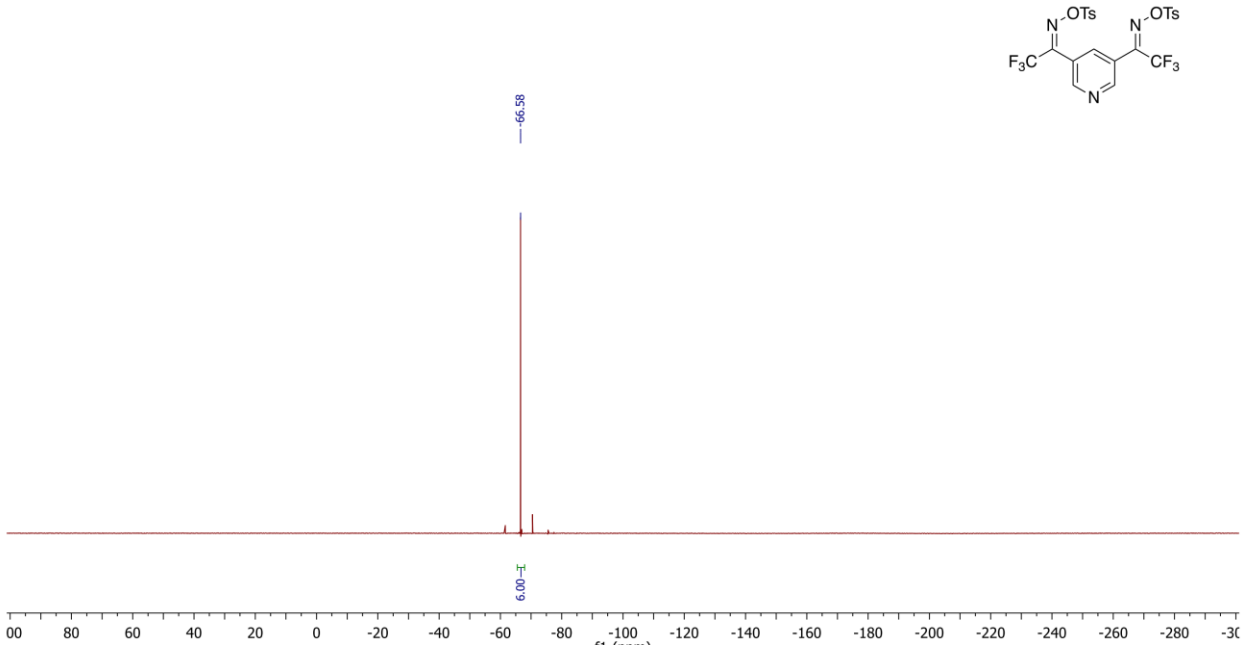
To a suspension of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) dioxime (1 eq., 1.181 g, 3.92 mmol) in DCM (10 mL) at room temperature was added tosyl chloride (2.1 eq., 1.57 g, 8.23 mmol), triethylamine (3.0 eq., 1.64 mL, 11.8 mmol), and DMAP (5 mol%, 24 mg, 196 µmol). The mixture was stirred at room temperature for 1.5 h. The mixture was treated with sat. aq. NH_4Cl (50 mL) and extracted with DCM (3 x 50 mL). The combined organic extracts were washed with water (50 mL), dried with sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography (gradient of AcOEt/hexanes from 0% to 20%) to afford the desired bis-tosyloxime (2.23 g, 3.65 mmol) in 93% yield. ^{1}H NMR (500.27 MHz, chloroform-d) δ 8.79 (d, *J* = 2.1 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 4H), 7.77 (s, 1H), 7.41 (d, *J* = 8.1 Hz, 4H), 2.49 (s, 6H). ^{13}C NMR (126 MHz, chloroform-d) δ 151.41, 149.8 (q, *J* = 34.9 Hz), 146.9, 136.1, 130.7, 130.3, 129.5, 121.6, 119.3 (q, *J* = 278 Hz), 22.0. ^{19}F NMR (282.54 MHz, chloroform-d) δ -66.58. IR

(diamond-ATR) ν: 1597, 1394, 1197, 1181, 1151, 902, 815, 763, 685, 548. HRMS (ESI+) m/z [M+H] calculated for $C_{23}H_{18}F_6N_3O_6S_2$: 610.0536; found: 610.0535; [M+Na] calculated for $C_{23}H_{17}F_6N_3O_6S_2Na$: 632.0355; found: 632.0352.

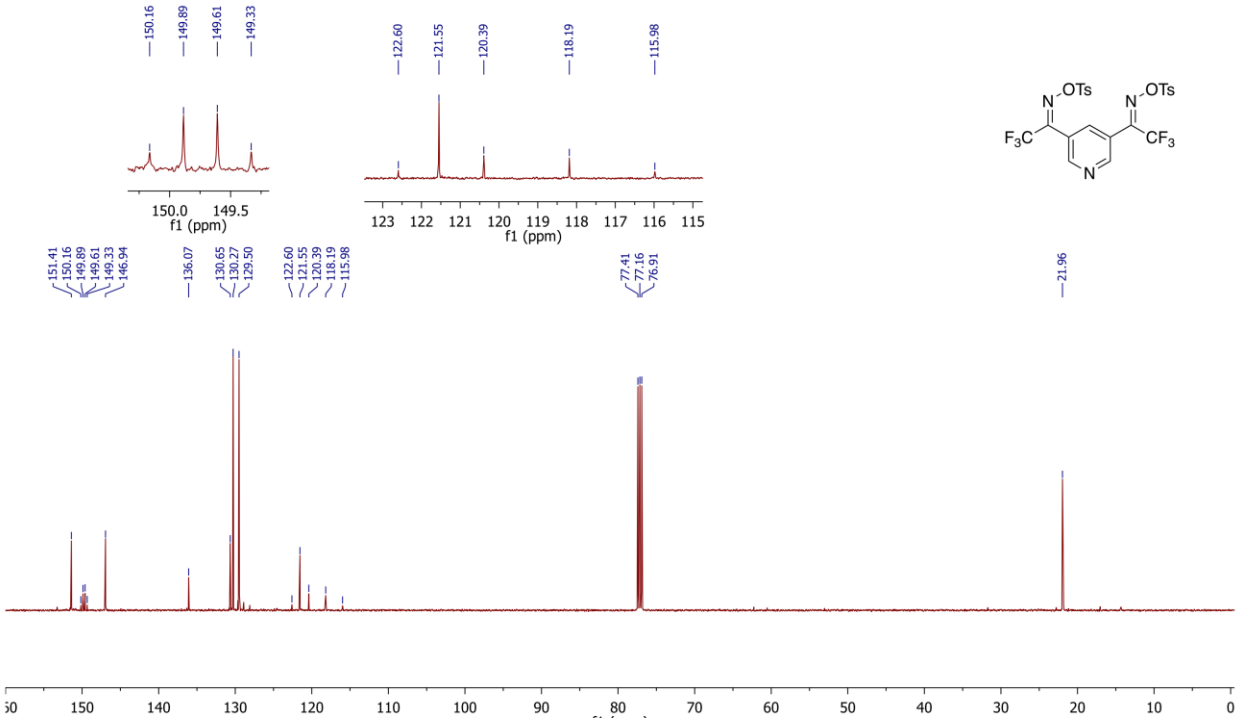
^{1}H NMR spectrum of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$:



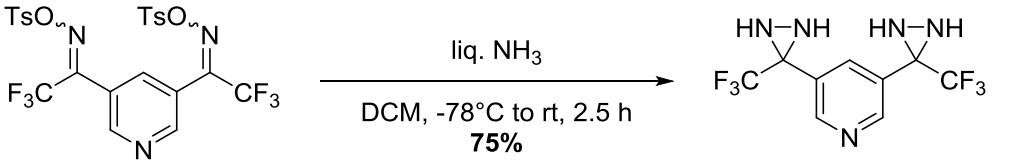
^{19}F NMR spectrum of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$:



^{13}C NMR spectrum of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$:



Synthesis of 3,5-bis(3-(trifluoromethyl)diaziridin-3-yl)pyridine



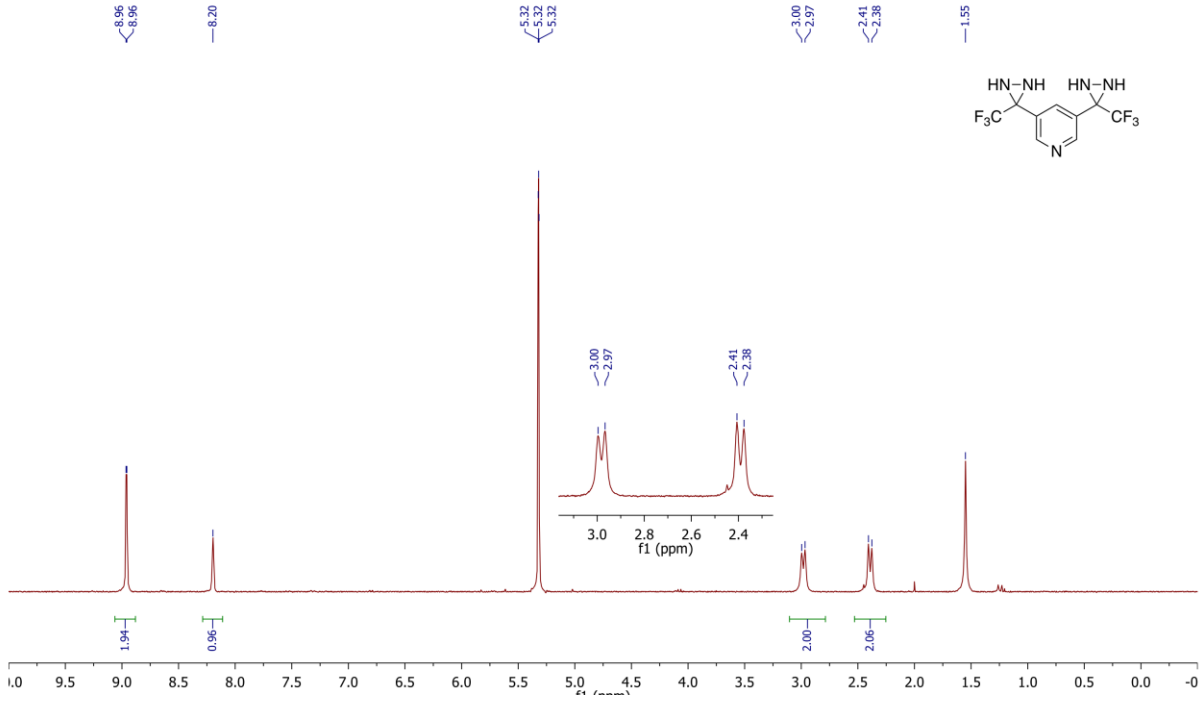
Chemical Formula: $C_{23}H_{17}F_6N_3O_6S_2$
Exact Mass: 609,0463
Molecular Weight: 609,5144

Chemical Formula: $C_9H_7F_6N_5$
Exact Mass: 299,0606
Molecular Weight: 299,1804

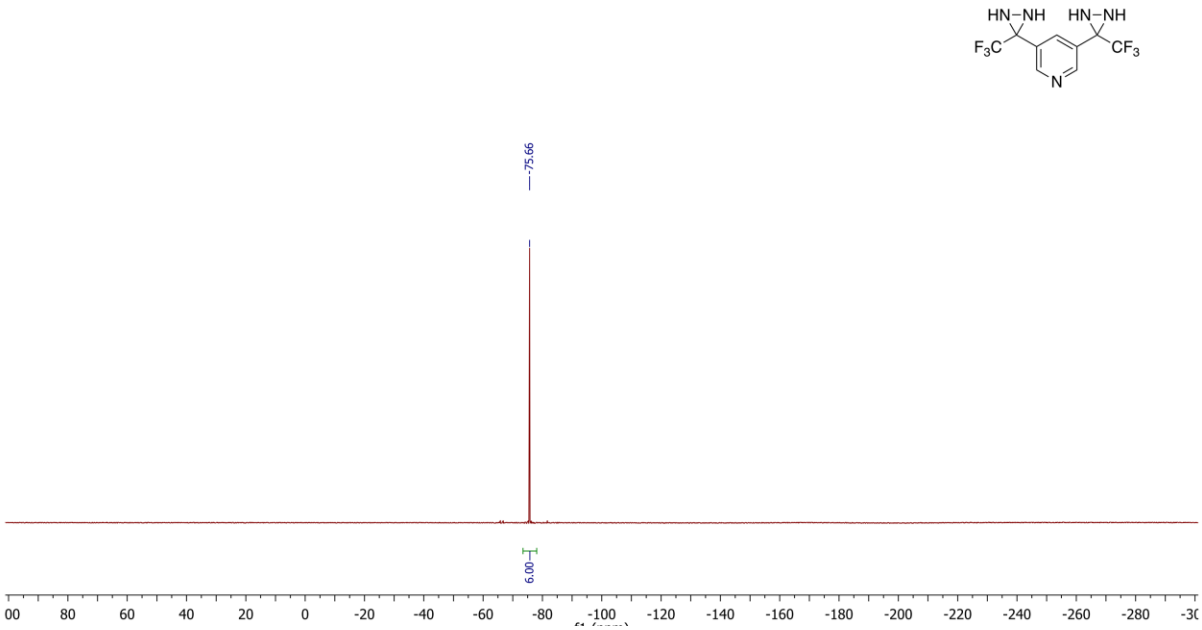
A flame-dried 3-neck flask under argon was equipped with a gas condenser and a circulation of anhydrous gaseous ammonia was set up. Upon cooling the system to –78 °C, ca. 125 mL of ammonia (ca. 1500 eq.) was condensed in the flask. A solution of 1,1'-(pyridine-3,5-diyl)bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime (1 eq., 2.19 g, 3.59 mmol) in anhydrous CH_2Cl_2 (10 mL) at room temperature was added dropwise over 10 min, maintaining the gaseous ammonia flow. The reaction mixture was stirred at –78 °C for 1 h. The mixture was allowed to warm up to room temperature over 1.5 h (a room temp water bath was used in the last hour). When the ammonia had all evaporated, water (50 mL) and CH_2Cl_2 (50 mL) were added to the flask and the layers separated. The aqueous layer was further extracted with CH_2Cl_2 (5 x 50 mL). The combined organic extracts were dried with sodium sulfate, filtered, and concentrated. The crude residue was purified by silica gel column chromatography (gradient of AcOEt/hexanes from 20% to 45%) to afford the desired bis-diaziridine (806 mg, 2.69 mmol) with 75% yield. ^{1}H NMR (300.27 MHz, methylene chloride-d_2) δ 8.96 (d, *J* = 2.1 Hz, 2H), 8.20 (s, 1H), 2.98 (d, *J* = 8.9

Hz, 2H), 2.39 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (126 MHz, acetone-d_6) δ 151.6 and 151.6, 137.4, 137.2, 129.3 and 129.2, 124.8 (q, *J* = 278 Hz), 57.0 (q, *J* = 36.4 Hz), 56.9 (q, *J* = 36.4 Hz). ^{19}F NMR (282.54 MHz, methylene chloride-d_2) δ -75.66. IR (diamond-ATR) v: 3210, 1586 1440, 1394, 1145, 718, 671. HRMS (ESI+) m/z [M+H] calculated for $C_9H_8F_6N_5$: 300.06784; found: 300.0678.

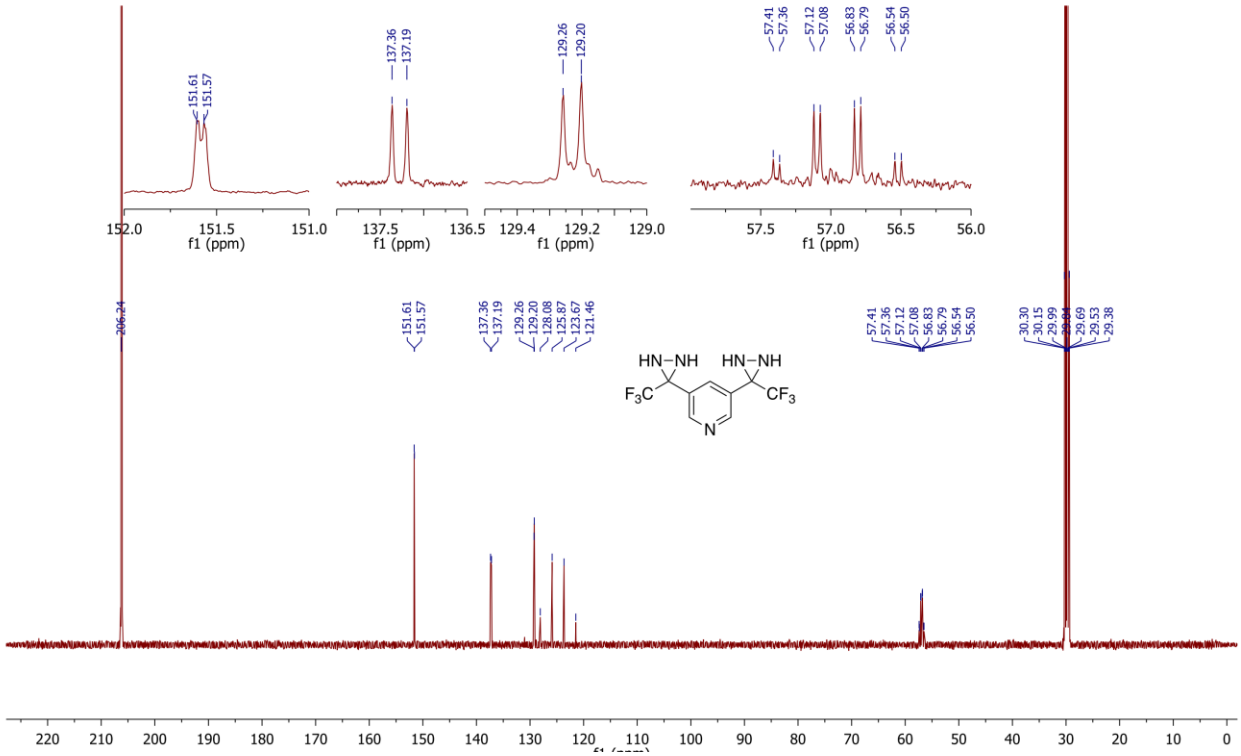
^{1}H NMR spectrum of 3,5-bis(3-(trifluoromethyl)diaziridin-3-yl)pyridine in CD_2Cl_2:



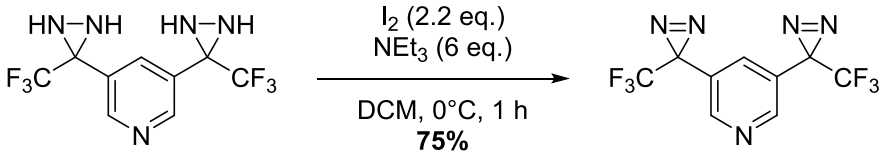
^{19}F NMR spectrum of 3,5-bis(3-(trifluoromethyl)diaziridin-3-yl)pyridine in CD_2Cl_2:



^{13}C NMR spectrum of 3,5-bis(3-(trifluoromethyl)diaziridin-3-yl)pyridine in acetone-d_6:



Synthesis of 3,5-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)pyridine (**2**)



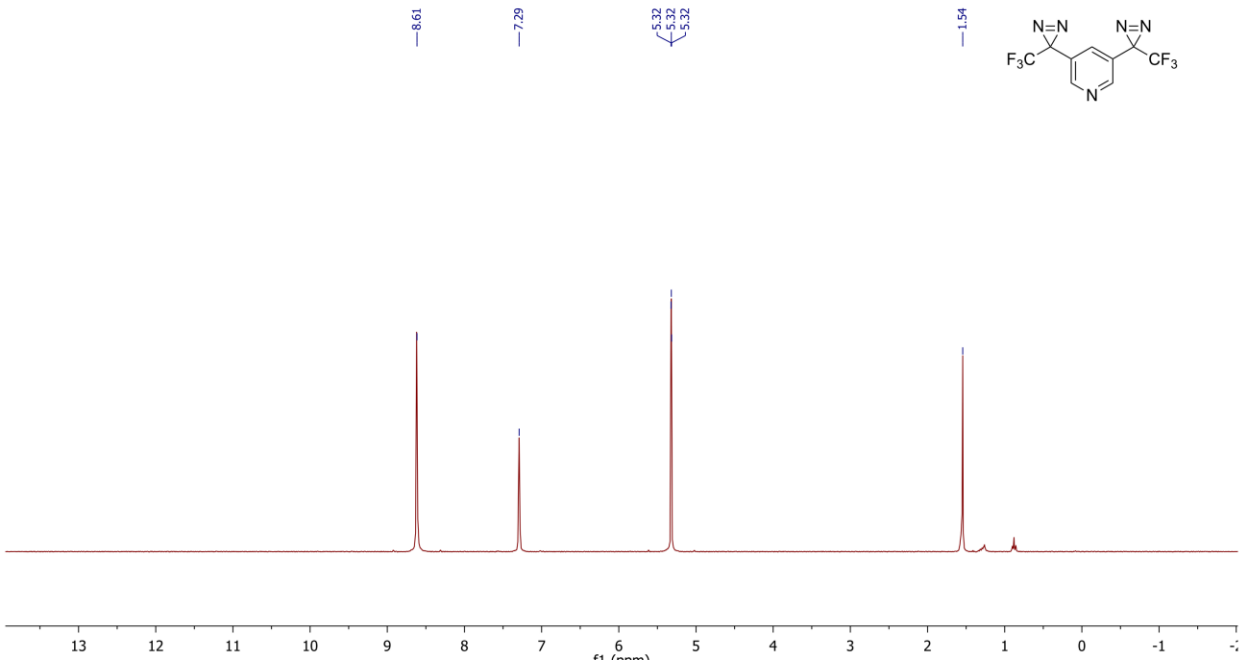
Chemical Formula: $C_9H_7F_6N_5$
Exact Mass: 299,0606
Molecular Weight: 299,1804

2

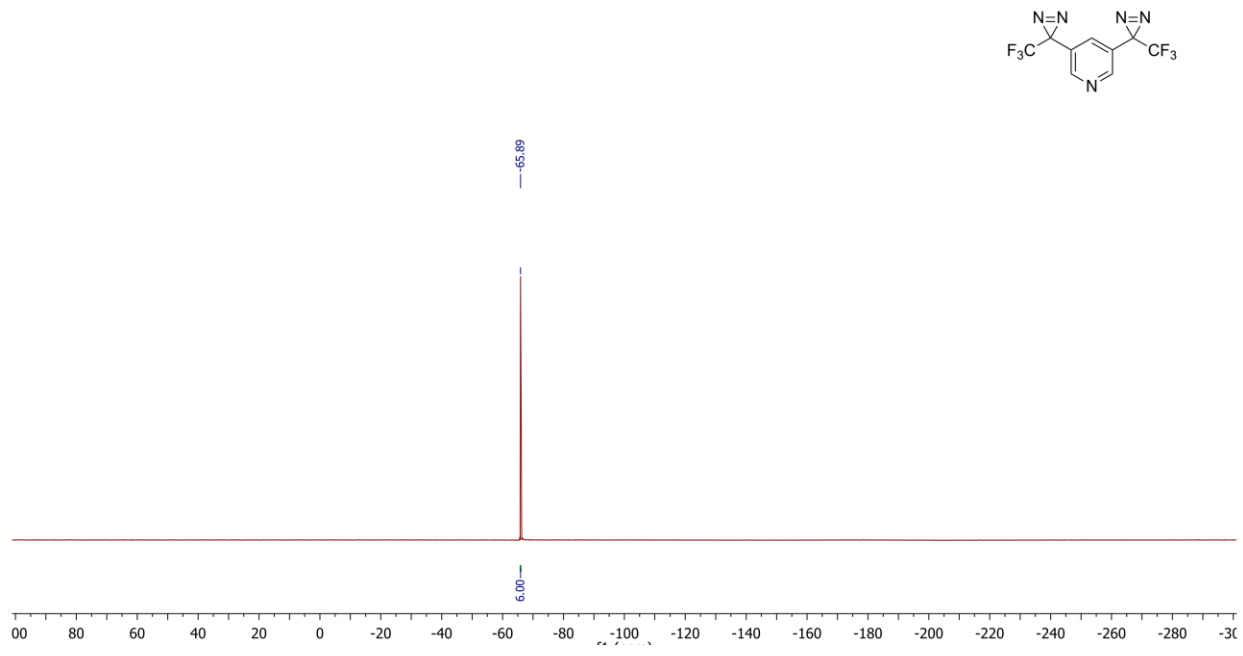
Chemical Formula: $C_9H_3F_6N_5$
Exact Mass: 295,0293
Molecular Weight: 295,1484

Reaction and workup were performed as in synthesis of **1**. Materials used in the reaction: 3,5-bis(3-(trifluoromethyl)diaziridin-3-yl)pyridine (0.40 g, 1.34 mmol) in DCM (10 mL), triethylamine (1.12 mL, 8.04 mmol), and iodine (0.75g, 2.95 mmol). The product (0.30 g, 75% yield) was obtained as a clear colorless liquid which solidified upon cooling. Melting point = +27°C. ^{1}H NMR (300.27 MHz, methylene chloride-d_2) δ 8.61 (s, 2H), 7.29 (s, 1H). ^{13}C NMR (126 MHz, methylene chloride-d_2) δ 149.5 (q, *J* = 2.0 Hz), 132.9, 125.9, 122.0 (q, *J* = 275 Hz), 27.4 (q, *J* = 42.0 Hz). ^{19}F NMR (282.54 MHz, methylene chloride-d_2) δ -65.89. IR (diamond-ATR) ν: 3058, 3025, 2949, 1622, 1452, 1332, 1260, 1181, 1144, 707, 681. HRMS (ESI+) m/z [M+H] calculated for $C_9H_4F_6N_5$: 296.03654, found: 296.03655.

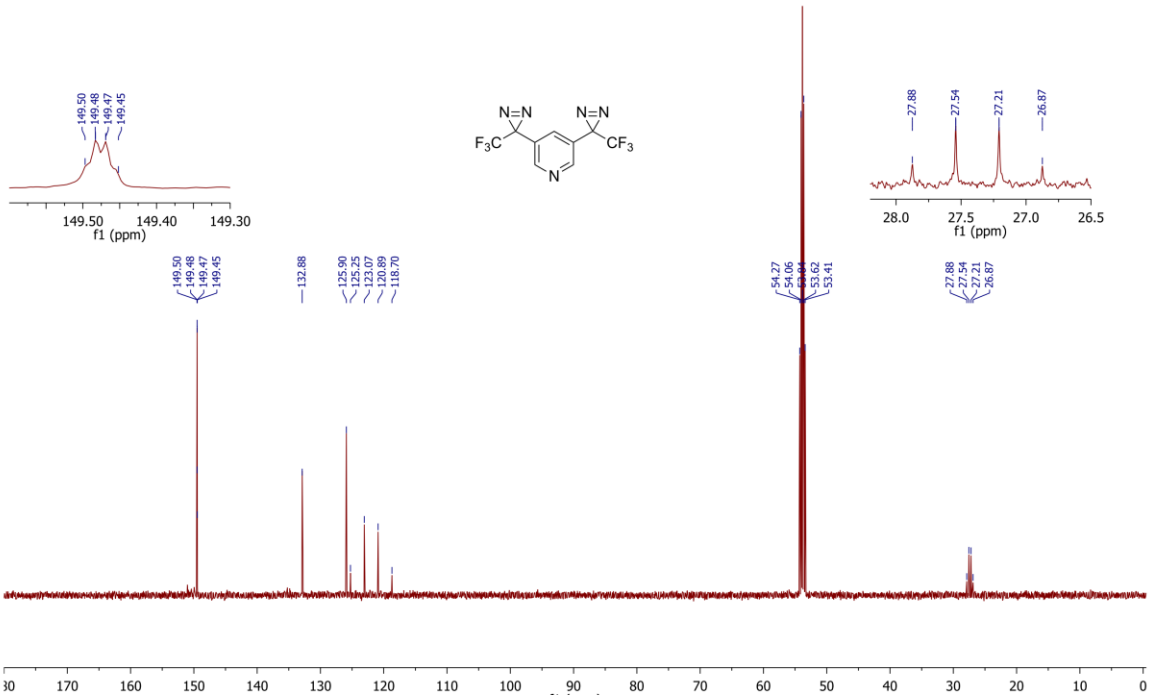
^{1}H NMR spectrum of 3,5-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)pyridine (2) in CD_2Cl_2:



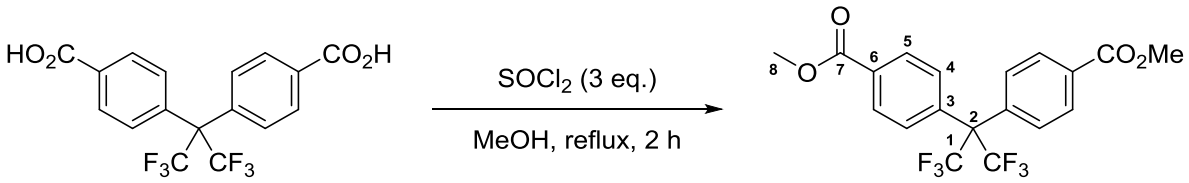
^{19}F NMR spectrum of 3,5-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)pyridine (2) in CD_2Cl_2:



^{13}C NMR spectrum of 3,5-bis(3-(trifluoromethyl)-3*H*-diazirin-3-yl)pyridine (2) in CD_2Cl_2:



Synthesis of dimethyl 4,4'-(perfluoropropane-2,2-diyl)dibenzoate

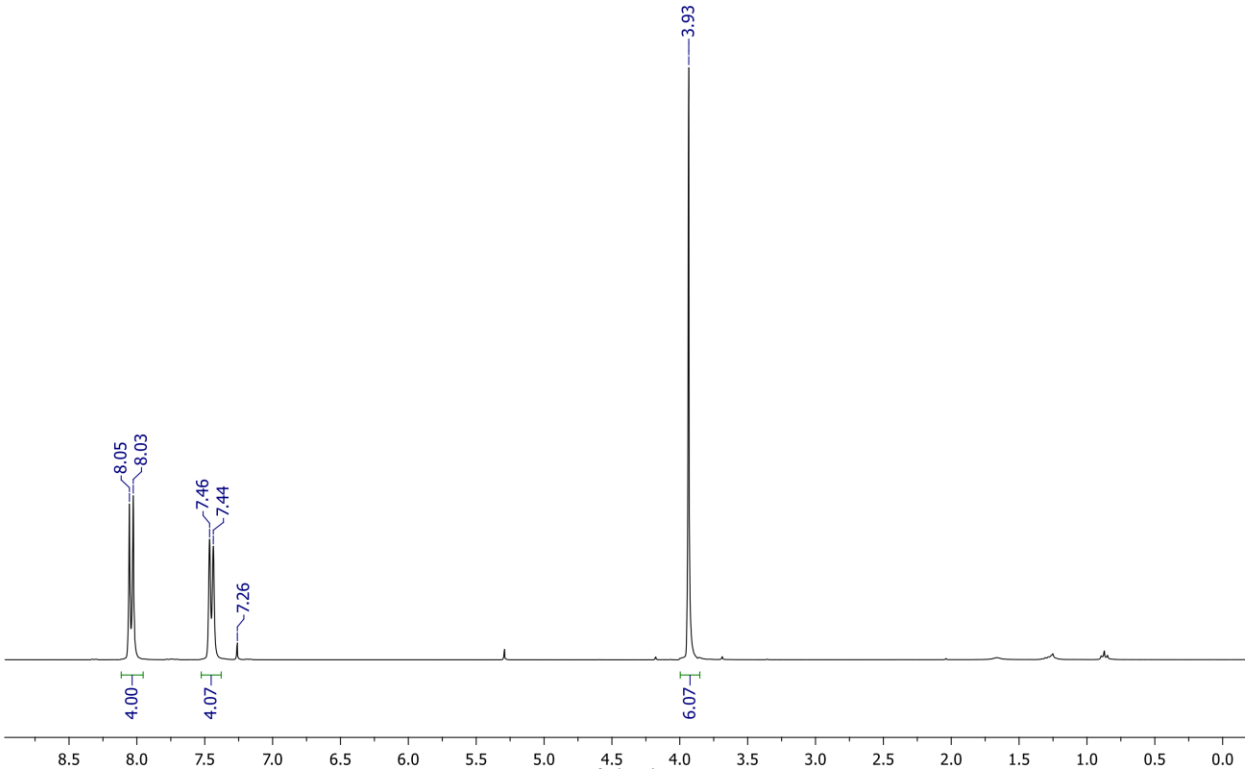


Chemical Formula: $C_{17}H_{10}F_6O_4$
Exact Mass: 392,05
Molecular Weight: 392,25

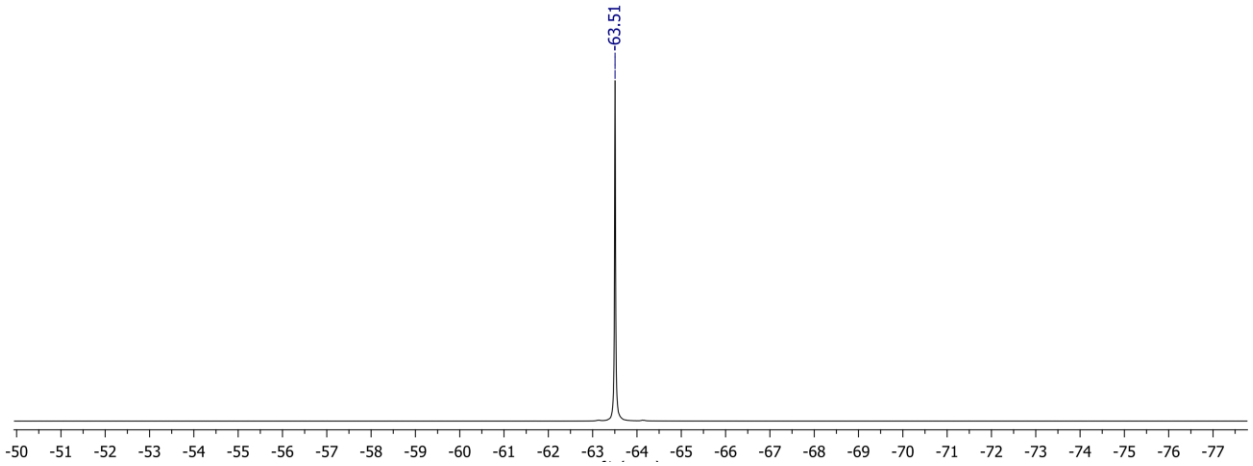
Chemical Formula: $C_{19}H_{14}F_6O_4$
Exact Mass: 420,08
Molecular Weight: 420,31

To a solution of 4,4'-(perfluoropropan-2,2-diyl)dibenzoic acid (10.00 g, 25.49 mmol) in MeOH (100 mL) was added dropwise thionyl chloride (3 eq., 5.55 mL, 76.48 mmol) at room temperature. The clear, colorless reaction mixture was heated to reflux for 2 h. The mixture was cooled down to room temperature and then concentrated in vacuo. The residue was treated with sat. aq. sodium bicarbonate (50 mL) and extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over sodium sulfate and concentrated to afford a colorless resin (10.72 g, 25.49 mmol, quantitative). ^{1}H NMR (300 MHz, chloroform-d) δ 8.05 (d, *J* = 8.4 Hz, 4H, H-5), 7.46 (d, *J* = 8.4 Hz, 4H, H-4), 3.94 (s, 6H, H-8). ^{13}C NMR (75 MHz, chloroform-d) δ 166.25 (C-7), 137.70 (C-3), 131.15 (C-6) 130.37 (C-4), 129.58 (C-5), 123.96 (q, *J* = 296 Hz, C-1), 64.68 (m, *J* = 26 Hz, C-2), 52.53 (C-8). ^{19}F NMR (282 MHz, chloroform-d) δ -63.51. IR (diamond-ATR) ν: 2956, 1726, 1612, 1577, 1513, 1438, 1417, 1326, 1279, 1252, 1239, 1208, 1171, 1111, 1022, 972, 959, 945, 929, 853, 825, 768, 748, 721, 709, 688. HRMS (ESI+) m/z [M+H] calculated for $C_{19}H_{15}F_6O_4$: 421.08690, found: 421.08689.

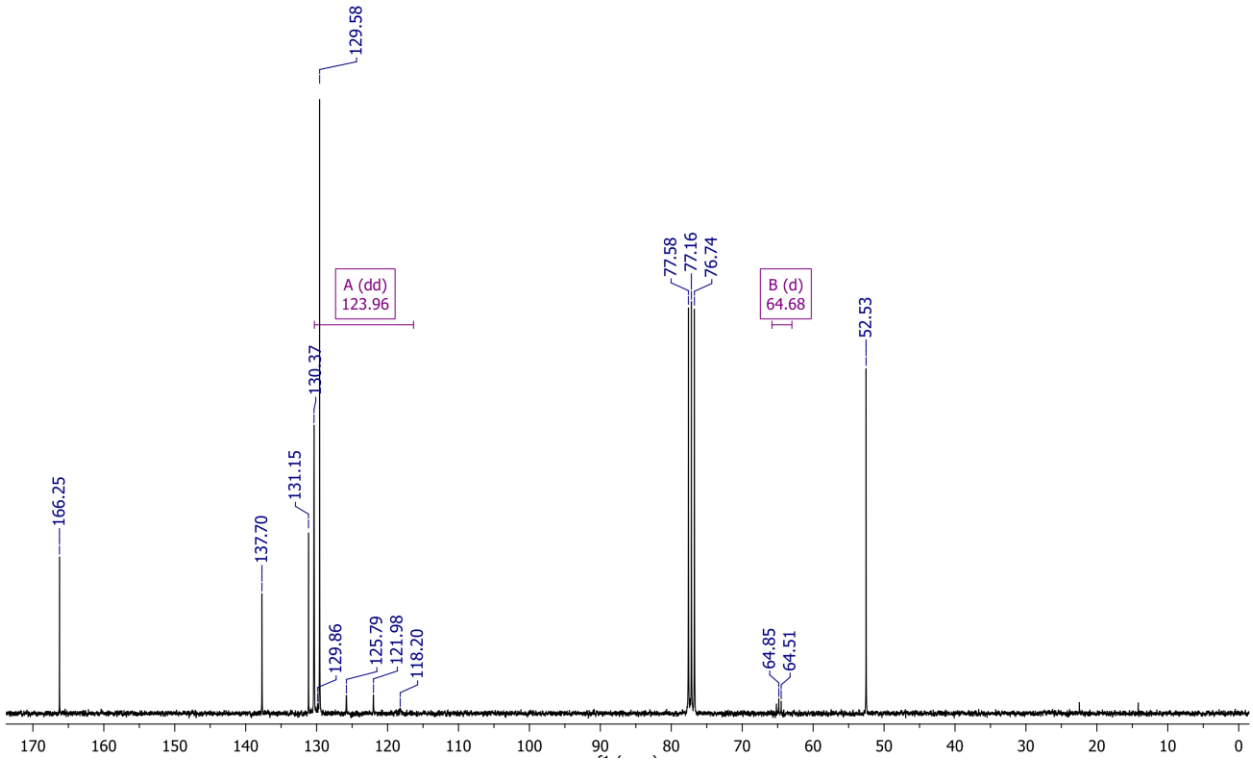
^{1}H NMR spectrum of dimethyl 4,4'-(perfluoropropane-2,2-diyl)dibenzoate in $CDCl_3$:



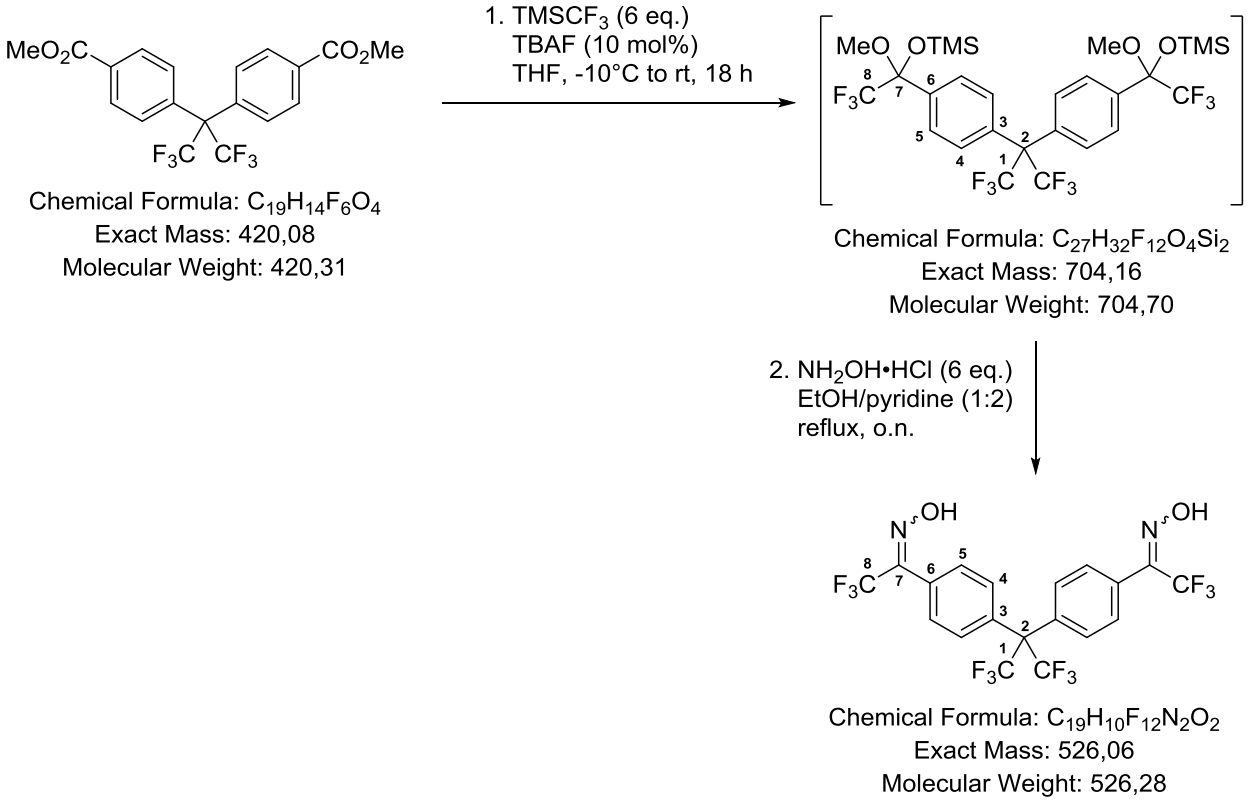
^{19}F NMR spectrum of dimethyl 4,4'-(perfluoropropane-2,2-diyl)dibenzoate in $CDCl_3$:



^{13}C NMR spectrum of dimethyl 4,4'-(perfluoropropane-2,2-diyl)dibenzoate in $CDCl_3$:



Synthesis of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)-3*H*-diazirine) (**3**)



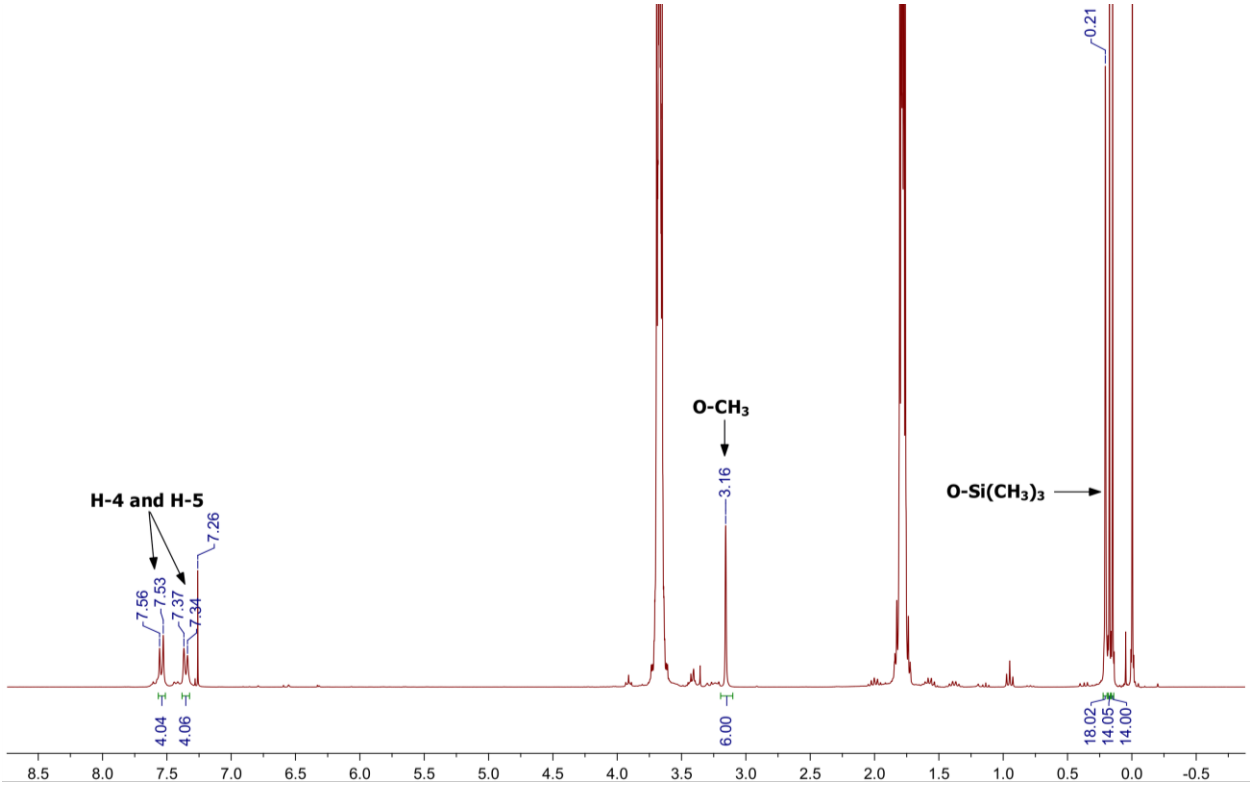
Chemical Formula: $C_{19}H_{14}F_6O_4$
Exact Mass: 420,08
Molecular Weight: 420,31

Chemical Formula: $C_{27}H_{32}F_{12}O_4Si_2$
Exact Mass: 704,16
Molecular Weight: 704,70

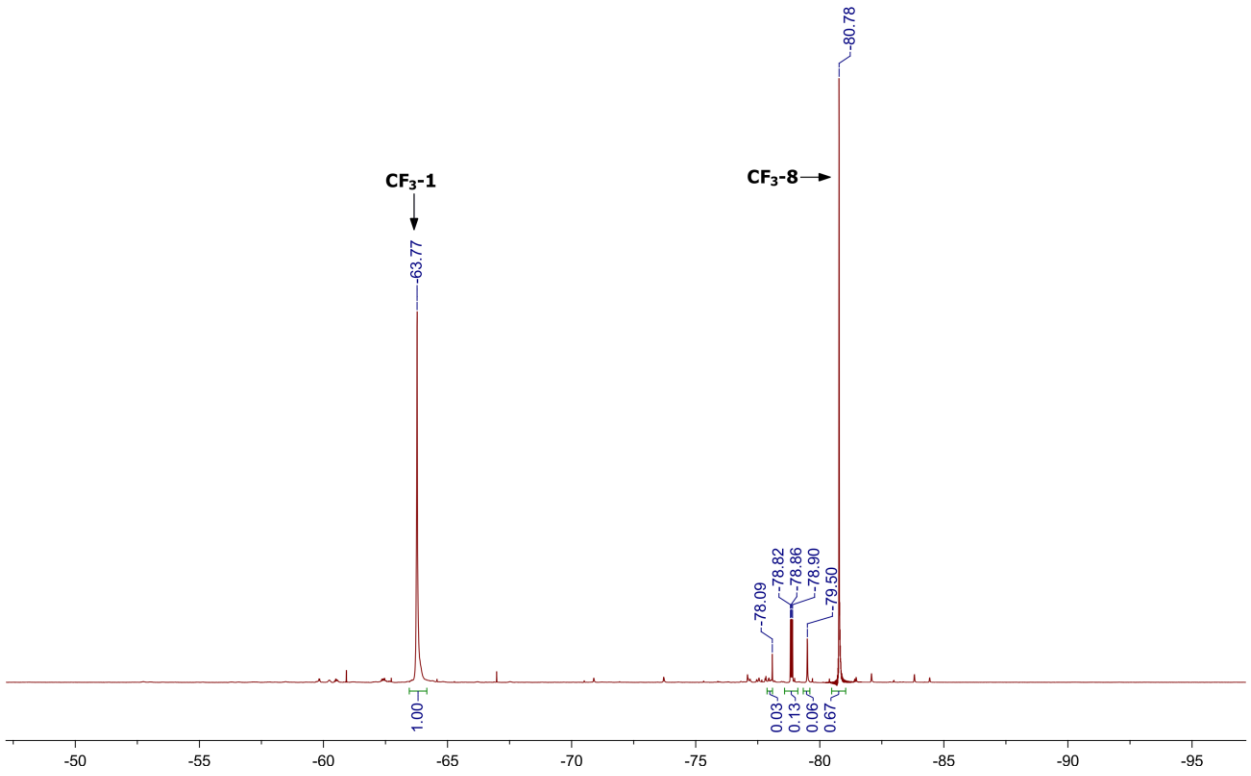
Chemical Formula: $C_{19}H_{10}F_{12}N_2O_2$
Exact Mass: 526,06
Molecular Weight: 526,28

In a flame-dried flask under argon, to a stirred solution of dimethyl 4,4'-(perfluoropropane-2,2-diyl)dibenzoate (1 eq., 5.37 g, 12.78 mmol) and $TMSCF_3$ (6.0 eq., 11.33 mL, 76.66 mmol) in anhydrous THF (30 mL) at –10 °C (ice/ethanol bath) was added dropwise a 1 M solution of TBAF in THF (10 mol%, 1.28 mL, 1.28 mmol). The mixture was then stirred, allowing the temperature to slowly raise to room temperature. As the temperature rose, the solution turned darker and darker orange. By diluting a few drops of the reaction mixture with $CDCl_3$, the reaction can be monitored by ^{1}H and ^{19}F NMR ($CDCl_3$, 300 and 282 MHz, resp.) in which the desired, unstable bis-methyl(trimethylsilyl)trifluoromethylketone acetal can be clearly observed.

^{1}H NMR spectrum of reaction mixture during trifluoromethylation, diluted in $CDCl_3$:



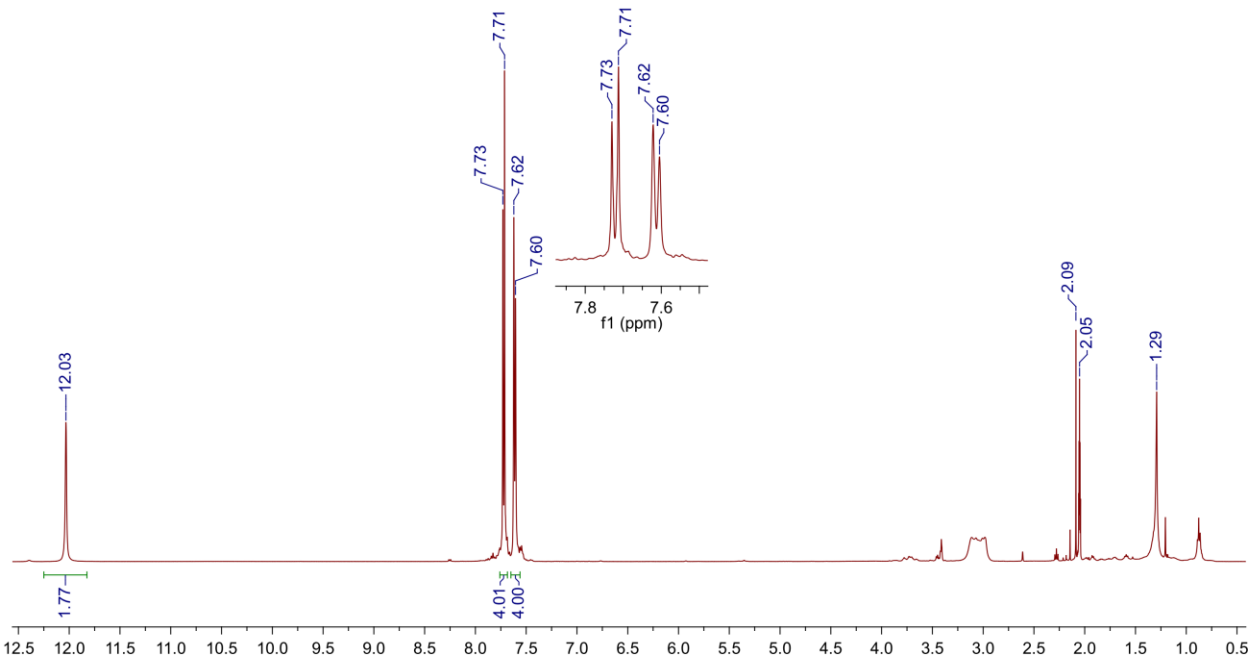
^{19}F NMR spectrum of reaction mixture during trifluoromethylation, diluted in $CDCl_3$:



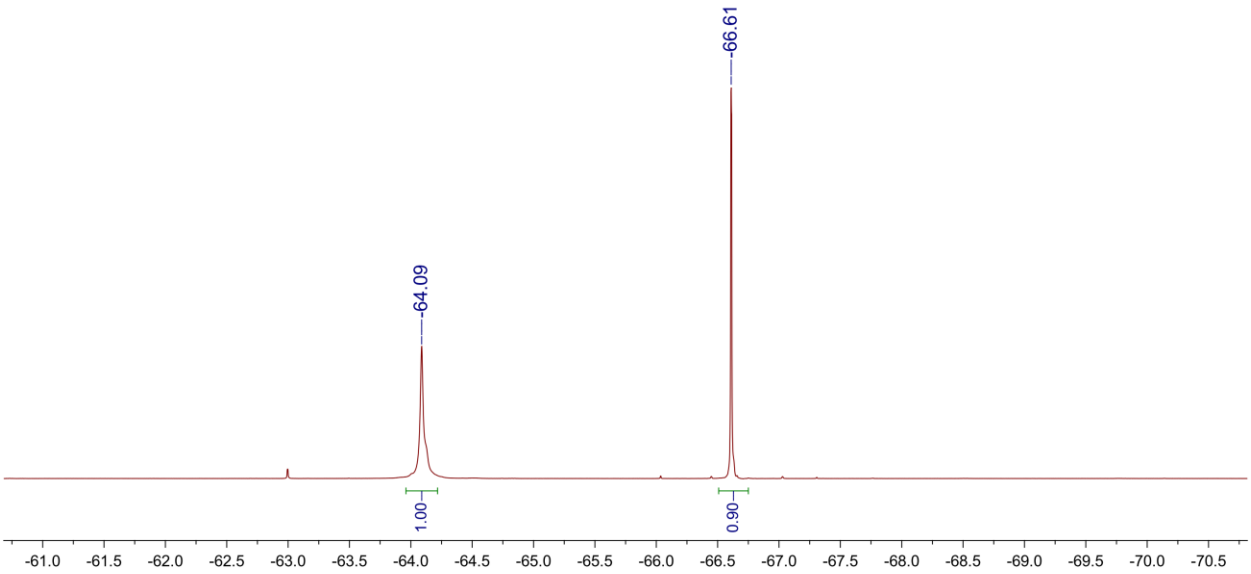
The mixture was quenched by the slow, careful addition of ethanol (20 mL). Hydroxylamine hydrochloride (6 eq., 5.33 g, 76.66 mmol) was added to the mixture, followed by the subsequent addition of pyridine (40 mL). The mixture was heated to reflux overnight (16 h). After cooling down to room temperature, the mixture was concentrated to remove most of the solvents. The resulting mixture was treated with 4M HCl (200 mL) and extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with distilled water until the pH of the washing layer became neutral. TLC confirmed efficient extraction. The combined organic extracts were then dried with sodium sulfate, filtered and concentrated. Then the residue was dried under high vacuum for a prolonged time to afford the desired crude bis-oxime (8.84 g), which was submitted to the next step without further purification.

On one occasion, for the purpose of NMR characterization, the residue was purified by silica gel column chromatography (gradient of AcOEt/hexanes from 2% to 30%) to afford the pure bis-oxime. ^{1}H NMR (500 MHz, acetone-d_6) δ 12.03 (s, 2H, N-OH), 7.72 (d, *J* = 8.4 Hz, 4H, H-5), 7.61 (d, *J* = 8.4 Hz, 4H, H-4). ^{13}C NMR (125 MHz, acetone-d_6) δ 145.87 (q, *J* = 32 Hz, C-7), 135.40 (C-6), 131.11 (C-4), 130.05 (C-5), 129.16 (C-3), 125.03 (q, *J* = 287 Hz, C-1), 122.03 (q, *J* = 273 Hz, C-8), 65.51 (m, *J* = 26 Hz, C-2). ^{19}F NMR (470 MHz, acetone-d_6) δ -64.09 (CF_3-1), -66.61 (s, CF_3-8).

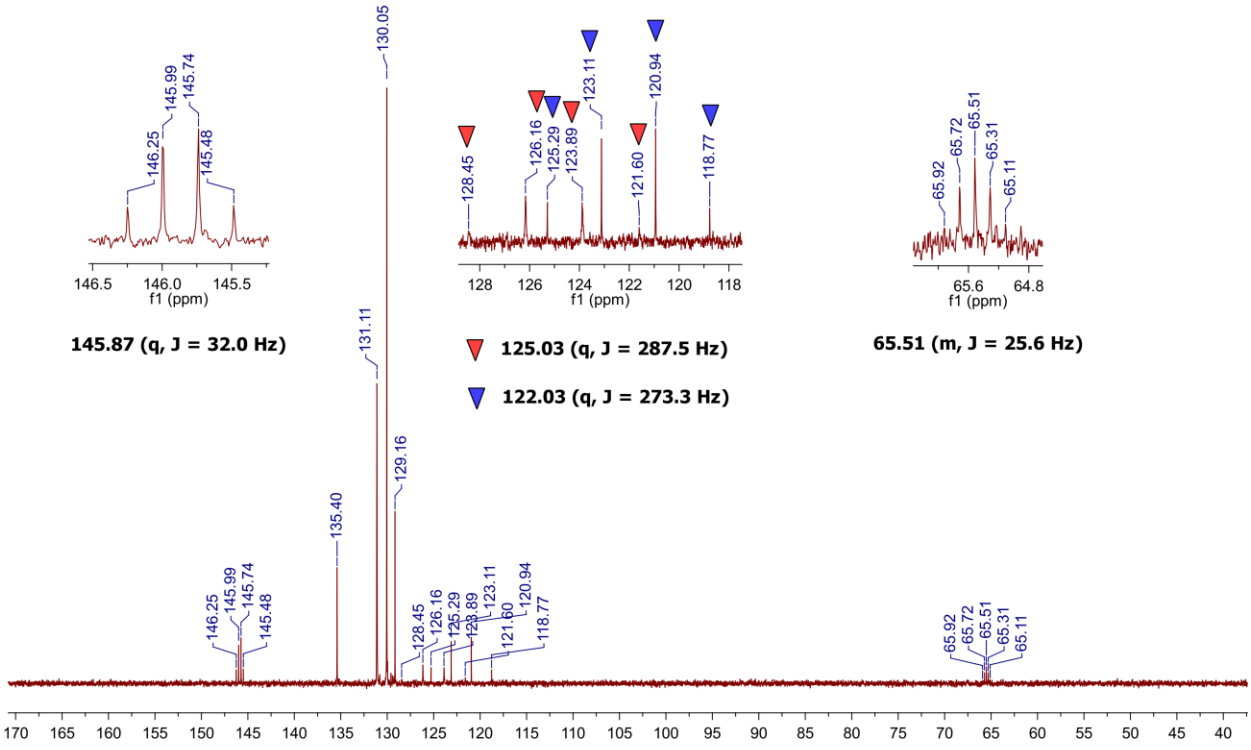
^{1}H NMR spectrum of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime in acetone-d_6:

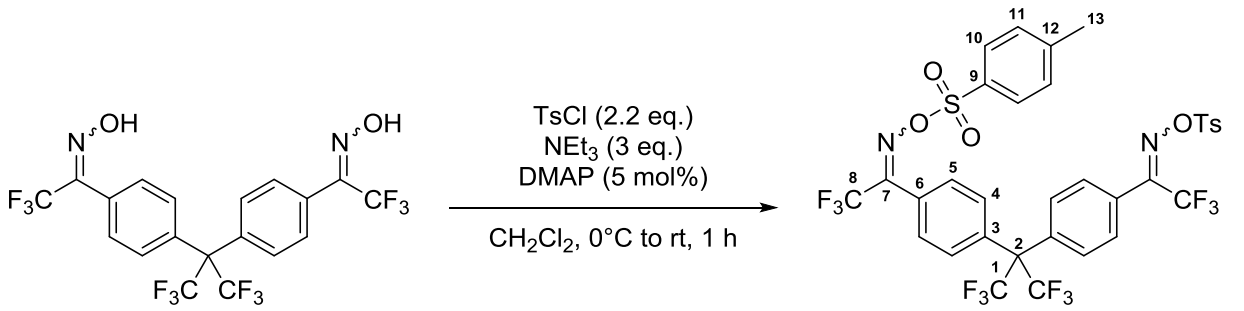


^{19}F NMR spectrum of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime in acetone-d_6:



^{13}C NMR spectrum of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime in acetone-d_6:





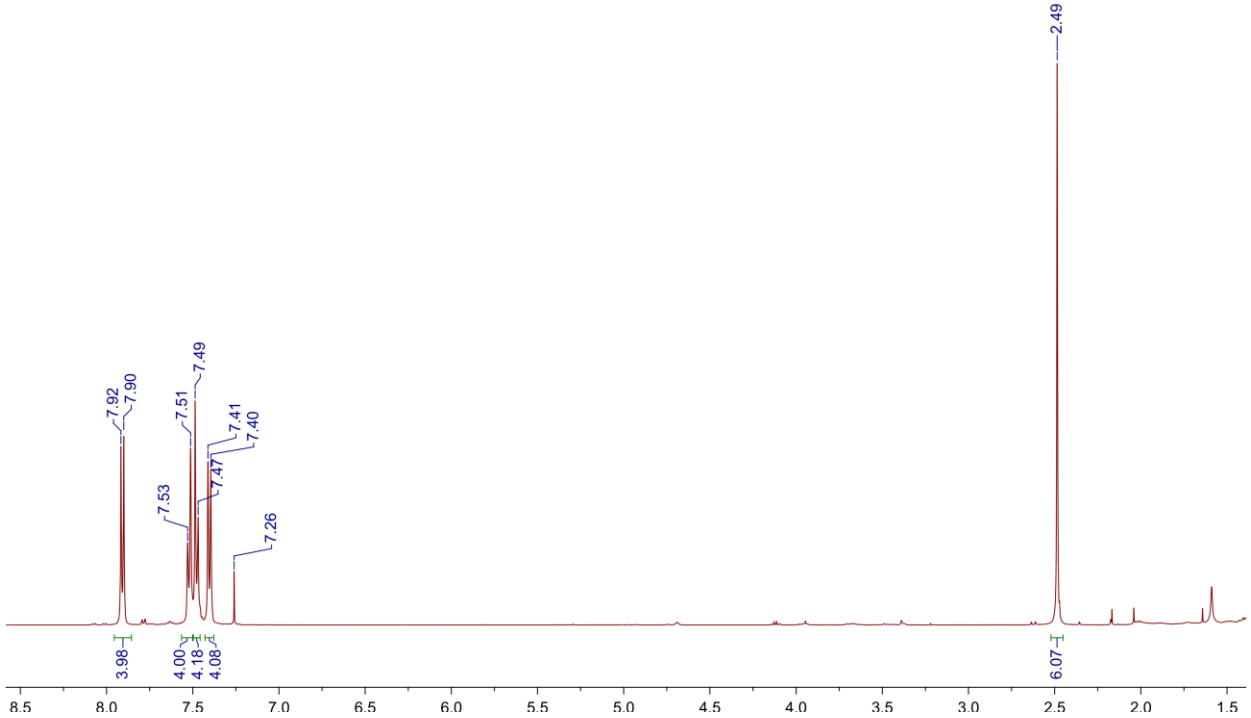
Chemical Formula: $C_{19}H_{10}F_{12}N_2O_2$
Exact Mass: 526,05507
Molecular Weight: 526,28184

Chemical Formula: $C_{33}H_{22}F_{12}N_2O_6S_2$
Exact Mass: 834,07
Molecular Weight: 834,65

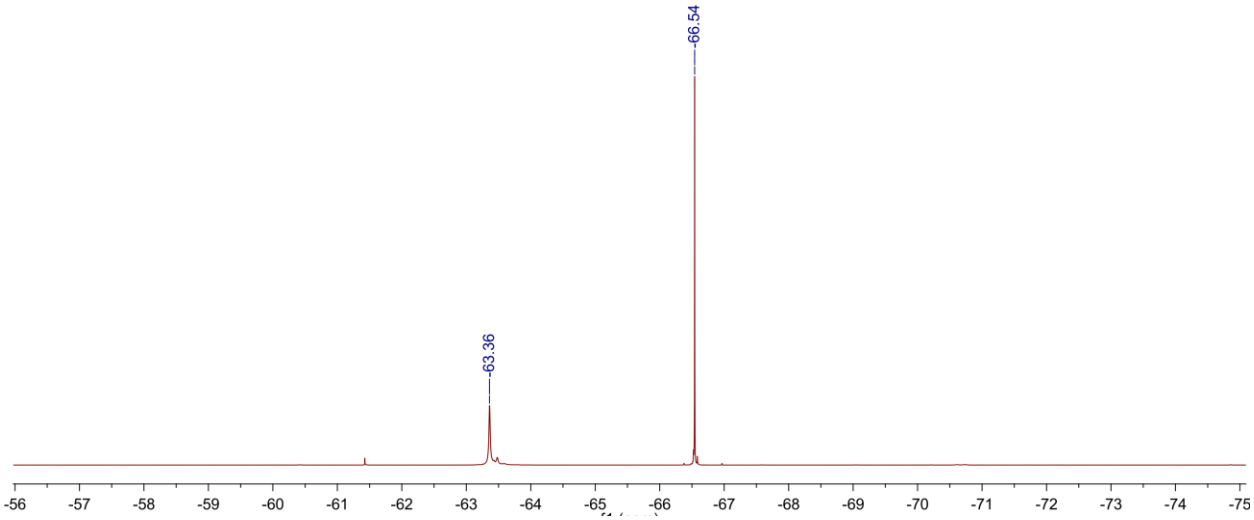
The crude residue from above (8.84 g) was dissolved in DCM (60 mL), and triethylamine (3.0 eq., 5.34 mL, 38.33 mmol), DMAP (5 mol%, 78.0 mg, 0.639 mmol) and tosyl chloride (2.2 eq., 5.36 g, 28.11 mmol) were successively added at 0 °C. The ice bath was removed after 5 min and the reaction mixture was stirred at room temperature for 1 h. The mixture was then treated with sat. aq. NH_4Cl (100 mL) and extracted with DCM (3 x 50 mL). The combined organic extracts were dried with sodium sulfate, filtered, and concentrated to afford the desired crude bis-tosyloxime (11.23 g), which was submitted to the next step without further purification.

On one occasion, for the purpose of NMR characterization, the residue was purified by silica gel column chromatography (gradient of AcOEt/hexanes from 0% to 25%) to afford the pure bis-tosyloxime. ^{1}H NMR (500 MHz, chloroform-d) δ 7.91 (d, *J* = 8.3 Hz, 4H, H-10), 7.52 (d, *J* = 8.5 Hz, 4H, H-5), 7.48 (d, *J* = 8.5 Hz, 4H, H-4), 7.40 (d, *J* = 8.3 Hz, 4H, H-11), 2.49 (s, 6H, H-13). ^{13}C NMR (125 MHz, chloroform-d) δ 152.70 (q, *J* = 34 Hz, C-7), 146.57 (C-9), 136.37 (C-12), 131.08 (C-6), 130.77 (C-5), 130.13 (C-11), 129.49 (C-10), 128.83 (C-4) 125.84 (C-3), 123.74 (q, *J* = 287 Hz, C-1), 119.60 (q, *J* = 277 Hz, C-8), 64.74 (m, *J* = 26 Hz, C-2). ^{19}F NMR (470 MHz, chloroform-d) δ -63.36 (CF_3-1), -66.54 (s, CF_3-8).

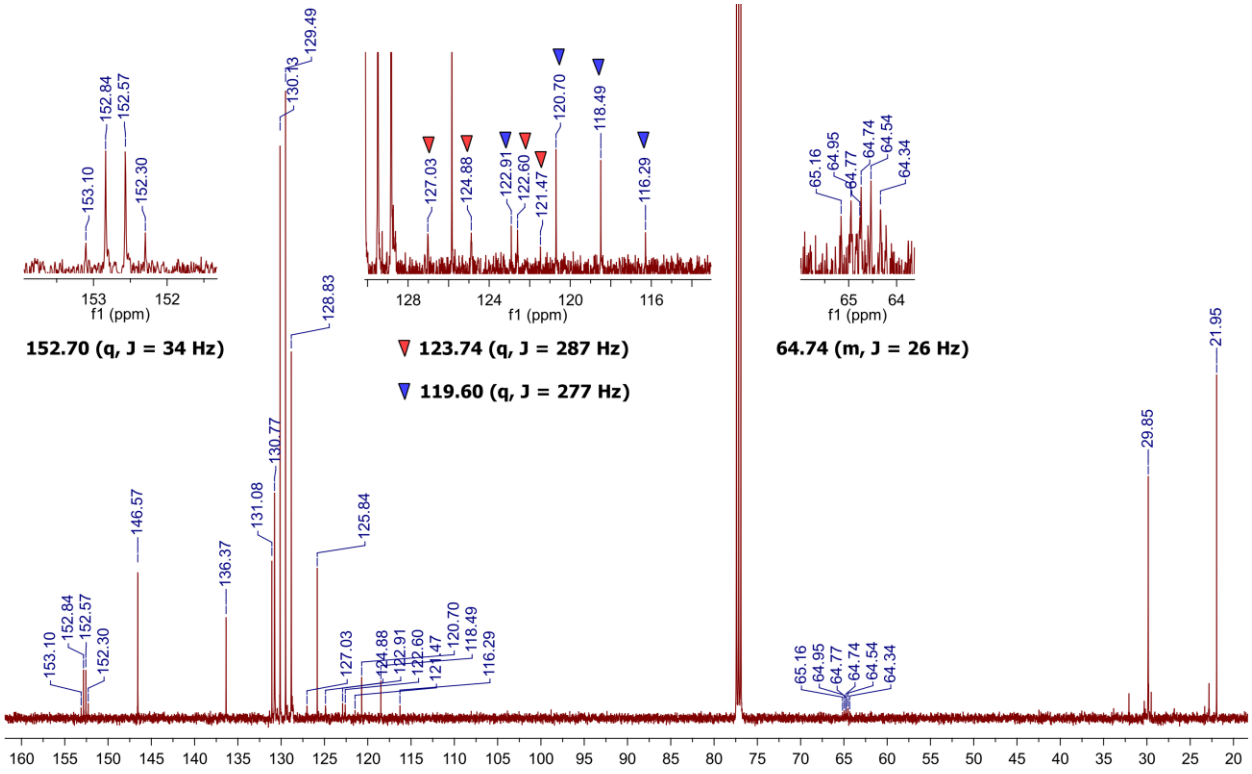
^{1}H NMR spectrum of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$:

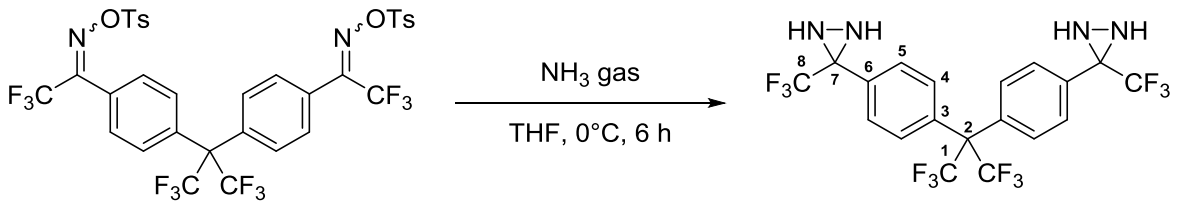


^{19}F NMR spectrum of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$



^{13}C NMR spectrum of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) *O*,*O*-ditosyl dioxime in $CDCl_3$





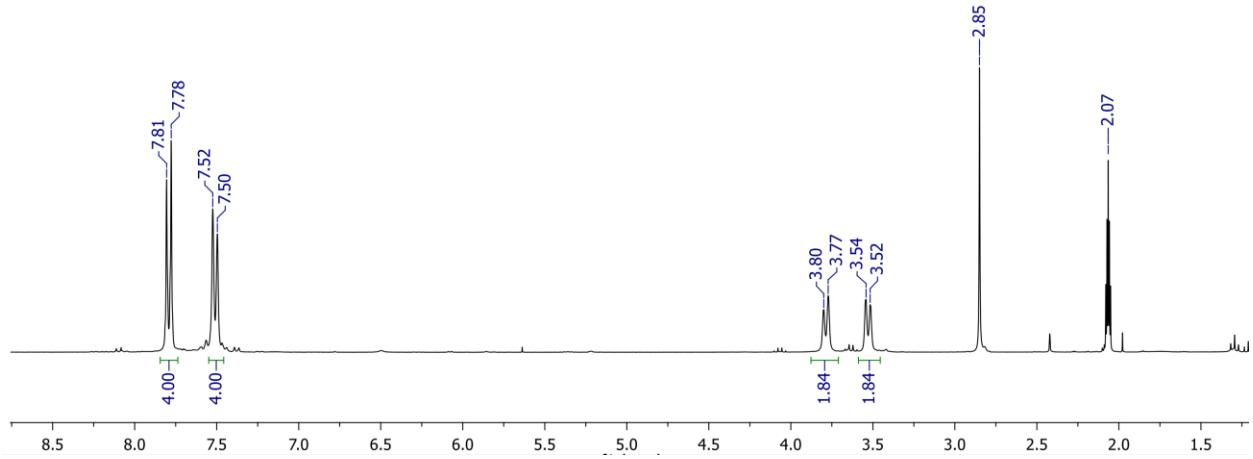
Chemical Formula: $C_{33}H_{22}F_{12}N_2O_6S_2$
Exact Mass: 834,07
Molecular Weight: 834,65

Chemical Formula: $C_{19}H_{12}F_{12}N_4$
Exact Mass: 524,09
Molecular Weight: 524,31

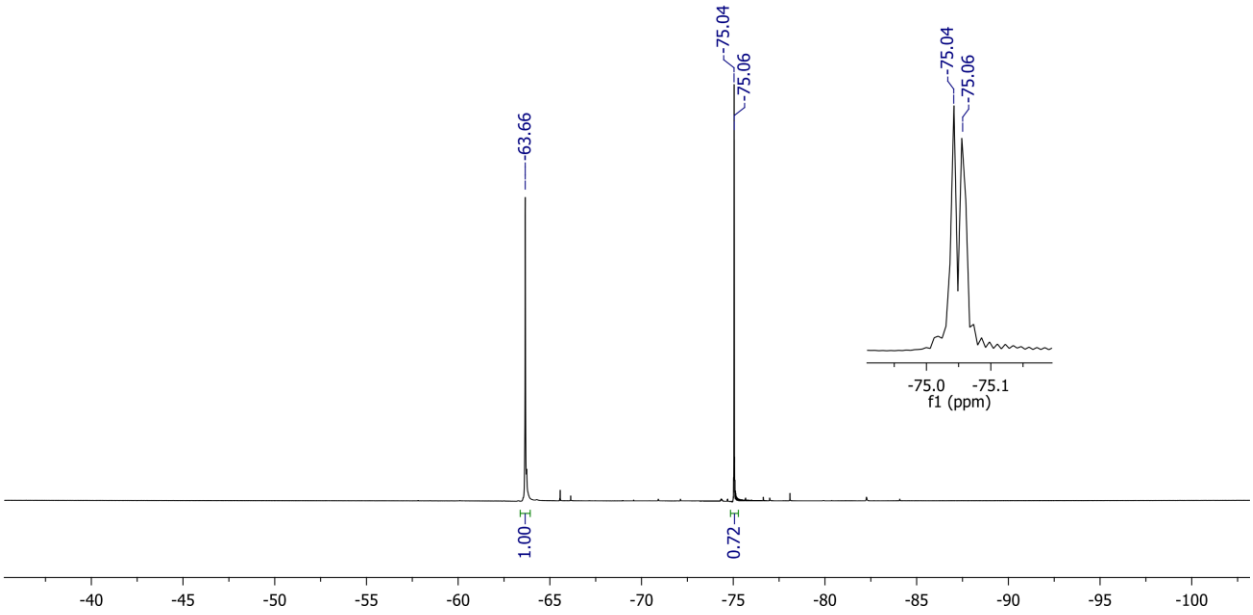
A solution of the bis-tosyloxime mixture (11.23 g) in anhydrous THF (60 mL) was transferred to a flame-dried 3-neck flask under argon and cooled to 0°C. Then anhydrous gaseous ammonia was bubbled into the stirred solution at 0°C for 6 h. The mixture was concentrated to remove THF. The residue was dissolved in DCM (70 mL) and washed with sat. aq. NH_4Cl (100 mL). Small portions of water were added to suppress emulsions and/or precipitation. The aqueous layer was separated and further extracted with DCM (2 x 70 mL). The combined organic extracts were dried with sodium sulfate, filtered and concentrated to afford the desired crude bis-diaziridine (9.28 g), which was submitted to the next step without further purification.

On one occasion, for the purpose of characterization, the residue was purified by silica gel column chromatography (gradient of AcOEt/hexanes from 5 % to 25%) to afford the pure bis-diaziridine. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.78 (d, *J* = 8.5 Hz, 4H, H-5), 7.50 (d, *J* = 8.5 Hz, 4H, H-4), 3.77 (d, *J* = 8.7 Hz, 2H, N–H), 3.52 (d, *J* = 8.7 Hz, N–H). ^{13}C NMR (125 MHz, acetone-d_6) δ 135.11 (C-3 or C-6), 134.83 (C-3 or C-6), 131.03 (C-4), 129.68 (C-5), 125.04 (q, *J* = 287 Hz, C-1), 125.03 (q, *J* = 278 Hz, C-8), 65.34 (m, *J* = 25 Hz, C-2), 58.13 (q, *J* = 36 Hz, C-7). ^{19}F NMR (470 MHz, acetone-d_6) δ -63.66 (CF3-1), -75.05 (two s, CF_3-8). IR (diamond-ATR) v: 3231, 1701, 1519, 1398, 1255, 1248, 1206, 1172, 1097, 1025, 972, 943, 930, 882, 831, 742, 719, 708, 669, 576, 549, 477. HRMS (ESI+) m/z [M+H] calculated for $C_{19}H_{13}F_{12}N_4$: 525.0943, found: 525.0943.

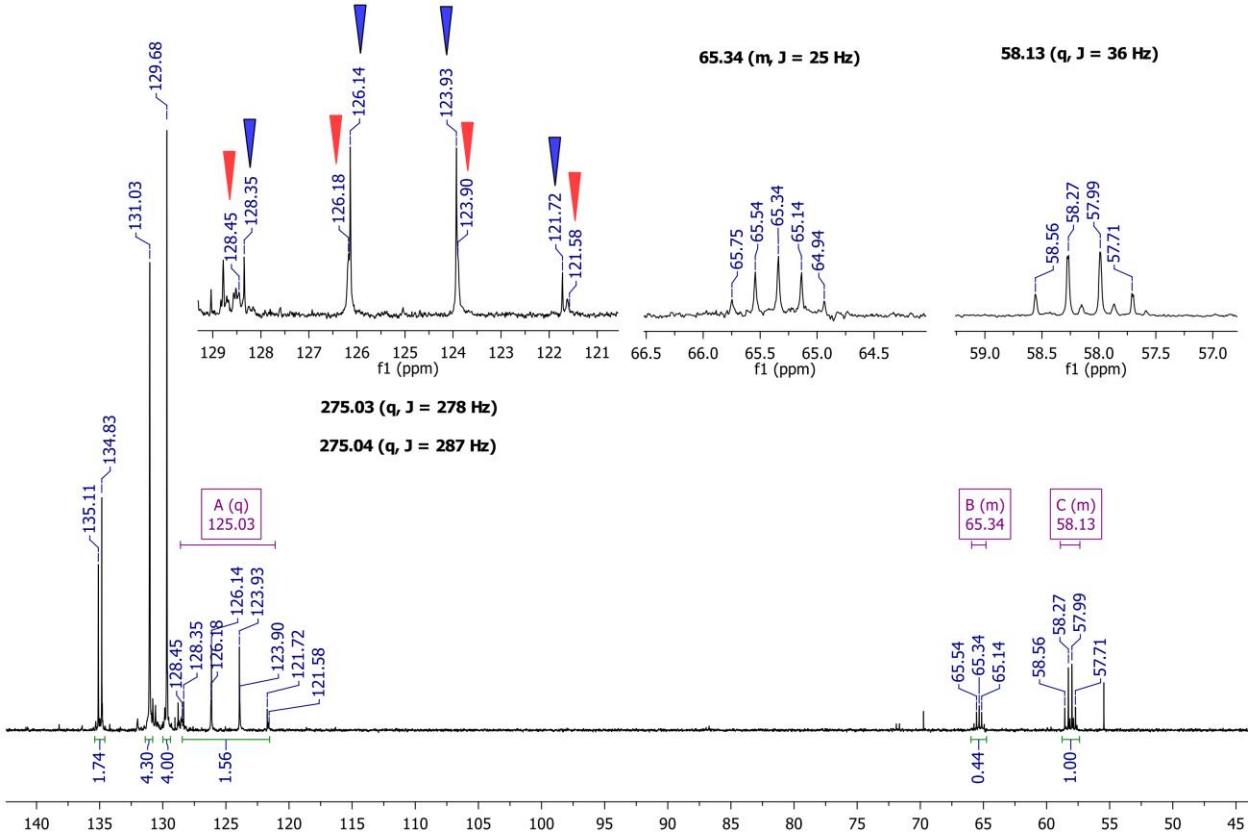
^{1}H NMR spectrum of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine) in acetone-d_6:

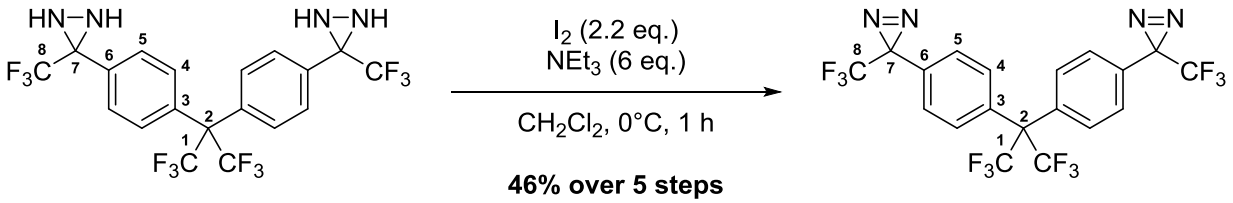


^{19}F NMR spectrum of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine) in acetone-d_6:



^{13}C NMR spectrum of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine) in acetone-d_6:



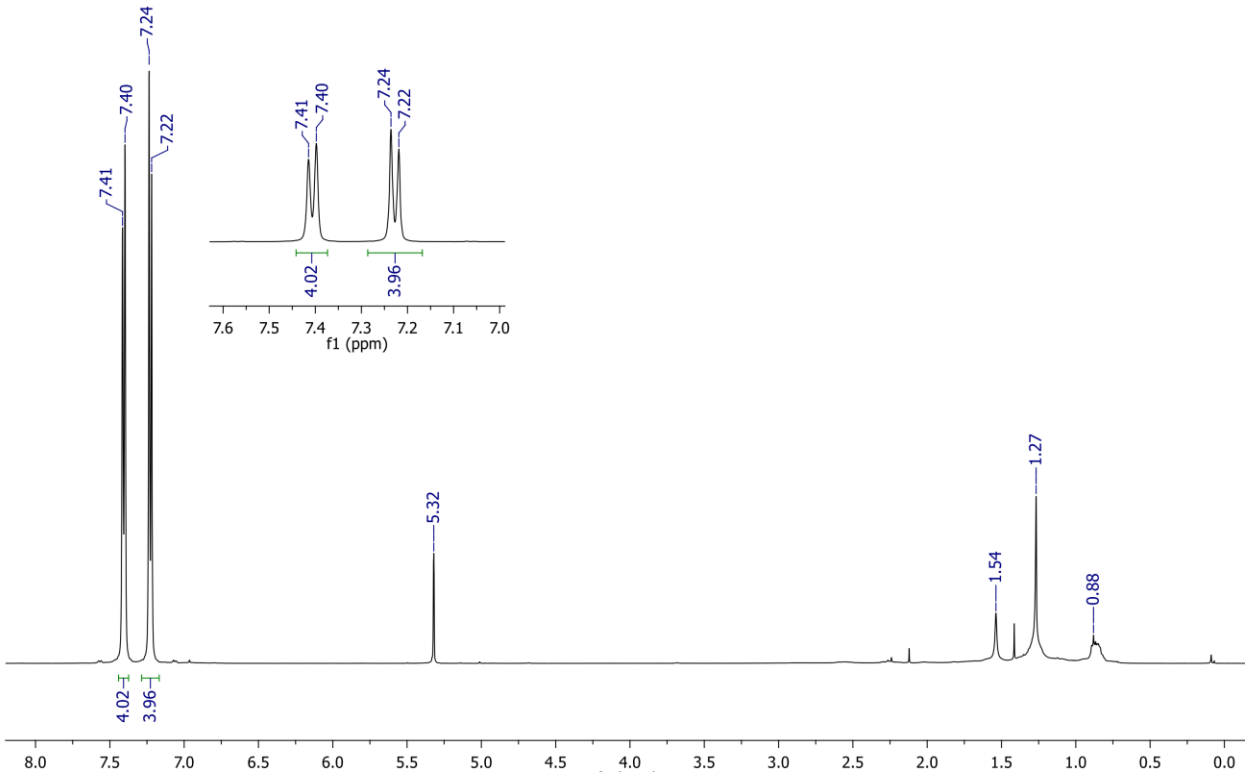


Chemical Formula: $C_{19}H_{12}F_{12}N_4$
Exact Mass: 524,09
Molecular Weight: 524,31

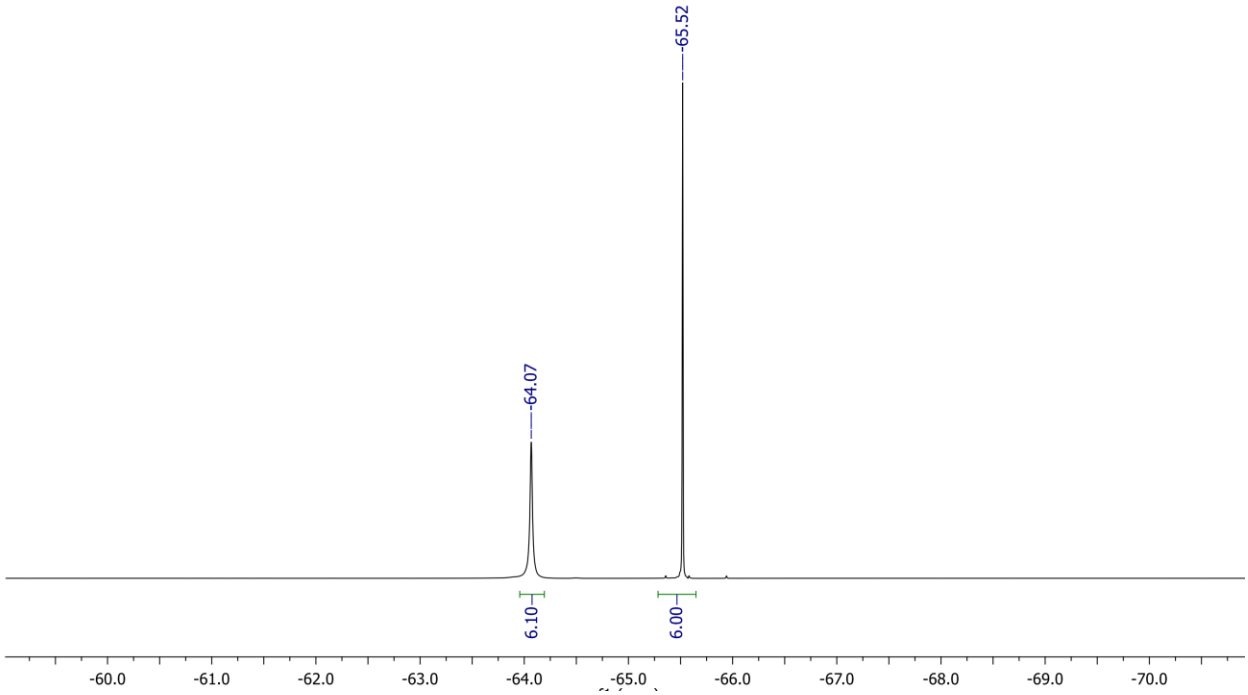
Chemical Formula: $C_{19}H_8F_{12}N_4$
Exact Mass: 520,06
Molecular Weight: 520,28

To a solution of the crude bis-diaziridine from above (9.28 g) in DCM (60 mL) at 0 °C were added successively triethylamine (6 eq., 12.64 mL, 90.57 mmol) and iodine (2.2 eq., 8.43 g, 33.21 mmol). The colored mixture was stirred at 0 °C for 1 h. The mixture was diluted with DCM (20 mL) and washed with a 1:1 mixture of sat. aq. sodium thiosulfate (70 mL) and water (70 mL). The phases were separated, and the aqueous layer was re-extracted with DCM (60 mL × 3). Then the combined organic extracts were washed with sat. aq. NH_4Cl (100 mL) following a similar procedure with DCM (50 mL × 3). The organic extracts were combined and dried with sodium sulfate, filtered and concentrated. The residue was purified by silica gel column chromatography (solid deposit, elution with pentane) to afford the desired bis-diazirine **3** (3.09 g, 5.95 mmol) as a colorless oil in 46% overall yield from dimethyl 4,4'-(perfluoropropane-2,2-diyl)dibenzoate. Melting point = +34°C. ^{1}H NMR (300 MHz, dichloromethane-d_2) δ 7.41 (d, *J* = 8.5 Hz, 4H, H-5), 7.23 (d, *J* = 8.5 Hz, 4H, H-4). ^{13}C NMR (125 MHz, dichloromethane-d_2) δ 134.75 (C-3), 130.98 (C-5), 130.87 (C-6), 126.86 (C-4), 124.23 (q, *J* = 287 Hz, C-1), 122.39 (q, *J* = 275 Hz, C-8), 64.68 (m, *J* = 26 Hz, C-2), 28.56 (q, *J* = 41 Hz, C-7). ^{19}F NMR (282 MHz, dichloromethane-d_2) δ -64.07 (CF_3-1), -65.52 (CF_3-8). IR (diamond-ATR) ν: 2362, 2093, 1729, 1616, 1522, 1351, 1338, 1289, 1207, 1177, 1153, 1055, 1025, 971, 942, 931, 875, 818, 746, 732, 709, 675, 553. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{19}H_8F_{12}N_4$: 520.0557, found: 520.0583.

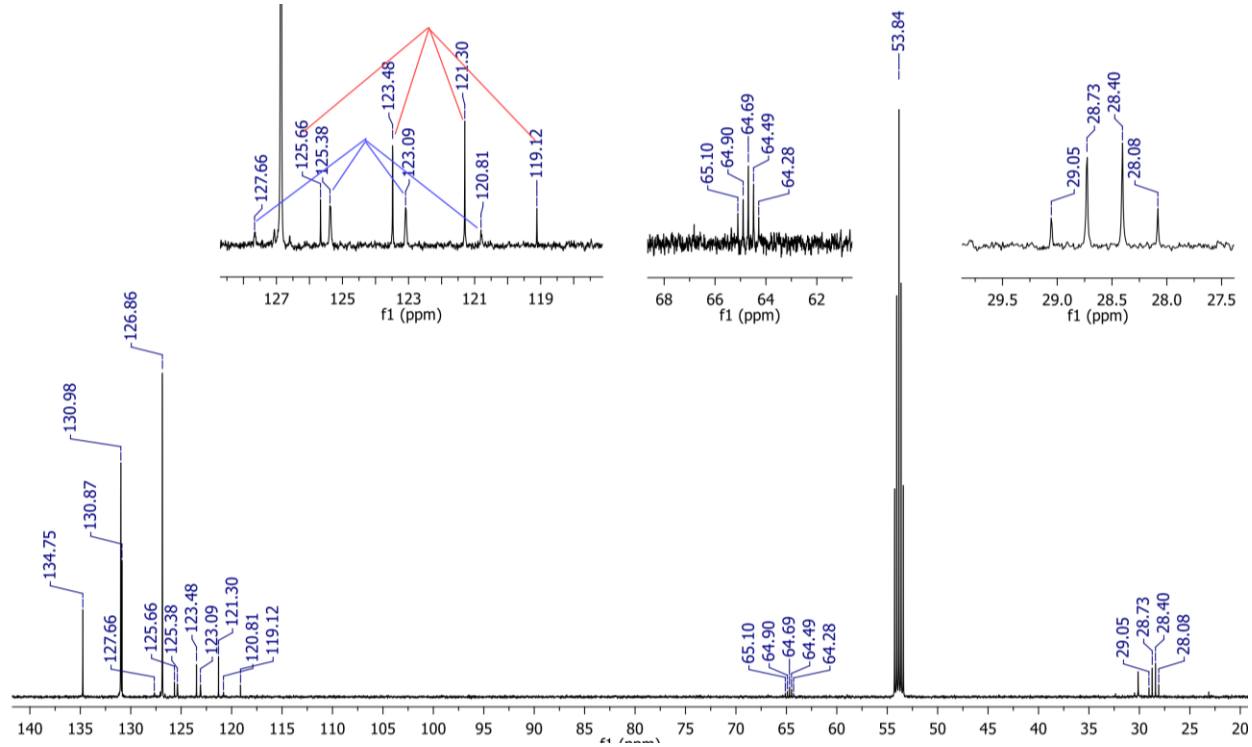
^{1}H NMR spectrum of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)-3*H*-diazirine) (3) in CD_2Cl_2:



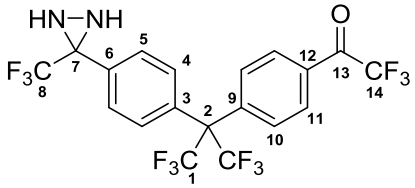
^{19}F NMR spectrum of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)-3*H*-diazirine) (3) in CD_2Cl_2:



^{13}C NMR spectrum of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)-3*H*-diazirine) (3) in CD_2Cl_2:



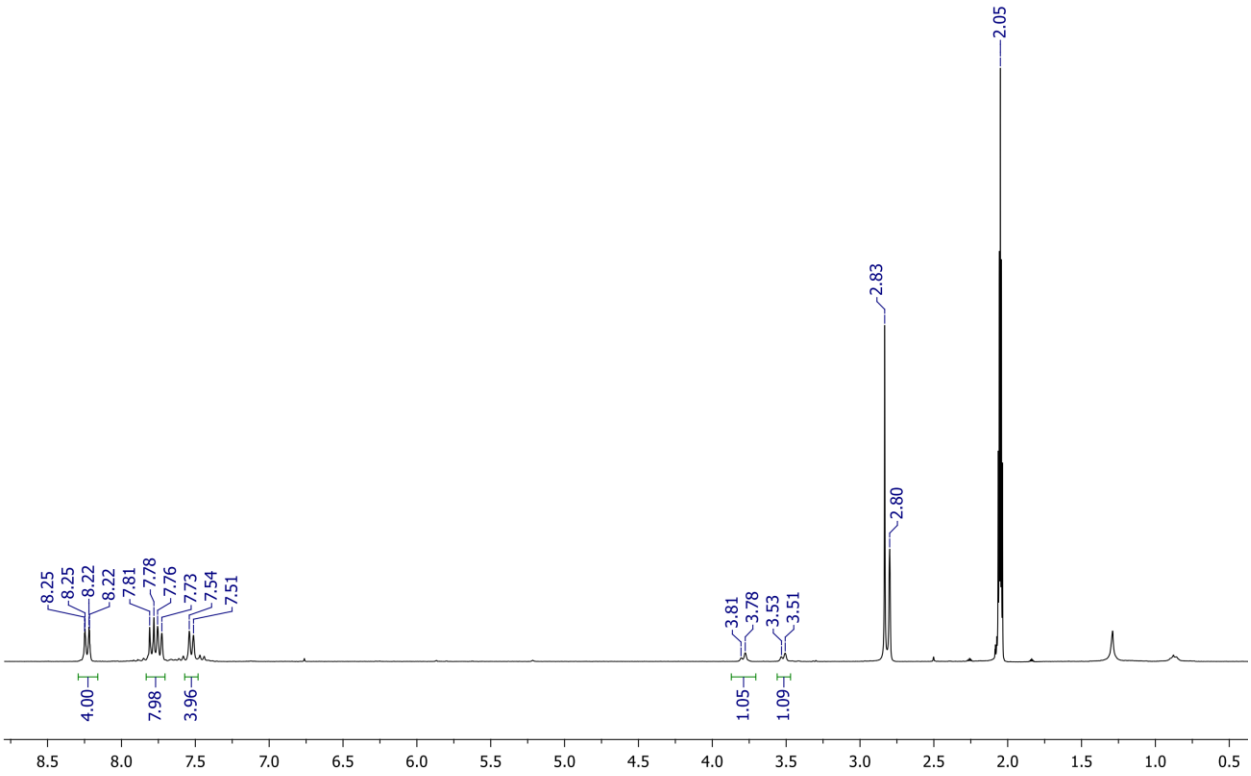
Isolation of the mono-diaziridine precursor of molecular control **7**



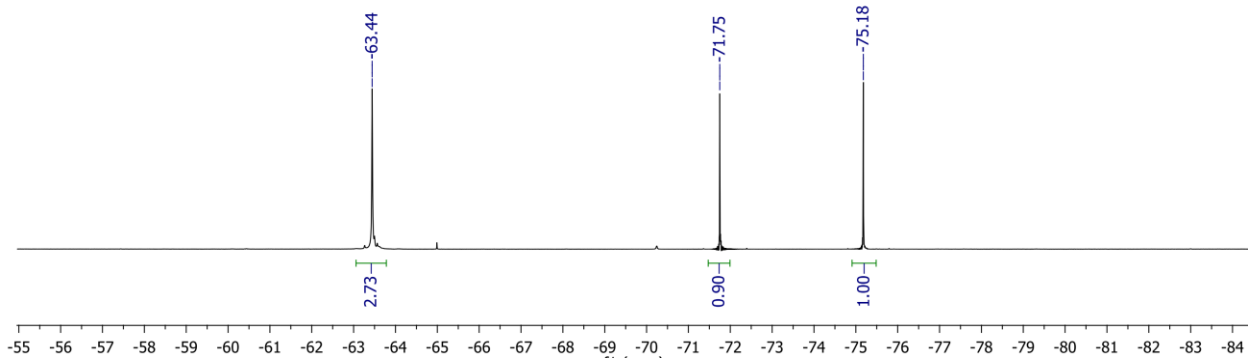
Chemical Formula: $C_{19}H_{10}F_{12}N_2O$
Exact Mass: 510,0602
Molecular Weight: 510,2828

During the purification of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine) described above, the corresponding mono-diaziridine, precursor of molecular control **7**, was isolated in small amounts. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.23 (d, *J* = 8.3 Hz, 2H, H-11), 7.80 (d, *J* = 8.5 Hz, 2H, H-5), 7.74 (d, *J* = 8.4 Hz, 2H, H-10), 7.53 (d, *J* = 8.4 Hz, 2H, H-4), 3.79 (d, *J* = 9.0 Hz, 1H, N-H), 3.52 (d, *J* = 8.8 Hz, 1H, N-H). ^{13}C NMR (125 MHz, acetone-d_6) δ 180.51 (q, *J* = 35 Hz, C-13), 140.83 (C-12), 135.09 (C-3) 134.54 (C-6), 131.98 (C-10), 131.46 (C-9), 131.08 (C-4), 130.92 (C-11), 129.85 (C-5), 125.02 (q, *J* = 290 Hz, C-1), 124.95 (q, *J* = 275 Hz, C-8), 117.47 (q, *J* = 291 Hz, C-14), 65.61 (m, C-2), 58.11 (q, *J* = 36 Hz, C-7). ^{19}F NMR (282 MHz, chloroform-d) δ -63.44 (CF_3-1), -71.75 (CF_3-14), -75.18 (CF_3-8). IR (diamond-ATR) ν: 3276, 2924, 1727, 1611, 1519, 1256, 1207, 1176, 1024, 972, 943, 930, 882, 832, 769, 741, 721, 690, 668, 533. HRMS (ESI+) m/z [M+H] calculated for $C_{19}H_{11}F_{12}N_2O$: 511.0674, found: 511.0675.

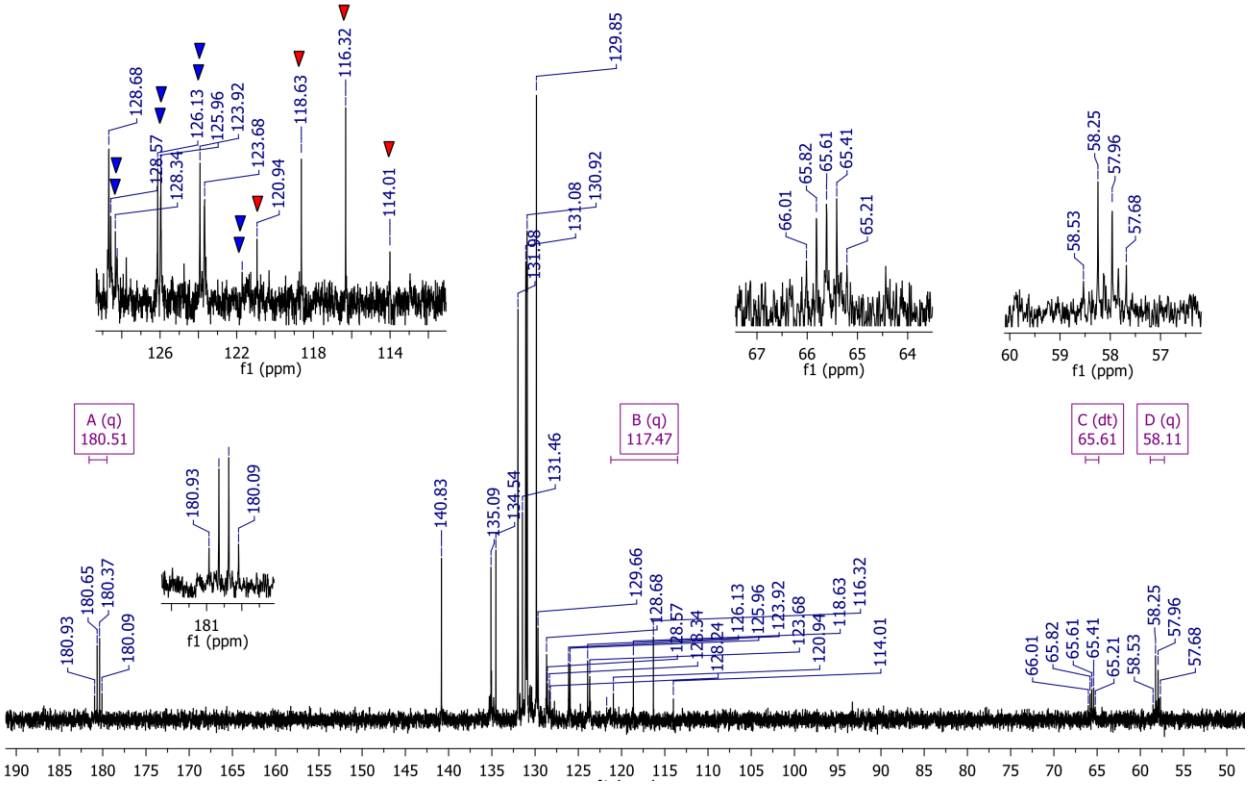
^{1}H NMR spectrum of the mono-diaziridine precursor of molecular control 7 in acetone-d_6:



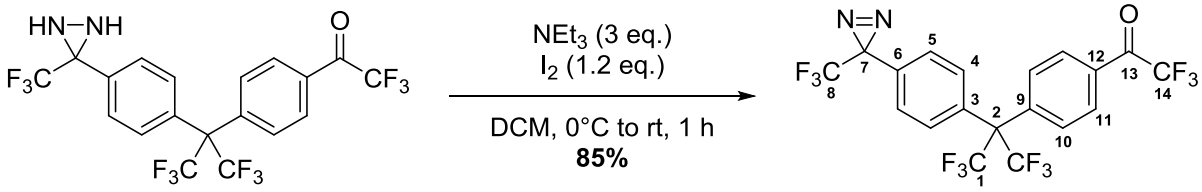
^{19}F NMR spectrum of the mono-diaziridine precursor of molecular control 7 in $CDCl_3$:



^{13}C NMR spectrum of the mono-diaziridine precursor of molecular control 7 in acetone-d_6:



Synthesis of molecular control (**7**)



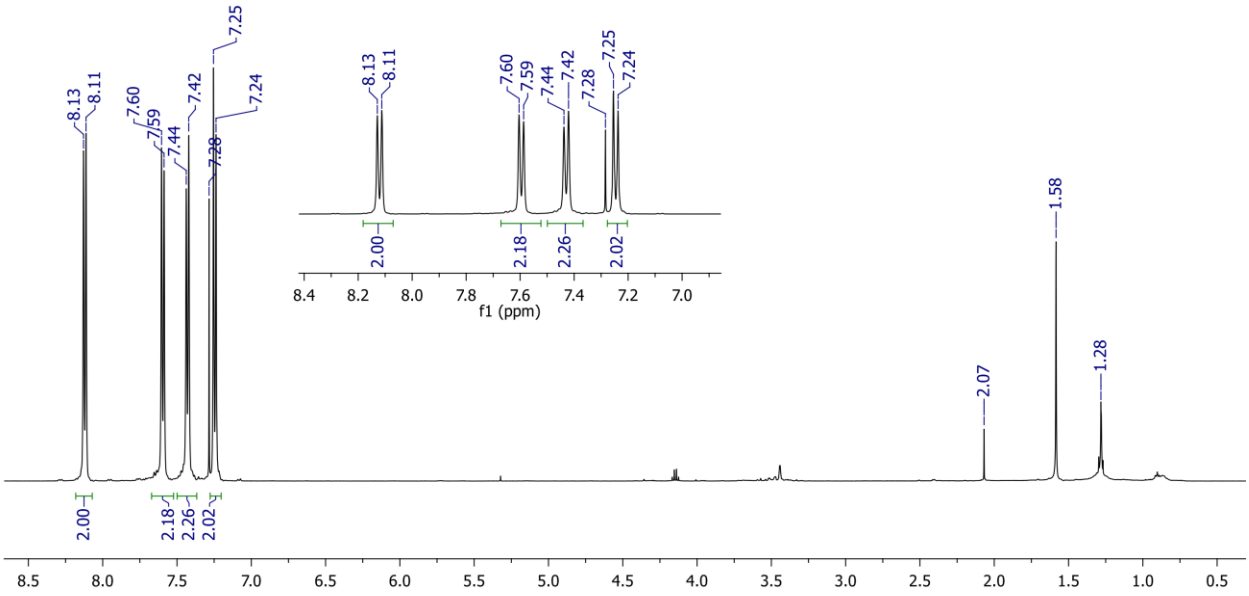
Chemical Formula: $C_{19}H_{10}F_{12}N_2O$
Exact Mass: 510,0602
Molecular Weight: 510,2828

Chemical Formula: $C_{19}H_8F_{12}N_2O$
Exact Mass: 508,0445
Molecular Weight: 508,2668

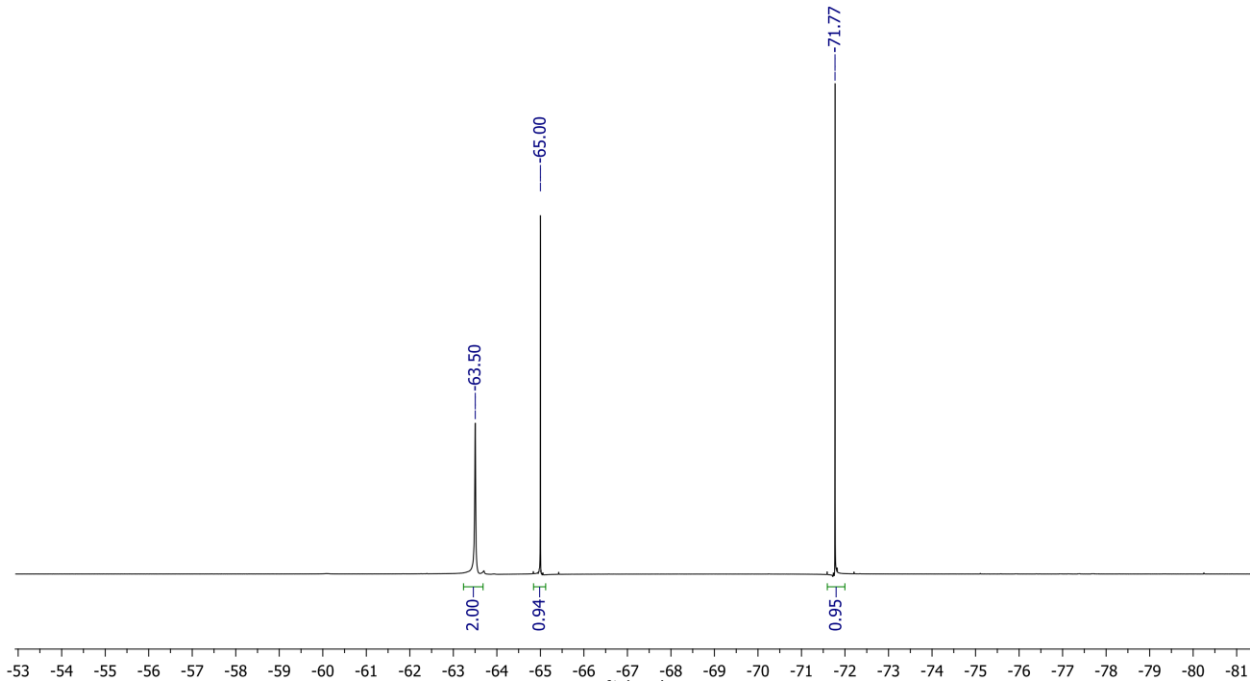
To a solution of the mono-diaziridine (1 eq., 150 mg, 294 µmol) in DCM (5 mL) at 0 °C were added successively triethylamine (3 eq., 123 µL, 882 µmol) and iodine (1.2 eq., 90 mg, 353 mmol). The colored mixture was stirred at 0 °C for 30 min, then at room temperature for another 30 min. The mixture was diluted with DCM (30 mL) and washed with a 1:1 mixture of sat. aq. sodium thiosulfate (15 mL) and water (15 mL). The phases were separated, and the aqueous layer was re-extracted with DCM (30 mL). The organic extracts were combined and dried with sodium sulfate, filtered and concentrated. The residue was purified by silica gel column chromatography (solid deposit, elution with a gradient from 5% to 30% AcOEt/pentane) to afford the desired mono-diazirine **7** (127 mg, 250 µmol) as a colorless oil in 85% yield. ^{1}H NMR (500 MHz, chloroform-d) δ 8.12 (d, *J* = 8.4 Hz, 2H, H-11), 7.60 (d, *J* = 8.5 Hz, 2H, H-10), 7.43

(d, *J* = 8.5 Hz, 2H, H-4), 7.25 (d, *J* = 8.6 Hz, 2H, H-5). ^{13}C NMR (125 MHz, chloroform-d) δ 176.92 (q, *J* = 36 Hz, C-13), 140.31 (C-12), 134.10 (C-6), 131.08 (C-10), 130.97 (C-9), 130.63 (C-4), 130.51 (C-3), 130.05 (C-11), 126.65 (C-5), 123.72 (q, *J* = 286 Hz, C-1), 122.01 (q, *J* = 275 Hz, C-8), 116.57 (q, *J* = 291 Hz, C-14), 64.73 (m, C-2), 28.28 (q, *J* = 41 Hz, C-7). ^{19}F NMR (470 MHz, chloroform-d) δ -63.50 (CF_3-1), -71.77 (CF_3-14), -65.00 (CF_3-8). IR (diamond-ATR) v: 1727, 1611, 1521, 1421, 1333, 1265, 1241, 1206, 1177, 1139, 1055, 1025, 972, 941, 930, 876, 850, 820, 769, 761, 736, 719, 704, 690, 675, 605, 550, 533. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{19}H_8F_{12}N_2O$: 508.4445, found: 508.0442.

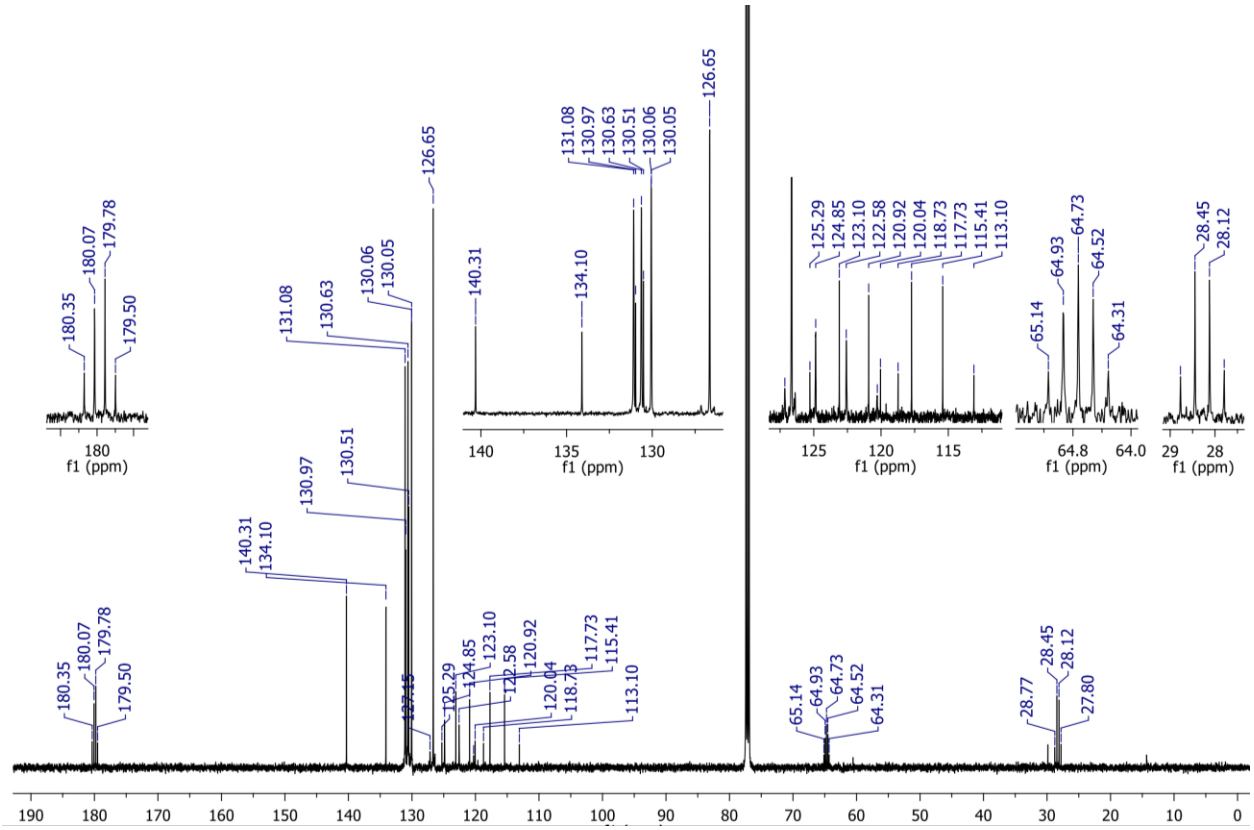
^{1}H NMR spectrum of molecular control (7) in $CDCl_3$:



^{19}F NMR spectrum of molecular control (7) in $CDCl_3$:



^{13}C NMR spectrum of molecular control (7) in $CDCl_3$:

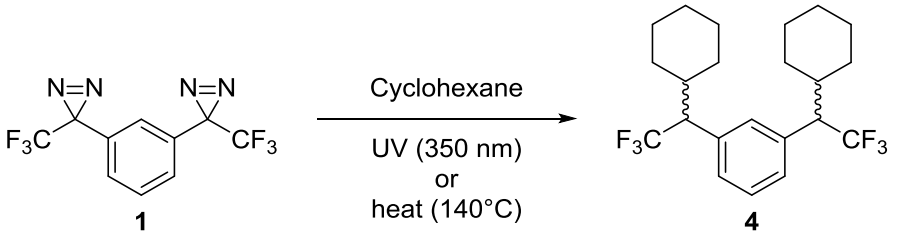


General procedure for the crosslinking of cyclohexane $(CH_2)_6$, as a small-molecule model for linear polyethylene $(CH_2)_n$

a) UV activation: a 1 mM solution of bis-diazirine in cyclohexane was prepared in a 500 mL round-bottom flask and the contents were flushed gently with argon. The flask was sealed with a septum and placed under a balloon of argon to maintain an inert atmosphere. The reaction was carried out at room temperature. The round bottom flask was suspended into a Rayonet UV chamber that was equipped with eight 350 nm UV lamps and an operating fan. The reaction contents were irradiated for 4 h. Upon confirming the absence of peaks at ~ −65 ppm (bis-diazirine) and ~ −54 ppm (diazo species) in the ^{19}F NMR spectra (benzene-d_6), the reaction was concentrated in vacuo to provide crude product.

b) Thermal activation: a 10 mM solution of bis-diazirine in cyclohexane was placed in a 100 mL sealed tube, flushed gently with argon and capped. The mixture was heated with stirring at 140 °C for 2 h. After cooling the mixture to room temperature, the contents were transferred into a round bottom flask and concentrated in vacuo to provide crude product.

Crosslinking of cyclohexane using **1** – preparation of 1,3-bis(1-cyclohexyl-2,2,2-trifluoroethyl)benzene (**4**)



1

Chemical Formula: $C_{10}H_4F_6N_4$
Exact Mass: 294,0340
Molecular Weight: 294,1604

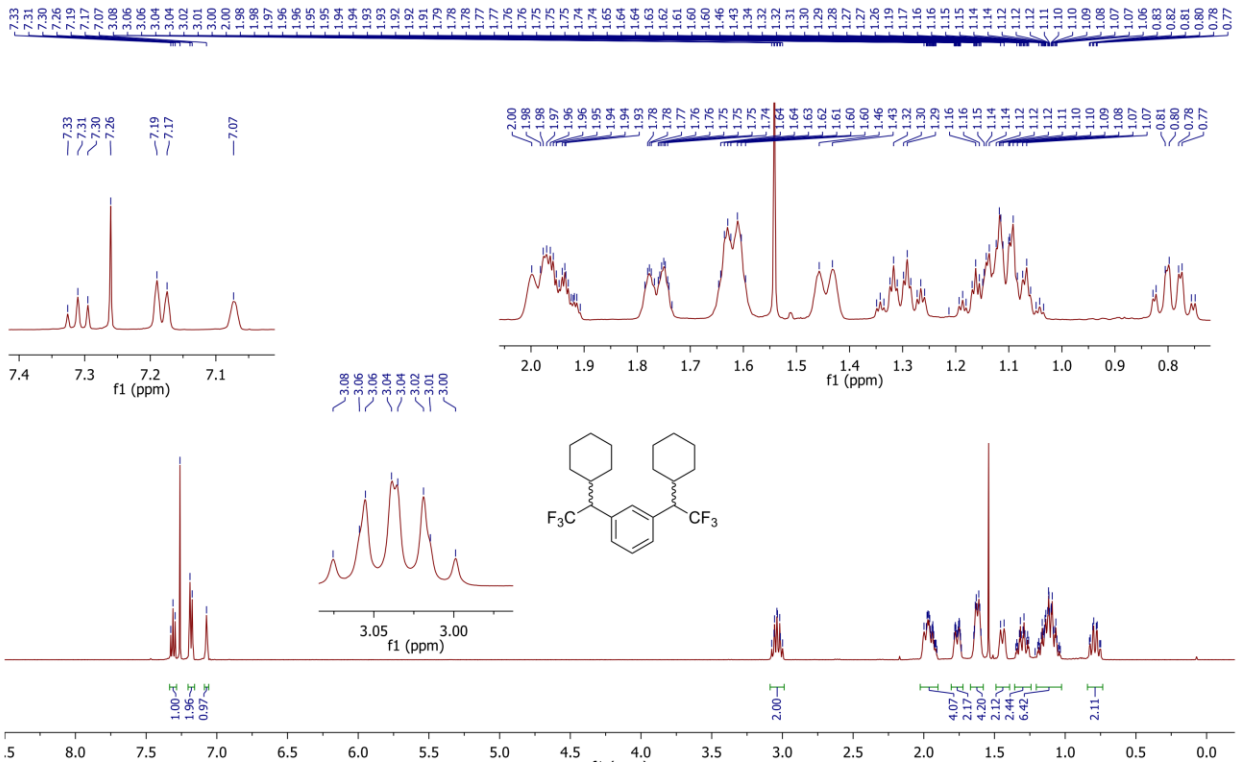
4

Chemical Formula: $C_{22}H_{28}F_6$
Exact Mass: 406,2095
Molecular Weight: 406,4564

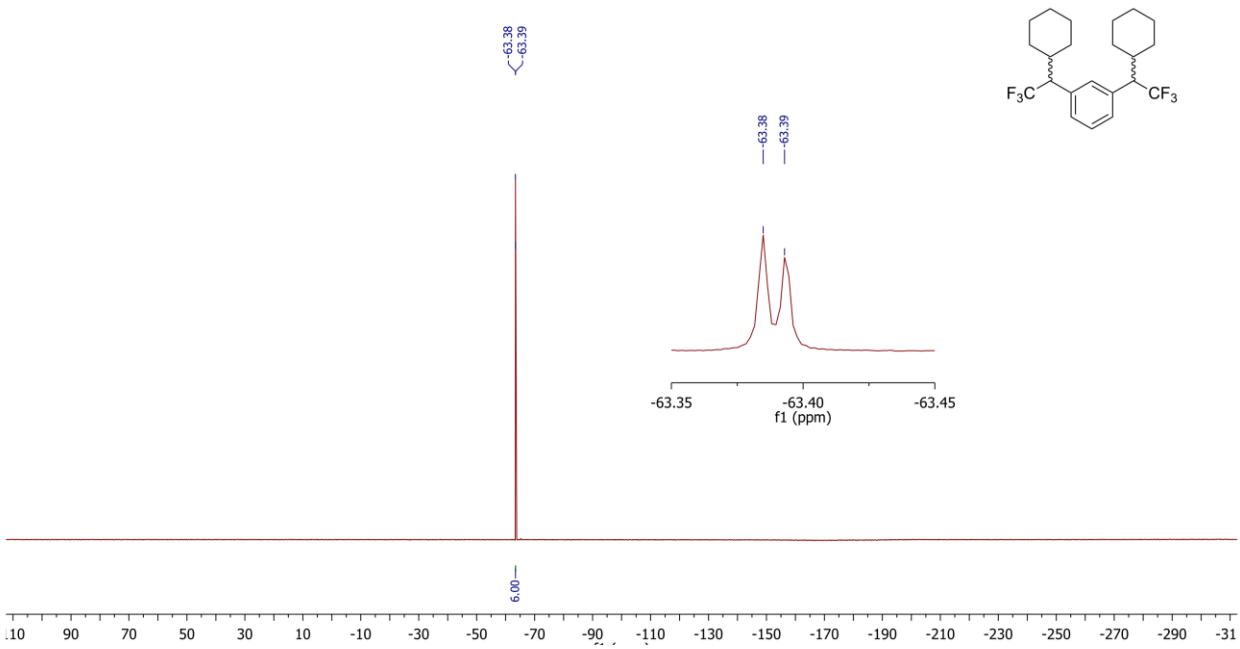
Reactions were performed as described in the above general procedure for crosslinking experiments. UV activation reaction: bis-diazirine **1** (102 mg in 347 mL cyclohexane) was used, and product (11.5 mg, 8.2%) was isolated following chromatography. Thermal activation reaction: bis-diazirine **1** (121 mg in 40.8 mL cyclohexane) was used and product (14.3 mg, 8.6%) was isolated following chromatography. In both cases, crude material was purified in a similar manner as described herein and the product was isolated as mixture of diastereomers, as a light yellow oil. The crude product was dissolved in 10% diethyl ether in pentane (~2 mL), loaded onto a column packed with silica gel and eluted with pentane. Several 2-4 mL fractions were collected in 12 x 75 mm test tubs. Fractions that contain the product (as determined by $^1H/^{19}F$ spectra), were combined and concentrated together to give the product. ^1H NMR (500.27 MHz, chloroform-d) δ 7.31 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.07 (s, 1H), 3.04 (qd, *J* = 10.1, 8.1 Hz, 2H), 2.04–1.88 (m, 4H), 1.82–1.71 (m, 2H), 1.68–1.58 (m, 4H) 1.44 (d, *J* = 12.4 Hz, 2H), 1.30 (qt, *J* = 13.1, 3.5 Hz, 2H), 1.21–1.02 (m, 6H), 0.79 (qd, *J* = 12.0, 3.3 Hz, 2H). ^{13}C NMR (126 MHz, chloroform-d) δ 135.5 (m), 130.5 and 130.4, 128.7, 128.6 and 128.5, 127.3 (q, *J* = 281 Hz), 56.2 (q, *J* = 25.1 Hz), 56.1 (q, *J* = 25.1 Hz), 38.7, 31.7 (d, *J* = 2.2 Hz), 30.8 (d, *J* = 3.2 Hz),

26.3, 26.2, 26.2. ^{19}F NMR (470.72 MHz, chloroform-d) δ -63.39, -63.38. IR: 2926, 2855, 1451, 1252, 1151, 1102, 714. HRMS (ESI+) m/z [M+Na] calculated for $C_{22}H_{28}F_6Na$: 429.19929, found: 429.19918.

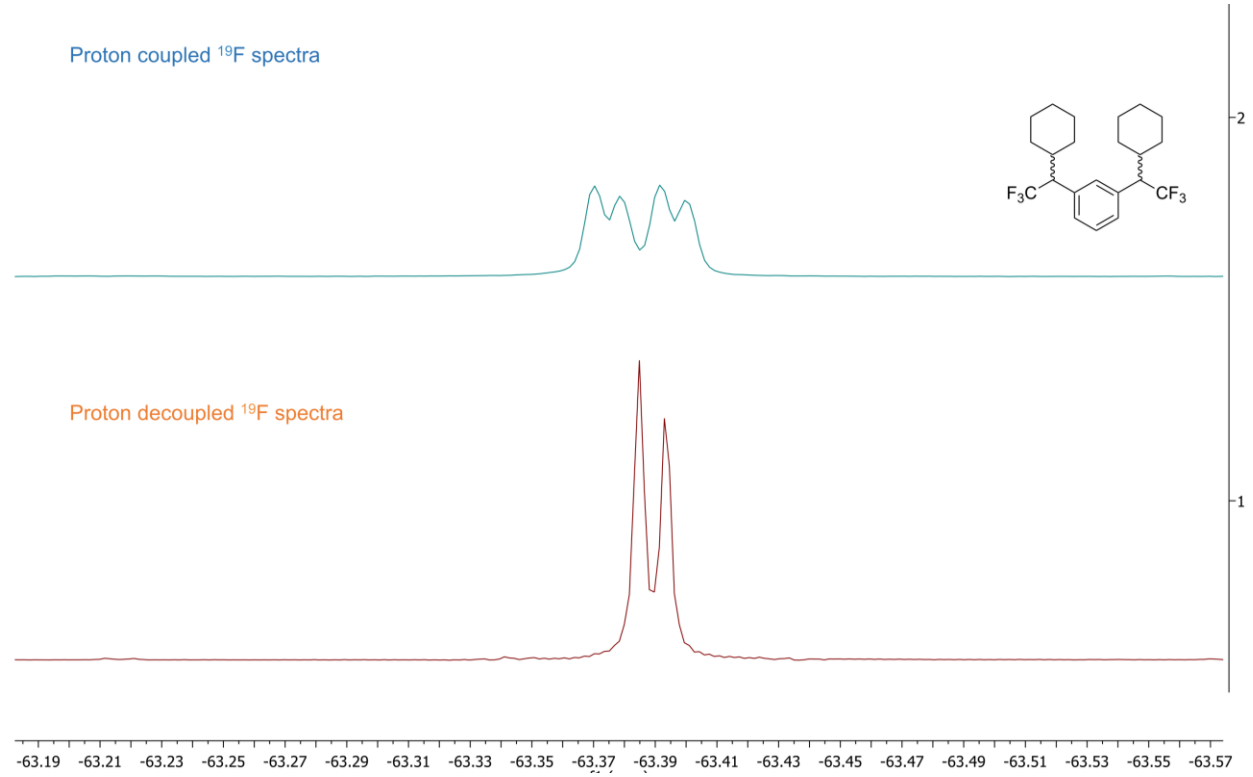
^{1}H NMR spectrum of cyclohexane adduct 4 in $CDCl_3$:



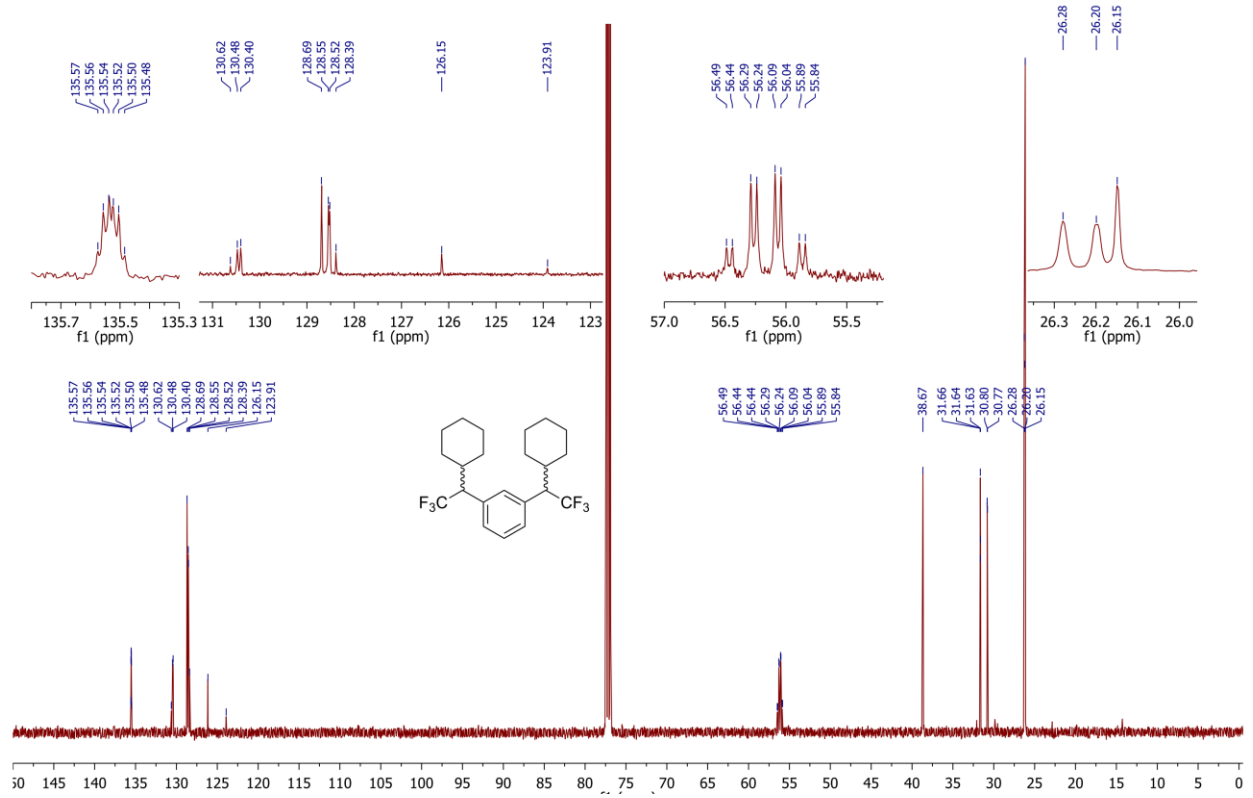
^{19}F NMR spectrum of cyclohexane adduct 4 in $CDCl_3$:



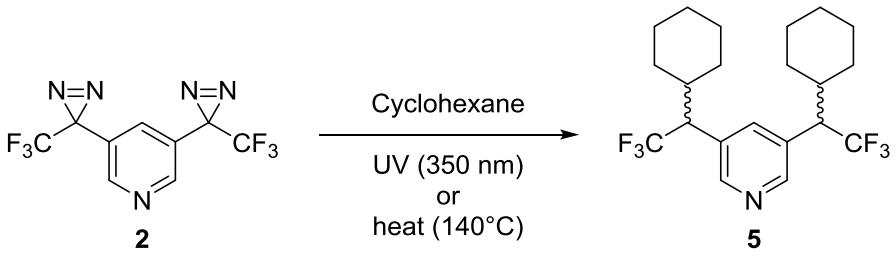
Comparison of ^{1}H-coupled and ^{1}H-decoupled ^{19}F spectra for cyclohexane adduct 4:



^{13}C NMR spectrum of cyclohexane adduct 4 in $CDCl_3$:



Crosslinking of cyclohexane using **2** – preparation of 3,5-bis(1-cyclohexyl-2,2,2-trifluoroethyl)pyridine (**5**)



2

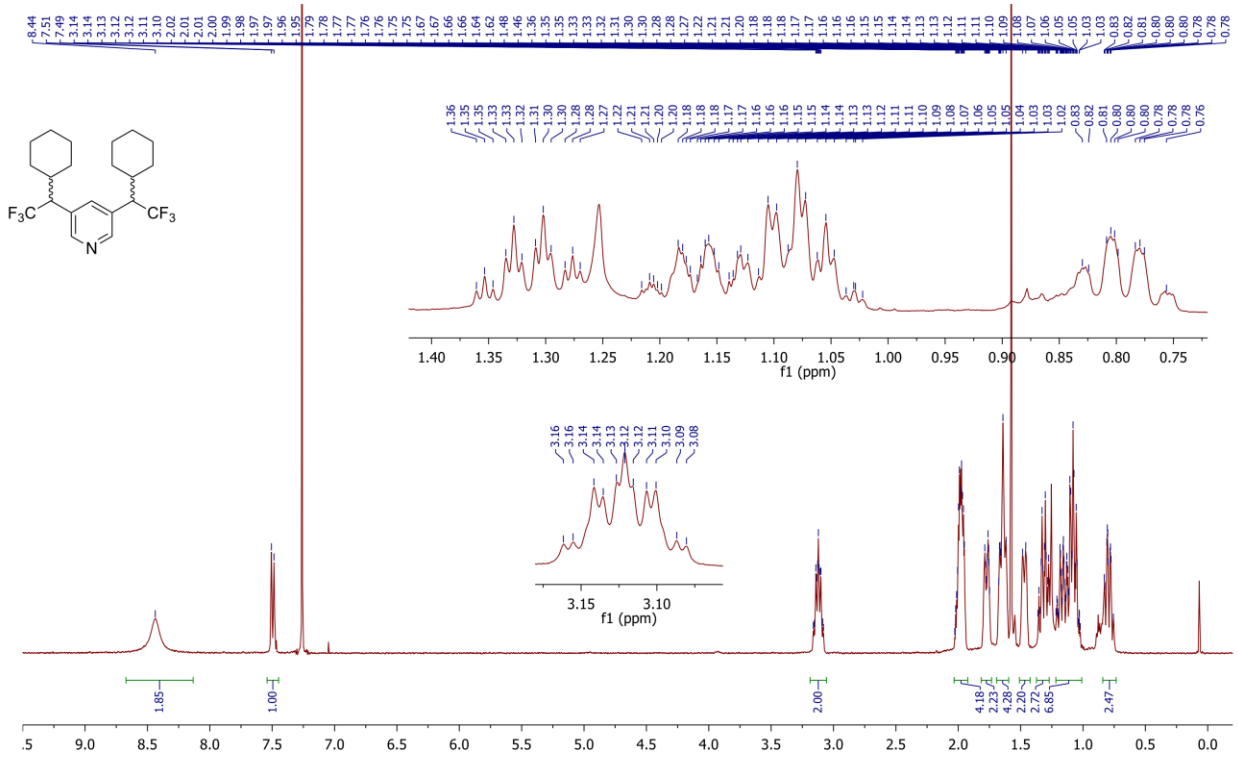
Chemical Formula: $C_9H_3F_6N_5$
Exact Mass: 295,0293
Molecular Weight: 295,1484

5

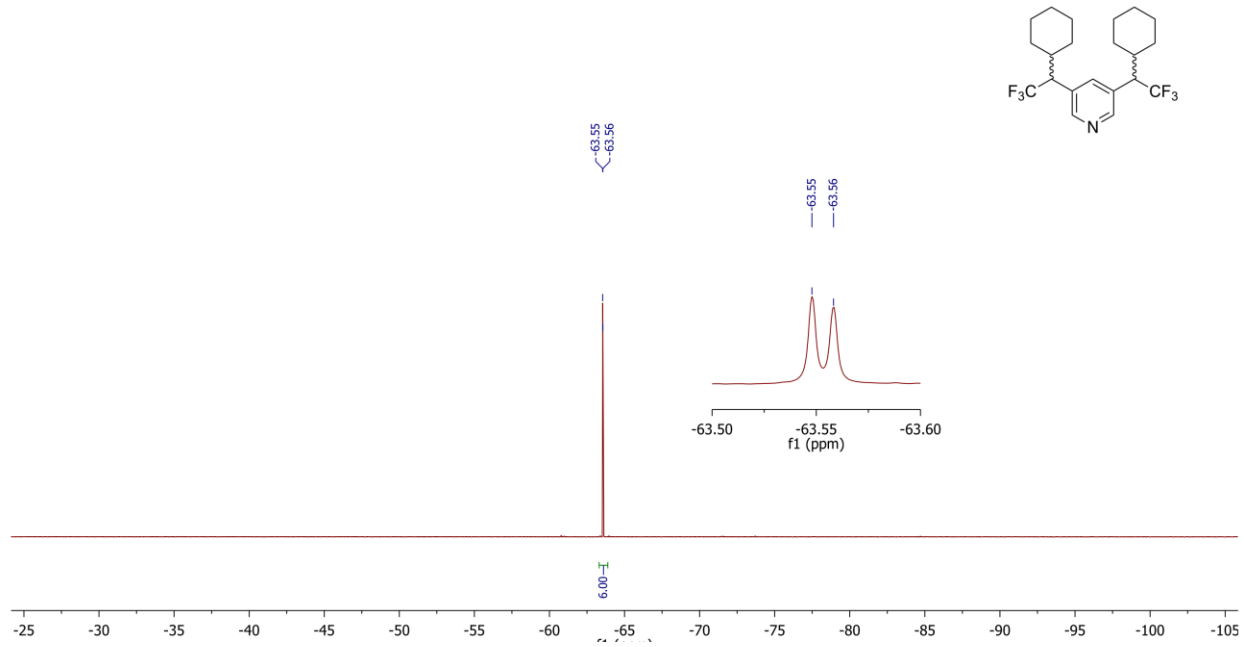
Chemical Formula: $C_{21}H_{27}F_6N$
Exact Mass: 407,2048
Molecular Weight: 407,4444

Reactions were performed as described in the above general procedure for crosslinking experiments. For UV activation reaction: bis-diazirine **2** (97 mg in 328 mL solvent) was used, and product (10 mg, 7.4%) was isolated following chromatography. For thermal activation reaction: bis-diazirine **2** (118 mg in 40 mL solvent) was used and product (12.3 mg, 7.5%) was isolated following chromatography. In both cases, crude material was purified in a similar manner as described herein and the product was isolated as mixture of diastereomers, as a light yellow solid. The crude product was dissolved in DCM (~1 mL) and loaded onto a column that was packed with silica gel and eluted with 12-15% EtOAc in hexane. ^{1}H NMR (500.27 MHz, chloroform-d) δ 8.44 (br s, 2H), 7.50 (d, *J* = 10.2 Hz, 1H), 3.12 (ddt, *J* = 14.4, 10.0, 5.0 Hz, 2H), 1.99 (m, 4H), 1.82-1.76 (m, 2H), 1.68–1.60 (m, 4H), 1.47 (d, *J* = 12.7 Hz, 2H), 1.31 (qt, *J* = 12.8, 3.5 Hz, 2H), 1.22–0.99 (m, 6H), 0.85–0.70 (m, 2H). ^{13}C NMR (126 MHz, chloroform-d) δ 150.2, 150.1, 136.9, 136.6, 130.8, 126.9 (q, *J* = 281 Hz), 126.8 (q, *J* = 281 Hz), 53.8 (q, *J* = 25.8 Hz), 53.7 (q, *J* = 25.8 Hz), 38.4, 31.6 (d, *J* = 4.7 Hz), 30.7, 30.5, 26.2, 26.1, 26.0. ^{19}F NMR (470.72 MHz, chloroform-d) δ -63.55, -63.56. IR (diamond-ATR) ν: 2928, 2856, 1452, 1252, 1154, 1101, 729. HRMS (ESI+) m/z [M+H] calculated for $C_{21}H_{28}F_6N$: 408.21205, found: 408.21202.

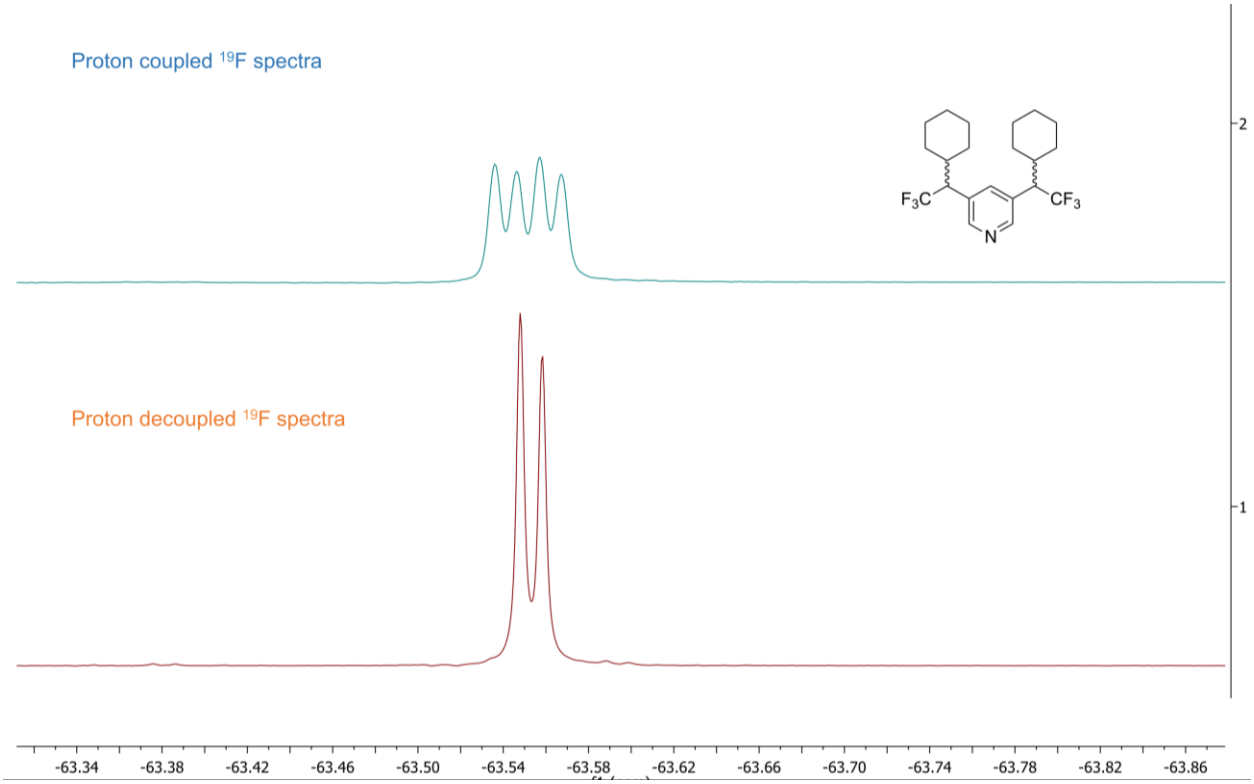
^{1}H NMR spectrum of cyclohexane adduct 5 in $CDCl_3$:



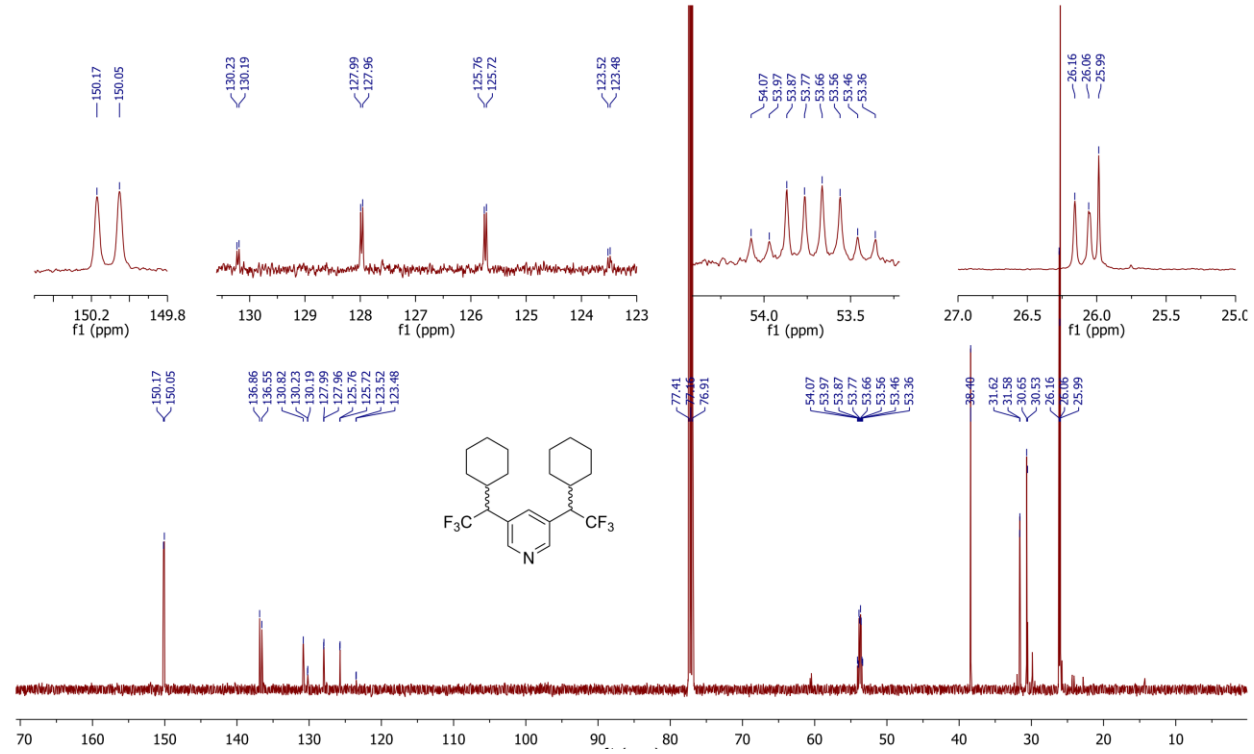
^{19}F NMR spectrum of cyclohexane adduct 5 in $CDCl_3$:



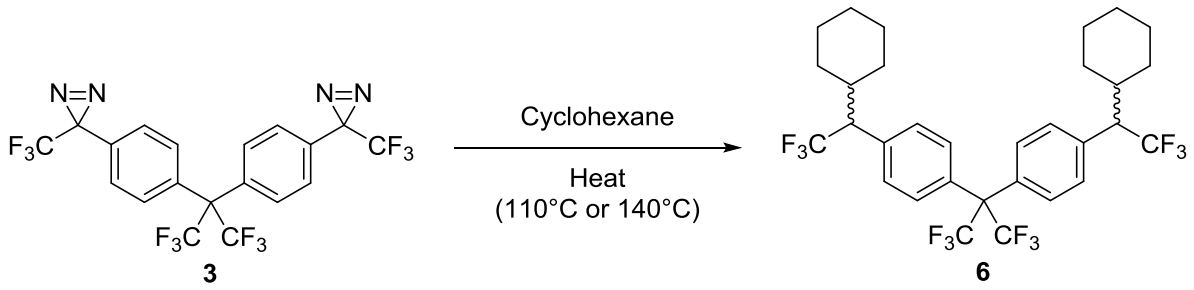
Comparison of ^{1}H-coupled and ^{1}H-decoupled ^{19}F spectra for cyclohexane adduct 5:



^{13}C NMR spectrum of cyclohexane adduct 5 in $CDCl_3$:



Crosslinking of cyclohexane using **3** – preparation of 4,4'-(perfluoropropane-2,2-diyl)bis((1-cyclohexyl-2,2,2-trifluoroethyl)benzene) (**6**)



3

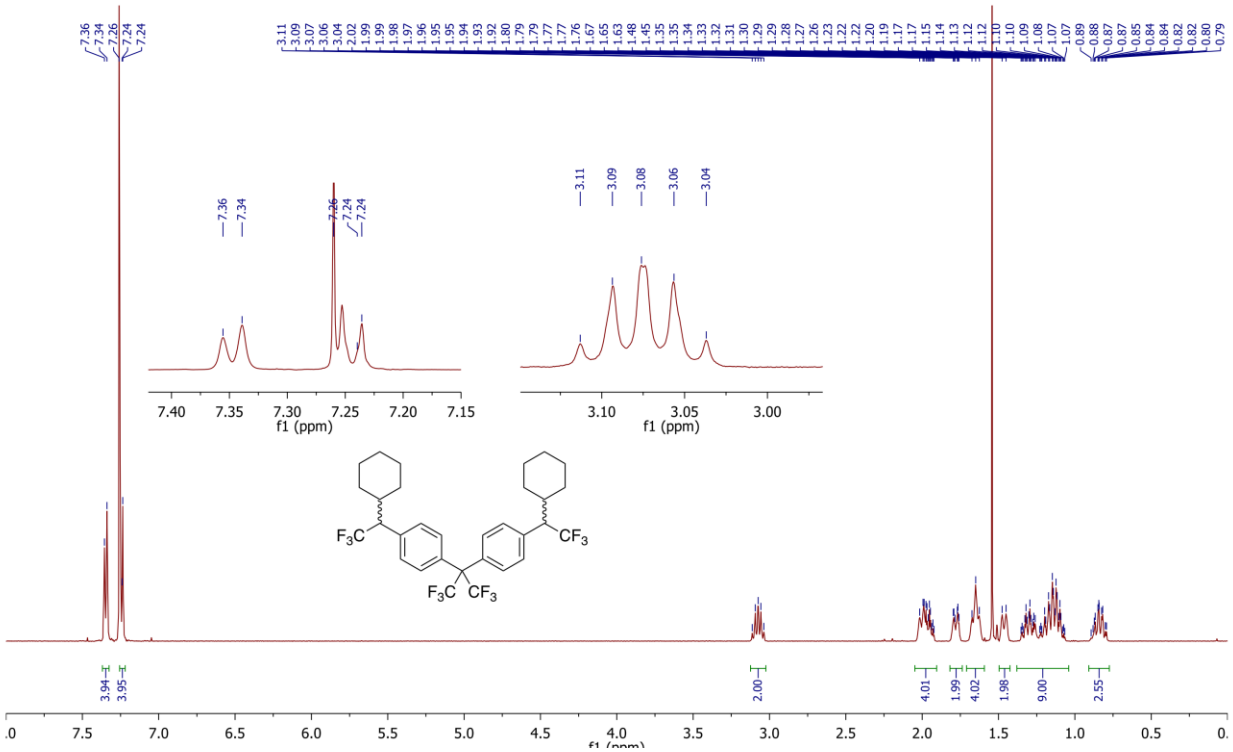
Chemical Formula: $C_{19}H_8F_{12}N_4$
Exact Mass: 520,0557
Molecular Weight: 520,2818

6

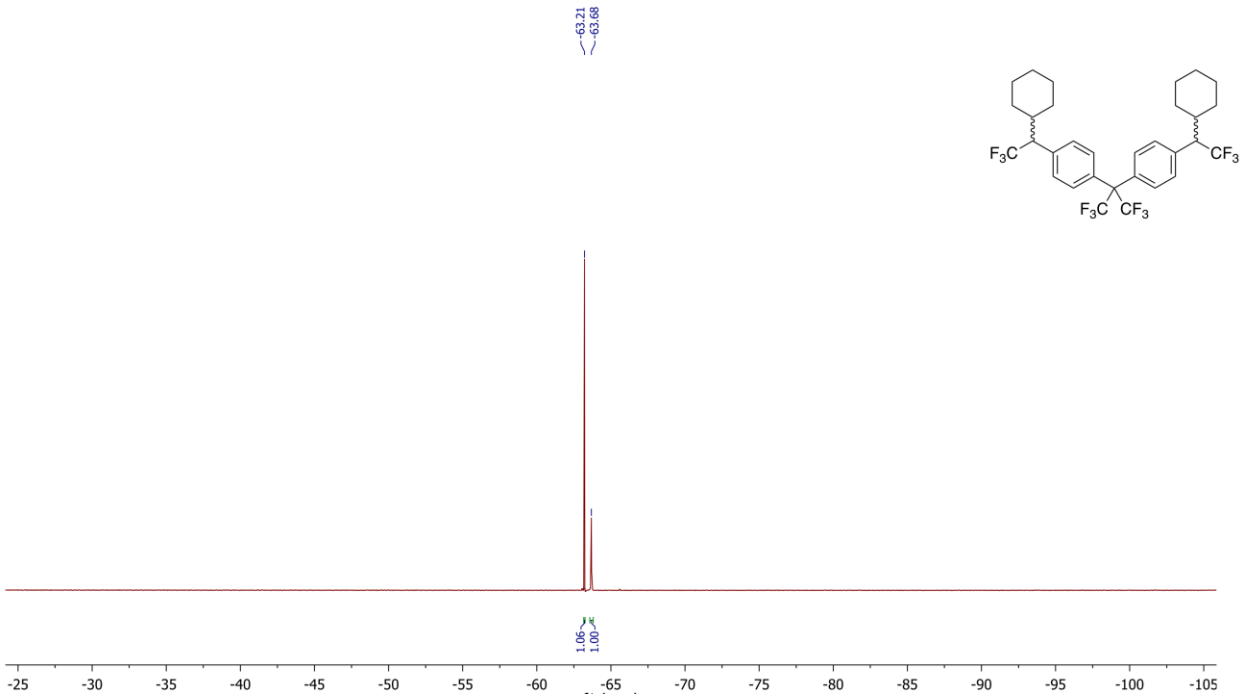
Chemical Formula: $C_{31}H_{32}F_{12}$
Exact Mass: 632,2312
Molecular Weight: 632,5778

Reactions were performed as described in the above general procedure for crosslinking experiments. Thermal activation under the standard conditions described above (with 115 mg of bis-diazirine **3** in 22 mL cyclohexane at 140 °C) afforded 9.7 mg product (7.0% yield) following chromatography. Thermal activation was repeated under slightly modified conditions (81.1 mg in 15.6 mL solvent) at 110 °C for 7 h to produce the identical product (9.4 mg, 9.5%). In both cases, crude material was purified in a similar manner as previously described and the desired product was isolated as mixture of diastereomers, as a white solid. ^{1}H NMR (500.27 MHz, chloroform-d) δ 7.35 (d, J = 8.4 Hz, 4H), 7.24 (d, J = 8.4 Hz, 4H), 3.07 (p, J = 9.7 Hz, 2H), 2.04–1.88 (m, 4H), 1.78 (m, 2H), 1.70–1.59 (m, 4H), 1.46 (d, J = 13.1 Hz, 2H), 1.37–1.06 (m, 9H), 0.91–0.78 (m, 2H). ^{13}C NMR (126 MHz, chloroform-d) δ 136.4 (d, J = 2.5 Hz), 132.8, 130.4, 129.2, 127.1 (q, J = 280 Hz), 124.3 (q, J = 282.54 Hz), 64.4 (q, J = 25.1 Hz), 56.0 (q, J = 25.3 Hz), 38.6, 31.6, 30.9, 26.3, 26.2, 26.1. ^{19}F NMR (470.72 MHz, chloroform-d) δ -63.21, -63.68 IR (diamond-ATR) ν: 2926, 2855, 1519, 1453, 1250, 1176, 1155, 1100, 713. HRMS (ESI+) m/z [M+CH_3CN+H] calculated for $C_{33}H_{36}F_{12}N$: 674.2656, found: 674.2648.

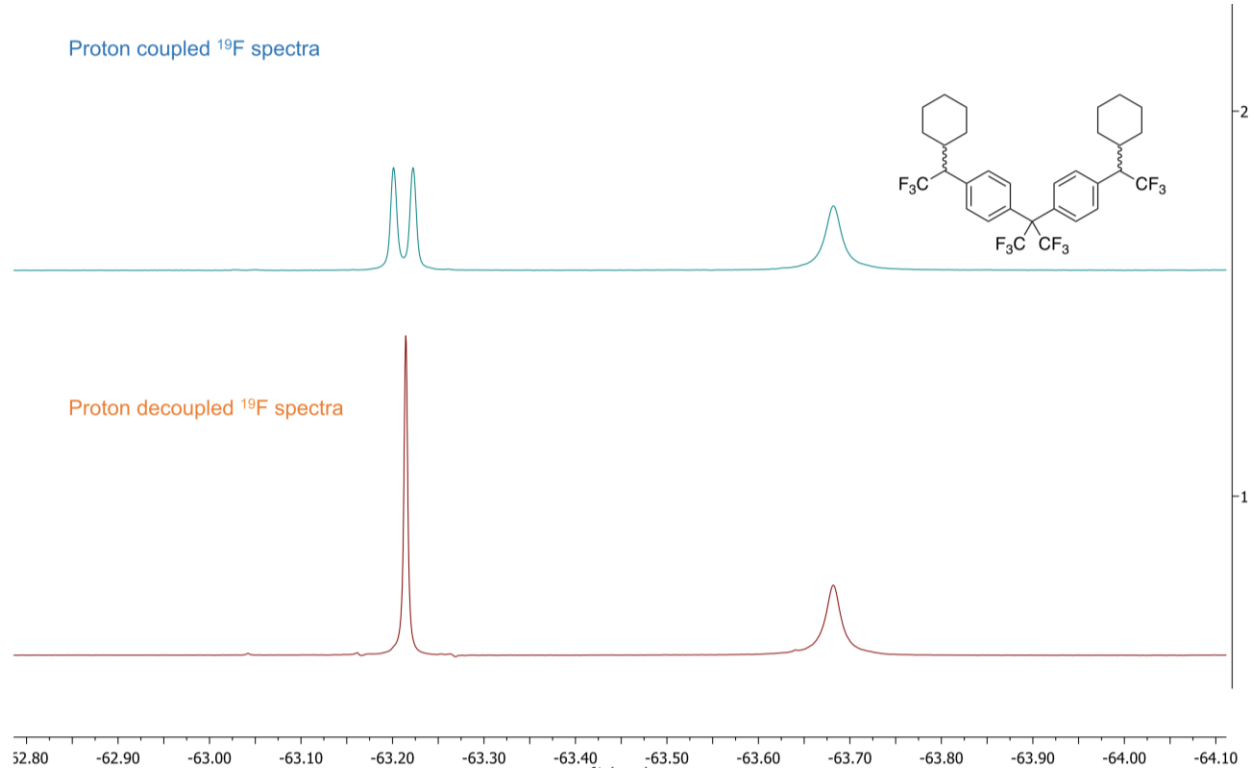
^{1}H NMR spectrum of cyclohexane adduct 6 in $CDCl_3$:



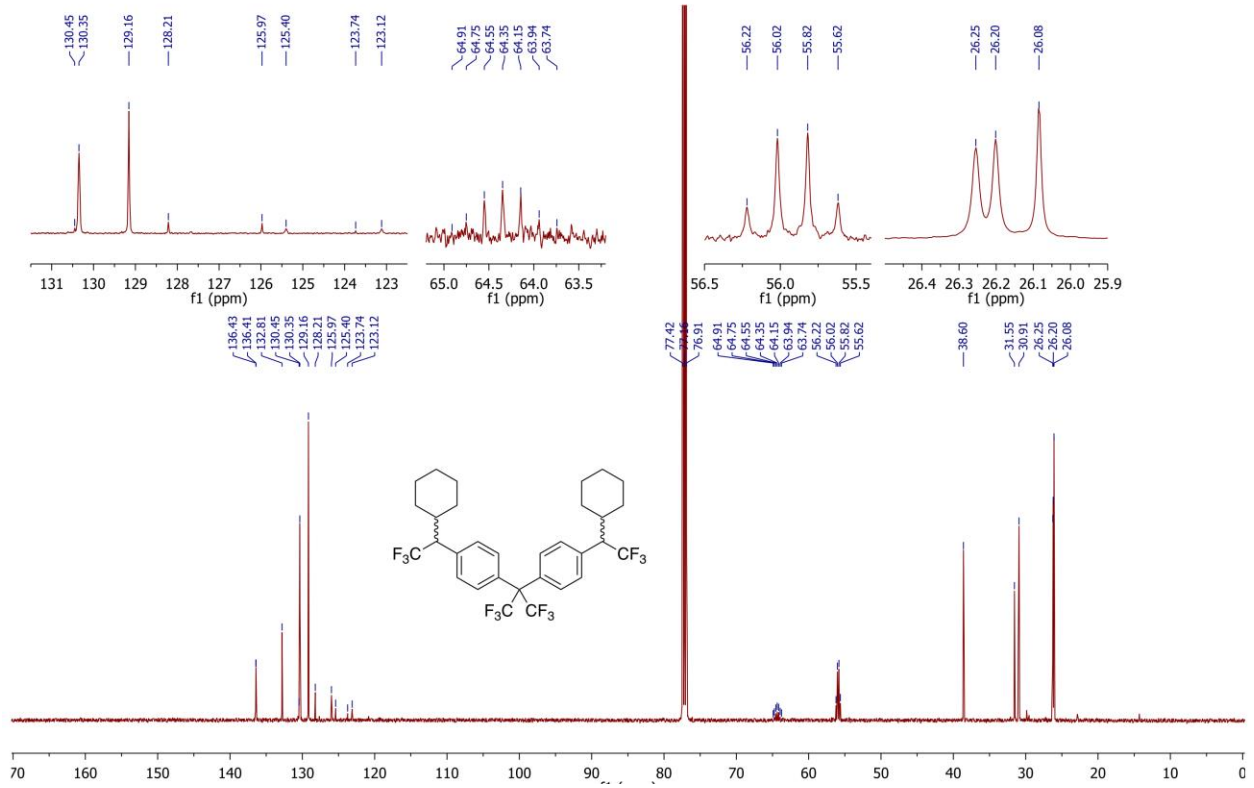
^{19}F NMR spectrum of cyclohexane adduct 6 in $CDCl_3$:



Comparison of ^{1}H-coupled and ^{1}H-decoupled ^{19}F spectra for cyclohexane adduct 6:



^{13}C NMR spectrum of cyclohexane adduct 6 in $CDCl_3$:



Thermogravimetric analysis (TGA)

A sample of the analyzed substance (typically 1 to 10 mg) was placed in a 90 µL alumina pan covered by a pinhole lid. This pan was placed in the oven of the SDT Q600 device and heated from 25°C to 200°C at a rate of 5°C/min, with an identical empty pan as a reference. The oven was constantly flushed by a 100 mL/min flow of nitrogen. The device recorded the initial weight and monitored the weight change over the heating process.

Differential Scanning Calorimetry (DSC)

A sample of the analyzed substance (typically 1 to 10 mg) was placed in a Tzero aluminum pan and sealed by a matching lid. In the case of compound **3**, the pan was pierced with a small pinhole to allow evolution of nitrogen gas. For compounds **1**–**2**, this was not possible due to their low boiling point. The pan was placed in the oven of the DSC25 device and heated from 40°C to 200°C at a rate of 5°C/min, with an identical empty pan as a reference. The oven was constantly flushed by a 50 mL/min flow of nitrogen. The device recorded the difference in heat flow between the reference and the studied sample.

Gel Permeation Chromatography (GPC)

GPC was carried out using a Malvern OMNISEC Tetra-Detector gel permeation chromatograph equipped with an automatic sampler, a pump, an injector, an inline degasser, and a column oven (30 °C). The elution columns T3000 and T5000 from Viscotek were used. Detection was conducted by means of a quadruple detector: light scattering, differential refractive index, viscosimeter and diode-array-based UV/Vis spectrometer. HPLC-grade tetrahydrofuran (Fisher) was used as the eluent, with a flow rate of 1.0 mL/min. The calibration was conducted using a PolyCALTM polystyrene standard (PS115K) from Viscotek. All samples were dissolved in the eluent (1-10 mg/mL) and filtered with a polytetrafluoroethylene membrane of 0.45 µm pore size before analysis.

Tear testing

Tear resistance of fabric was characterized according to ASTM D2261. In a sample of 100 mm × 100 mm, a centered edge cut of 50 mm in length was introduced using a hot wire cutter. The two “legs” of the sample were then clamped symmetrically, over a length of 25 mm on each, in a universal testing system (Instron, Series 5969), and pulled apart at a rate of 30 mm/min, while the force-extension curve was recorded.

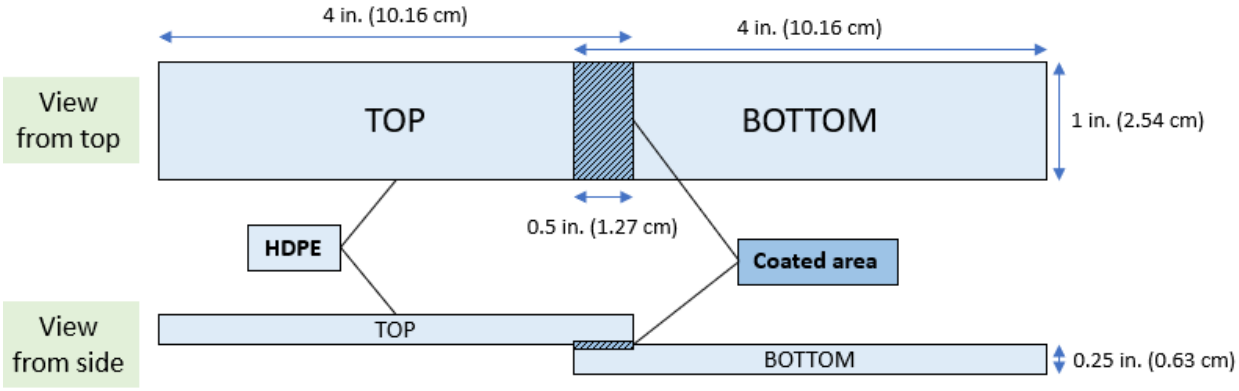
Drop-tower testing

A Gardner Impact Tester (PF-5545, BYK) was used to characterize the perforation resistance of fabrics. For each test, 5 fabric pieces of 40 mm × 40 mm were stacked together and placed on a rigid PET foam substrate (AIREX T92) for capturing the dent signature of each impact. A drop weight of 1.98 kg was released from a constant height to deliver an impact energy of 5.9 J to a

cylindrical perforator, which had a diameter of 3.65 mm and a conically shaped tip. The penetration depth of the perforator into the substrate was measured after the test.

Preparation of adhered HDPE samples

Pairs of 4''x1''x1/4'' bars of HDPE (obtained from Quadrant Plastics) were glued together by spreading 10 or 25 mg of SuperGlue®, **7** (molecular control) or **3** (bis-diazirine) on a 1''x 0.5'' area in between the bars (see figure below). Each pair of bars was held together with binder clamps and placed in an oven at 115°C for 15 h. After cooling down to room temperature, the samples were challenged on a lap-shear experiment.



Lap-shear test

The adhesion strength of the pair of HDPE bars crosslinked with **3** was measured according to ASTM D1002 using single-lap-joint bonded specimens. Two rectangular plastic sheets of 100 mm × 27 mm × 6 mm were bonded together over a length of 12 mm their longest edges. The two ends of the specimen were then clamped in a universal testing system (Instron, Series 5969), and pulled apart at a rate of 3 mm/min until breakage of the bond. The maximum force was recorded for each specimen.

Statistical significance

Throughout the manuscript and supporting information, the statistical significance of results of crosslinked materials versus the appropriate control was assessed using unpaired t tests with Welch's correction.

Supplementary Text

Challenges for high energy crosslinking processes

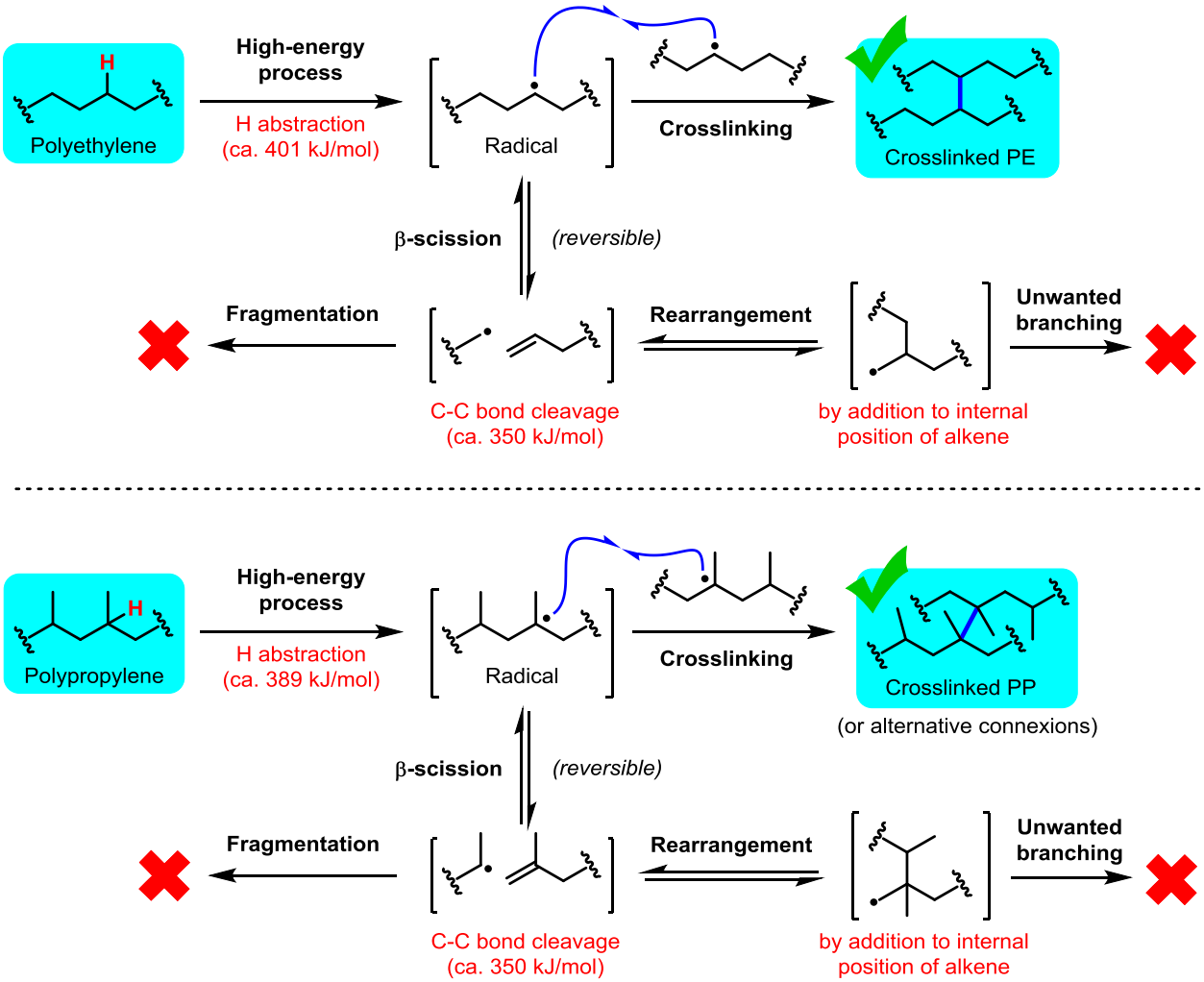


Figure S1. Challenges associated with high-energy crosslinking processes relying on the *in situ* generation of radical species. β-scission processes are particularly favored in the case of polypropylene, since a secondary radical would be produced following the cleavage reaction. This presumably accounts for the lack of commercial crosslinked polypropylene.

Convention

Throughout the manuscript, "wt%" refers to a weight:weight ratio of crosslinker/control to the treated material. For instance, "1wt%" means that 10 mg of crosslinker/control was added to a sample of 1 g material. Consequently, "100wt%" means that an equal amount of crosslinker/control and treated material were mixed together.

TGA measurements for crosslinkers **1**–**2**

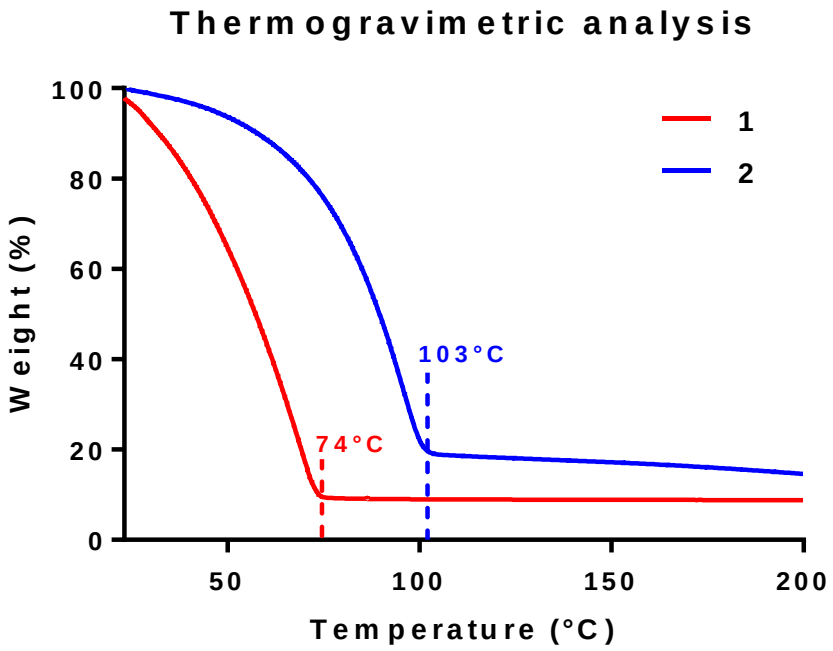


Figure S2. Thermogravimetric analyses of 1–2 showing their volatility.

TGA measurement for crosslinker **3**

Upon heating, **3** loses 10.7% of its weight (Fig. 2C in the manuscript), a remarkably good correlation with the weight of two molecules of elemental nitrogen being released (see below).

Equation S1. Correlation of thermogravimetric analysis of 3 with theoretical weight loss.

$$MW\ (N_2) = 28.01\ g/mol$$

$$MW\ (\mathbf{3}) = 520.28\ g/mol$$

$$(2 \times MW\ (N_2)) / MW\ (\mathbf{3}) = 56.02 / 520.28 = \mathbf{10.8\ \%}$$

DSC measurements for crosslinkers **1–2**

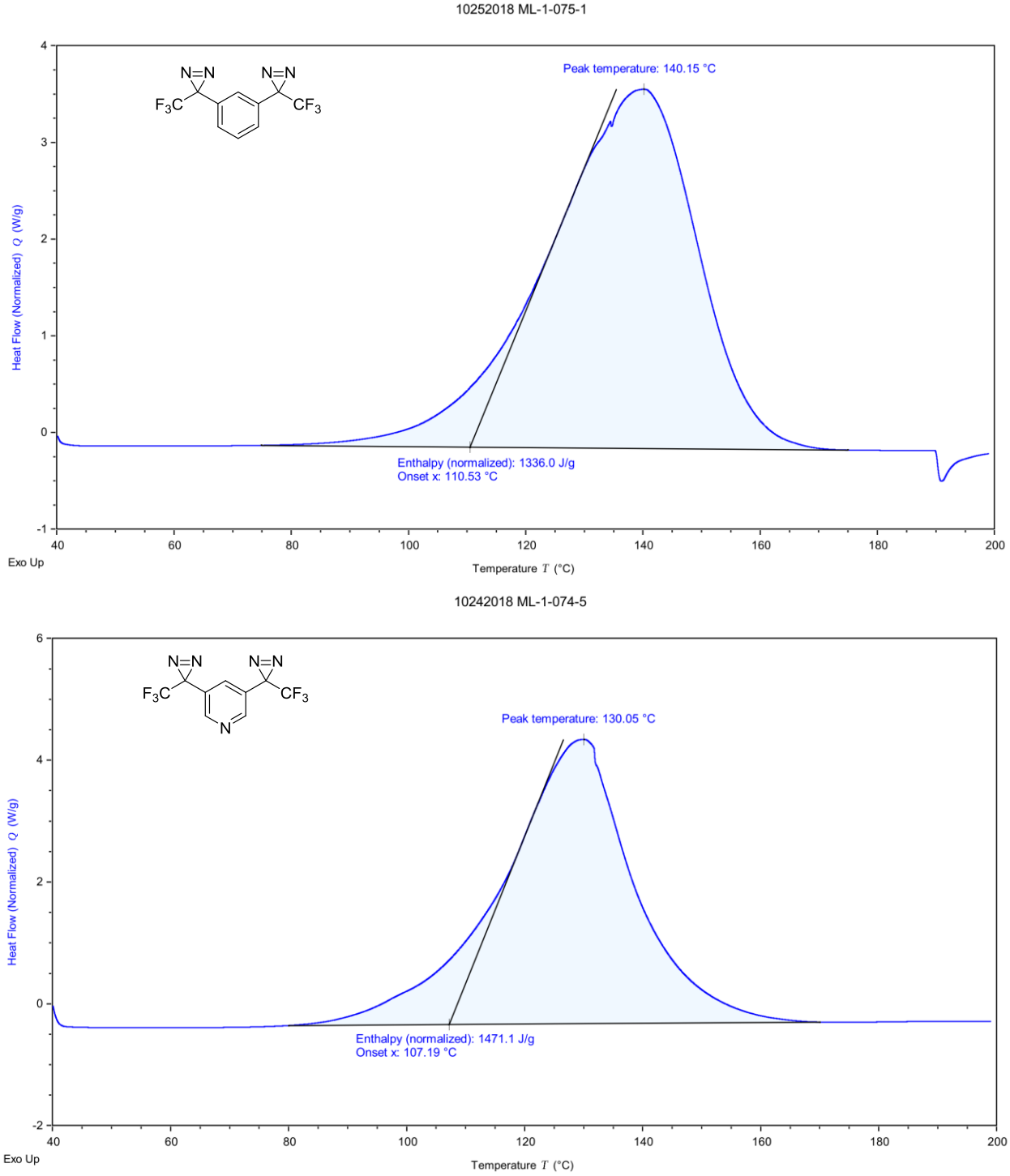


Figure S3. Representative DSC curves (40°C to 200°C at 5°C/min) for 1–2.

Assessment of explosivity

Equation S2. Shock sensitivity (SS) according to Yoshida correlations.

$$\text{Shock sensitivity} = \log (Q_{DSC}) - 0.72 \times \log (T_{onset} - 25) - 0.98$$

Equation S3. Explosive propagation (EP) according to Yoshida correlations.

$$\text{Explosive propagation} = \log (Q_{DSC}) - 0.38 \times \log (T_{onset} - 25) - 1.67$$

Q_{DSC} is in cal/g and T_{onset} is in °C.

A material is highly likely to be explosive if shock sensitivity and/or explosive propagation values are positive.

Table S1. Values of Yoshida correlations for shock sensitivity (SS) and explosive propagation (EP) for bis-diazirines 1–3.

Compound	1	2	3
# of replicates(N):	3	4	4
Enthalpy (J/g)	1242 ± 92	1395 ± 75	696 ± 24
Enthalpy (kJ/mol)	365 ± 27	412 ± 22	362 ± 13
Onset temperature (°C)	112.9 ± 2.1	106.5 ± 1.1	113.1 ± 0.2
Shock sensitivity	LIKELY (+0.09)	LIKELY (+0.17)	Not likely (-0.16)
Explosive propagation	LIKELY (+0.06)	LIKELY (+0.13)	Not likely (-0.19)

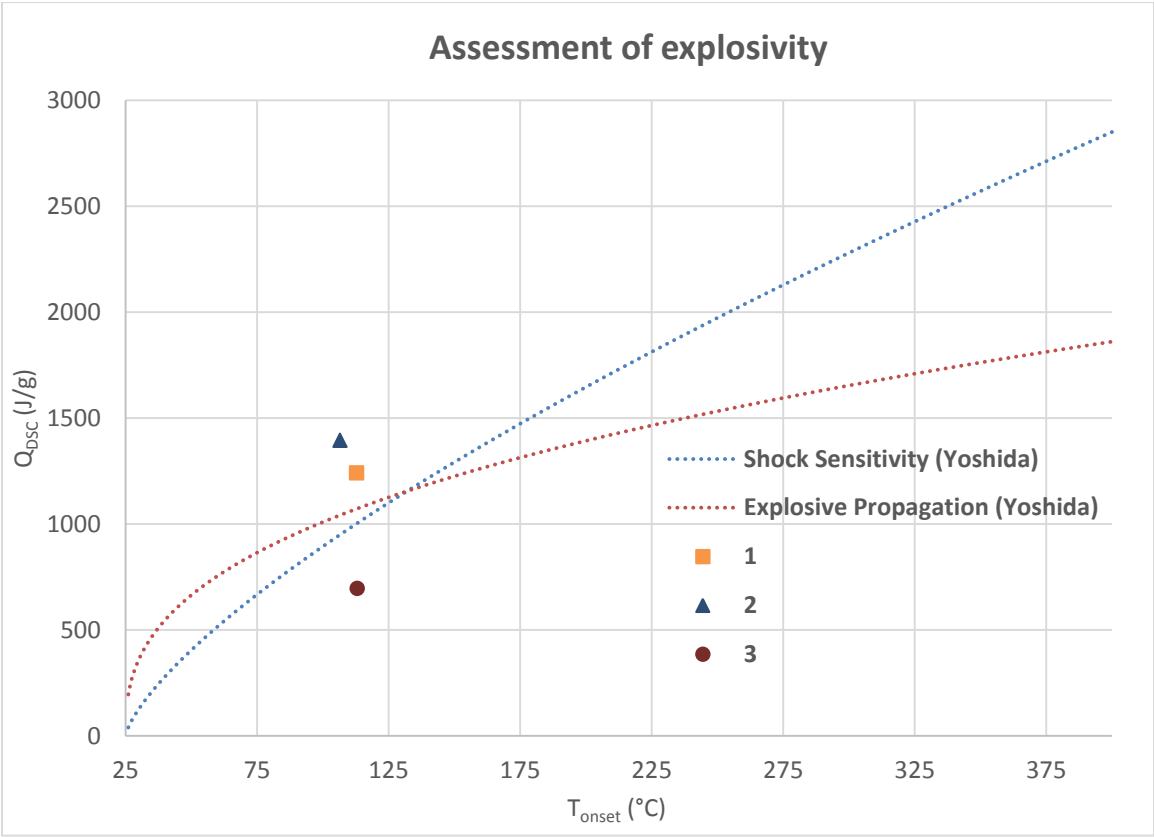


Figure S4. Assessment of explosivity according to Yoshida correlations for shock sensitivity and explosive propagation). Compounds are represented by a point of coordinates {T_{onset}, Enthalpy}. Compounds above either of the two curves are likely to be explosive.

Decomposition of **1**–**3** under UV irradiation or heating

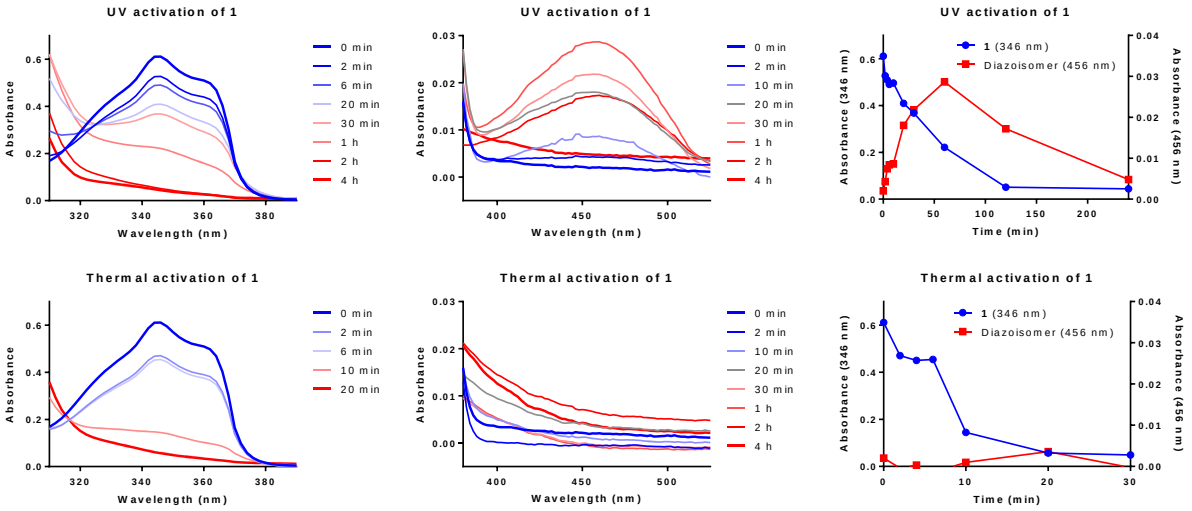


Figure S5. UV and thermal activation of bis-diazirine 1. *Top*: UV irradiation (350 nm). *Bottom*: Heating (140°C). *Left*: absorbance spectra in the 310-390 nm region showing consumption of starting material over time; *Middle*: absorbance spectra in the 380-525 nm region showing formation or absence of diazoisomers over time; *Right*: Absorbance values at 346 and 456 nm over time to estimate consumption of **1** and formation of its diazoisomers, respectively.

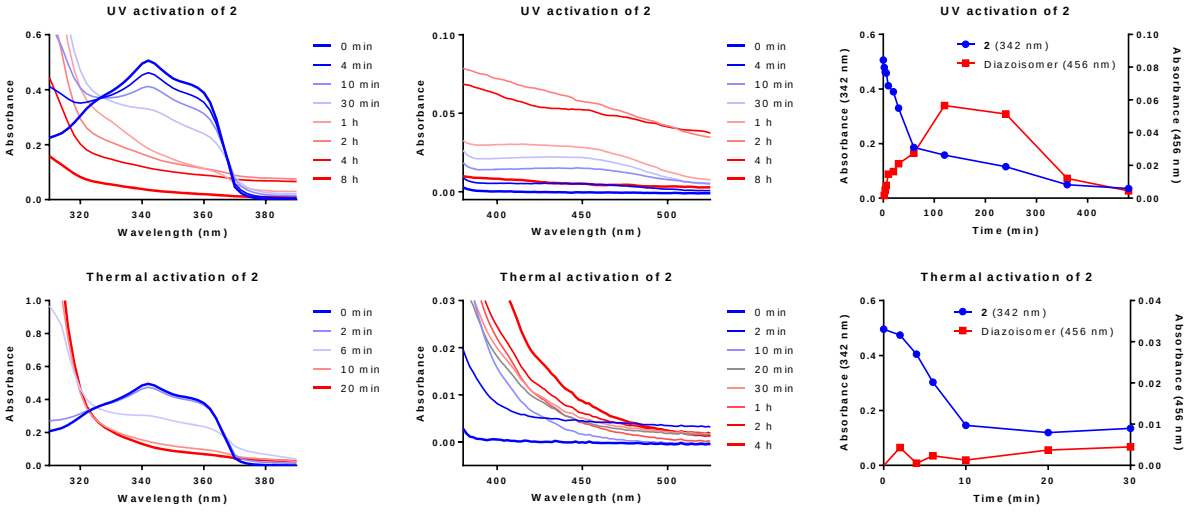


Figure S6. UV and thermal activation of bis-diazirine 2. *Top*: UV irradiation (350 nm). *Bottom*: Heating (140°C). *Left*: absorbance spectra in the 310-390 nm region showing consumption of starting material over time; *Middle*: absorbance spectra in the 380-525 nm region showing formation or absence of diazoisomers over time; *Right*: Absorbance values at 342 and 456 nm over time to estimate consumption of **2** and formation of its diazoisomers, respectively.

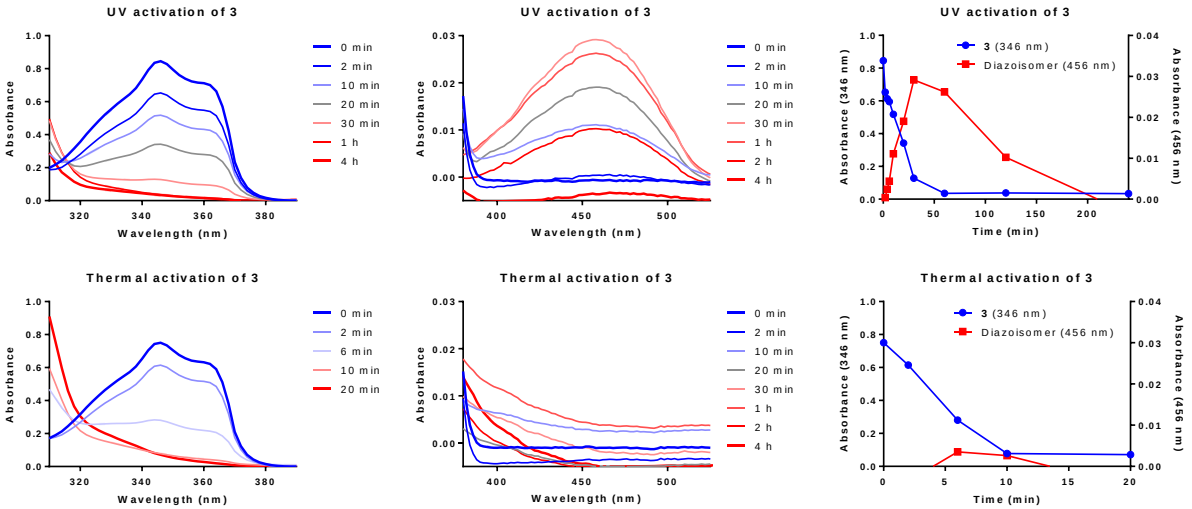


Figure S7. UV and thermal activation of bis-diazirine 3. *Top*: UV irradiation (350 nm). *Bottom*: Heating (140°C). *Left*: absorbance spectra in the 310-390 nm region showing consumption of starting material over time; *Middle*: absorbance spectra in the 380-525 nm region showing formation or absence of diazoisomers over time; *Right*: Absorbance values at 346 and 456 nm over time to estimate consumption of **3** and formation of its diazoisomers, respectively.

Detection of diazo intermediates during cyclohexane crosslinking with **1** and **2**

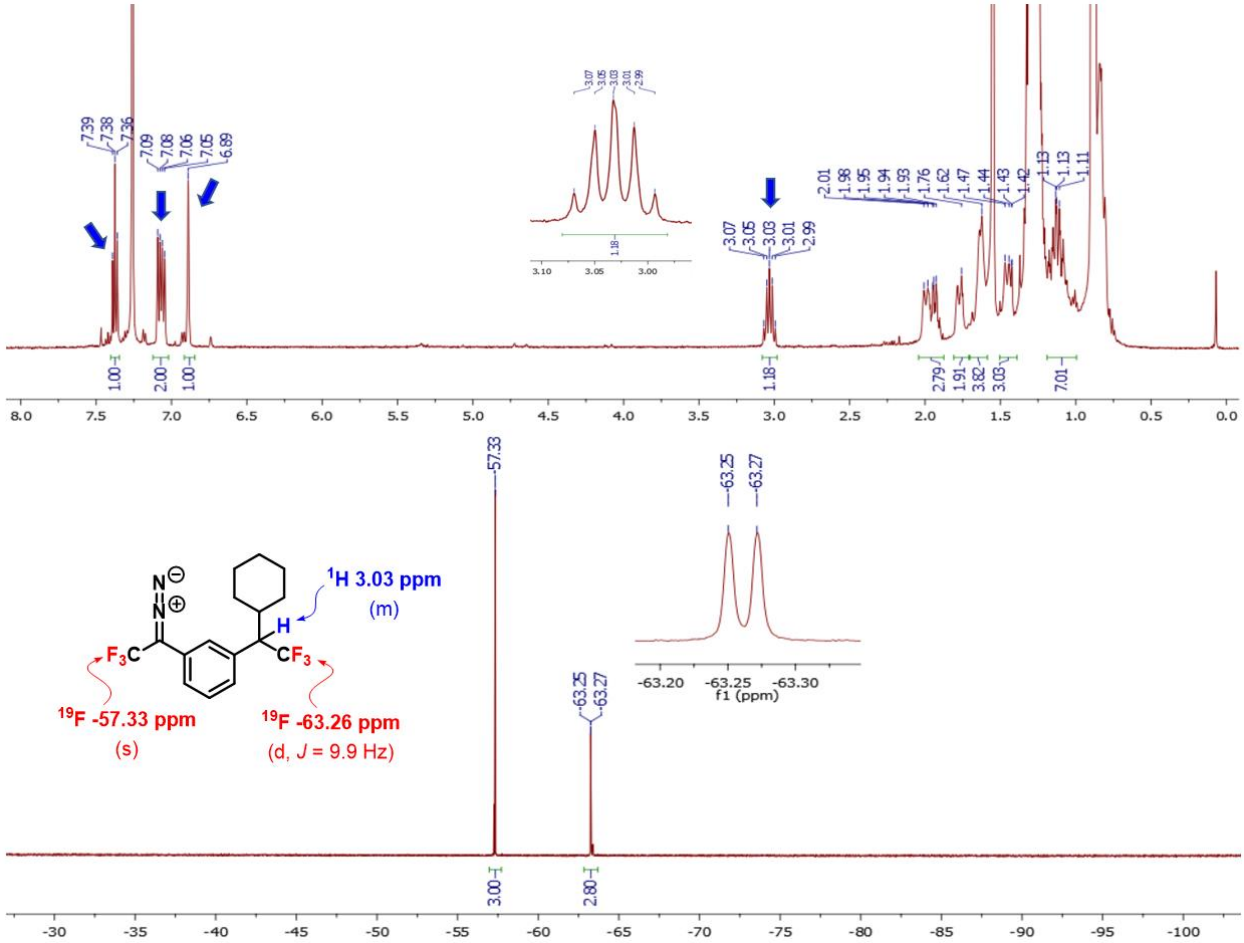


Figure S8. ^{1}H and ^{19}F NMR spectra of impure fractions containing a diazo intermediate/byproduct arising from the partial activation of crosslinker **1** under UV irradiation in cyclohexane.

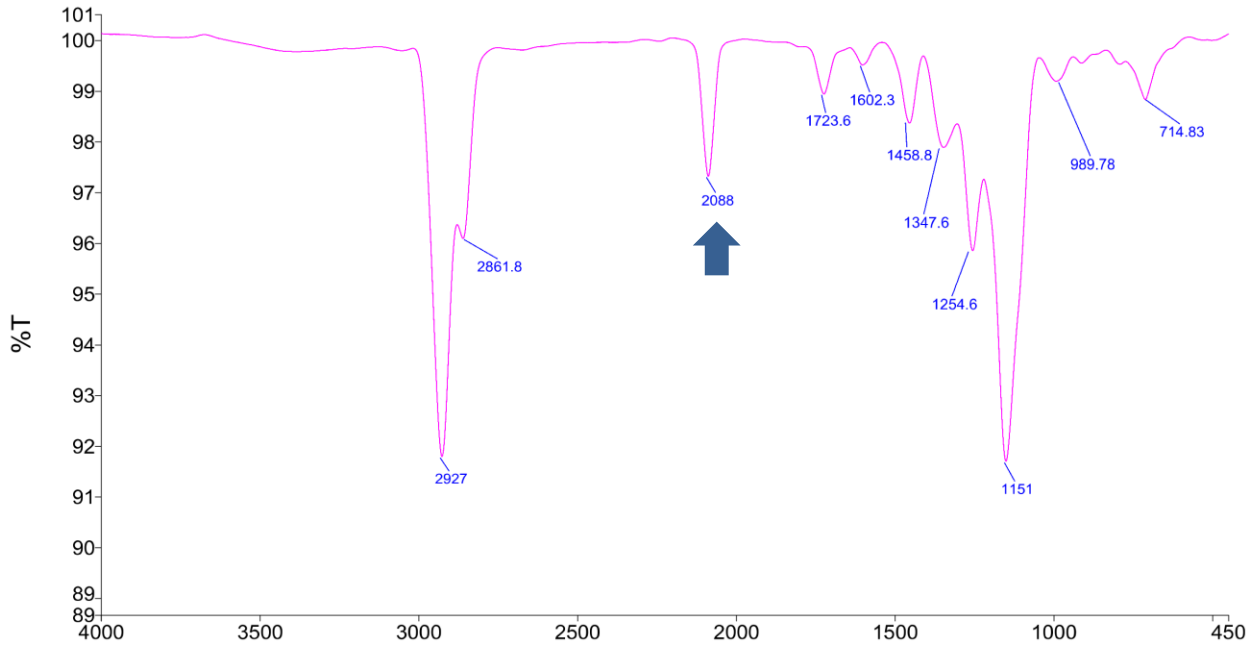


Figure S9. Infrared spectrum of impure fractions containing a diazo intermediate/byproduct arising from the partial activation of crosslinker **1** under UV irradiation in cyclohexane. The sharp band at 2088 cm^{-1} (indicated by the arrow) is characteristic of a linear diazo group.

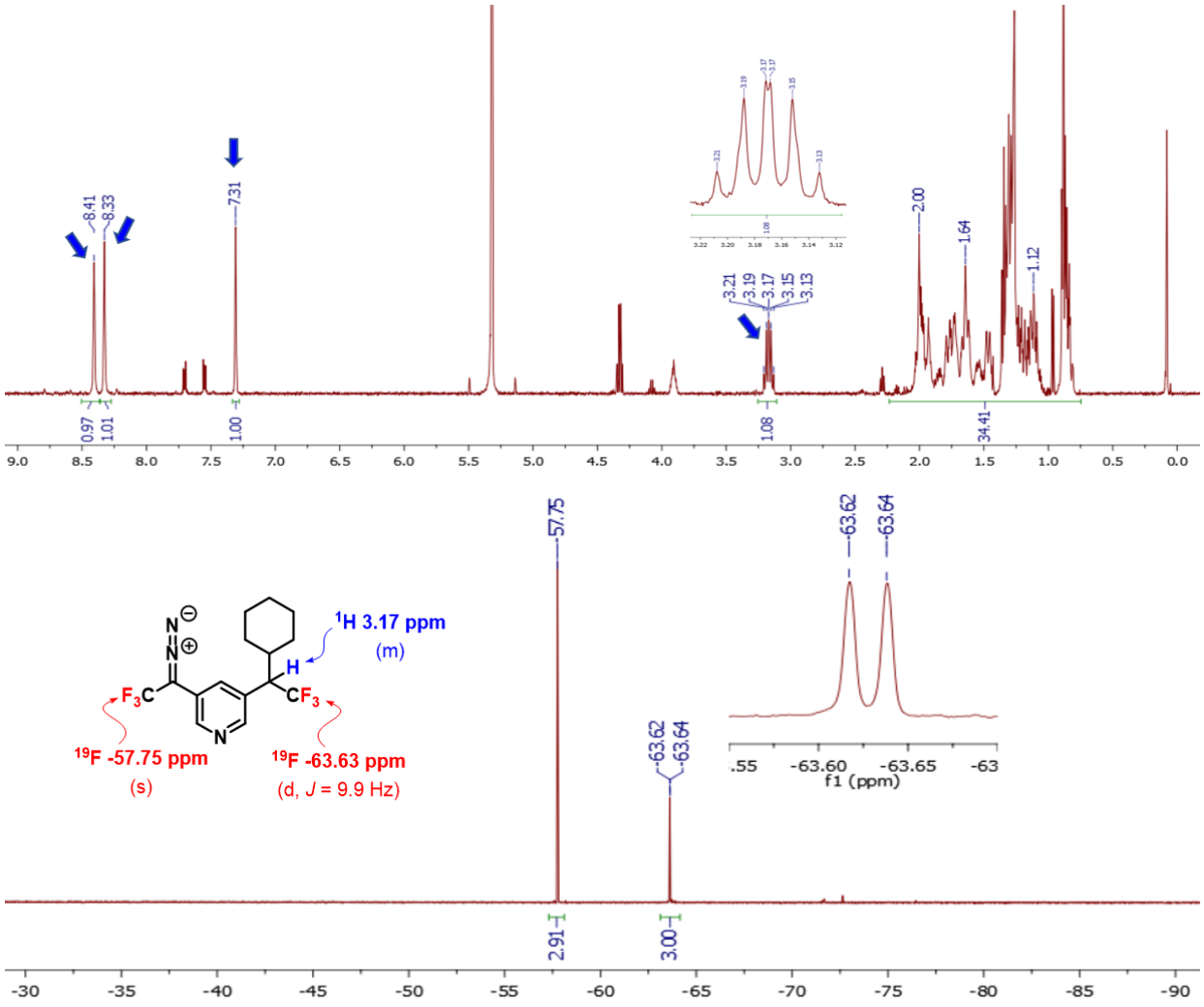


Figure S10. ^{1}H and ^{19}F NMR spectra of impure fractions containing a diazo intermediate/byproduct arising from the partial activation of crosslinker **2** under UV irradiation in cyclohexane.

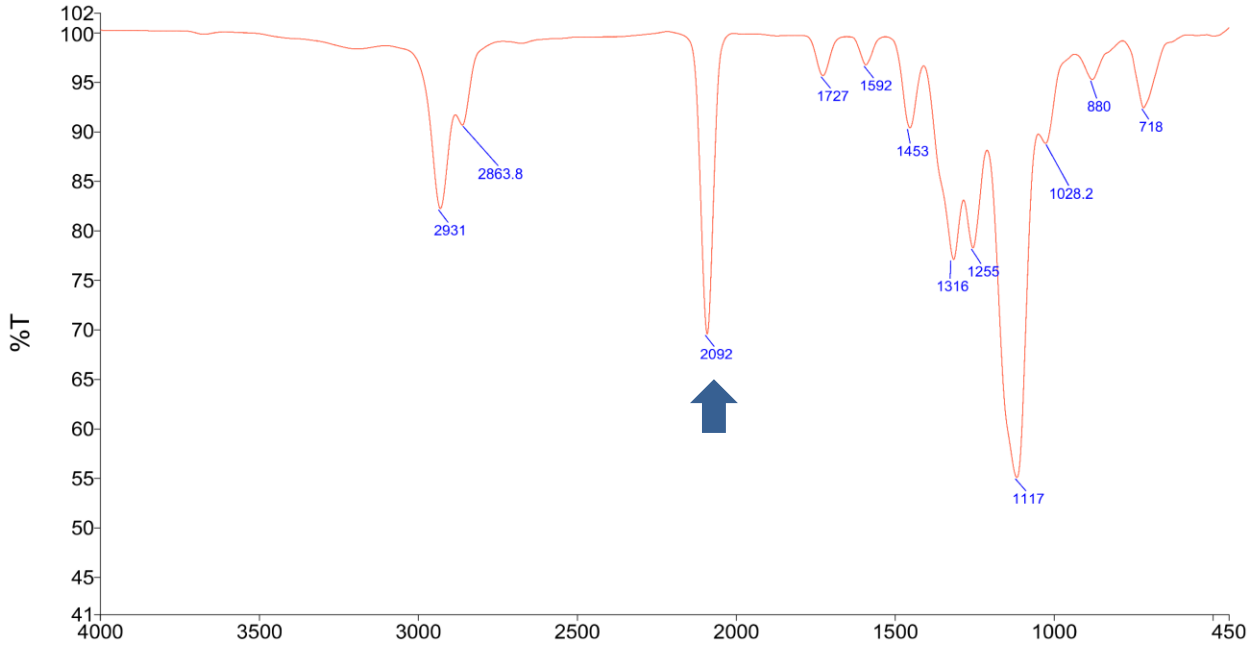


Figure S11. Infrared spectrum of impure fractions containing a diazo intermediate/byproduct arising from the partial activation of crosslinker **2** under UV irradiation in cyclohexane. The sharp band at 2092 cm^{-1} (indicated by the arrow) is characteristic of a linear diazo group.

Estimation of C–H insertion efficiency during heat-activation of **3** at 140°C for 2 h

Postulating that:

1) the ^{19}F resonances observed between -63.4 and -64.3 ppm correspond to geminal, unreactive trifluoromethyl groups in **6** and all byproducts (highlighted in red in Fig. S12);
2) the ^{19}F resonances observed between -62.7 and -63.4 ppm correspond to trifluoromethyl groups proximal to a C–H insertion site (highlighted in orange in Fig. S12);

it is possible to estimate the C–H insertion efficiency during the reaction of **3** in cyclohexane at 140°C for 2 h. The ratio between integration values (see full spectrum in Fig. S13) of the regions highlighted in orange (Int. = 25.2) and red (Int. = 48.9) is **0.52 : 1**. This suggests that **about 52%** of the diazirine groups reacted to give C–H insertion products. The spectra show no remaining diazirine functions (for which adjacent CF_3 groups come into resonance at ca. -65 ppm; see blue-highlighted region below), but the complexity of the crude NMR spectrum suggests that some degree of dimerization, oligomerization or self-reaction accompanies the C–H insertion process. Many of these dimers and oligomers will constitute molecular crosslinks.

Experimental support for the postulates detailed above comes from analysis of ^{1}H-coupled and ^{1}H-decoupled ^{19}F NMR spectra. As shown in Fig. S13, the ^{19}F signals between -62.7 and -63.4 ppm (orange-highlighted region) all show additional splitting upon coupling, while the signals between -63.4 and -64.3 ppm (red-highlighted region) do not. An additional region of the ^{19}F NMR spectrum at ca. -65.6 ppm (highlighted in green) also possesses signals that demonstrate coupling to protons. These signals likely correspond to additional C–H insertion products, beyond the 52% calculated above.

In summary, it appears that >50% of diazirine moieties reacted to afford C–H insertion products, although additional species beyond the canonical adduct **6** were formed.

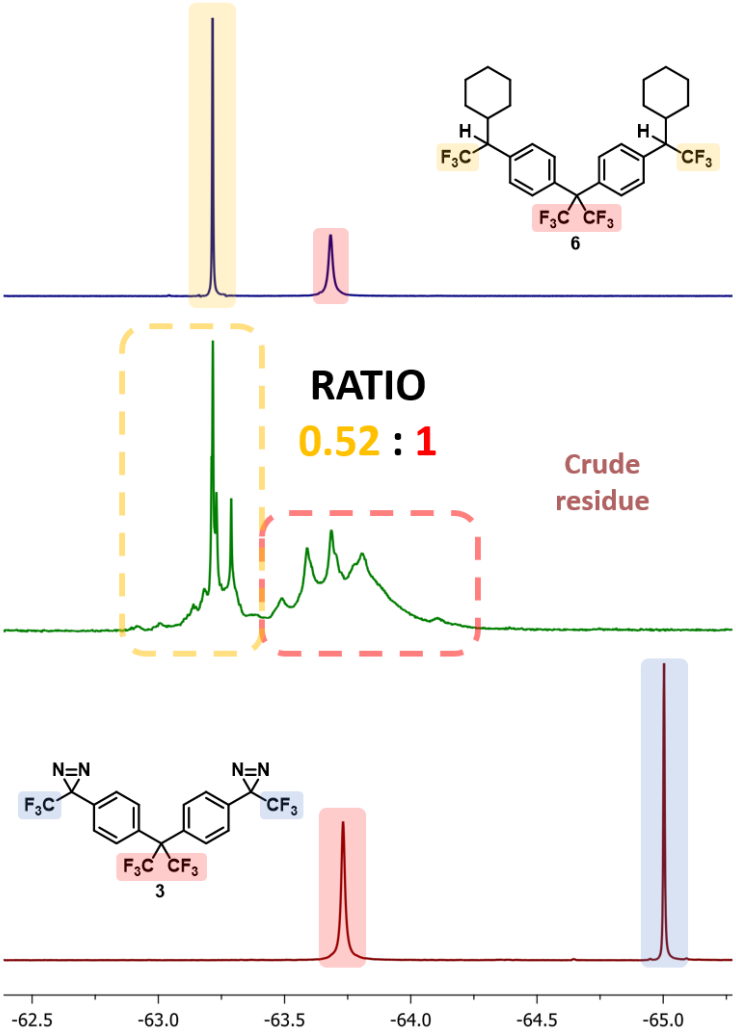


Figure S12. Comparison of $^{19}F\{^{1}H\}$ NMR spectra of crosslinker **3** (bottom) and purified cyclohexane adduct **6** (top) with the crude NMR spectrum resulting from the reaction of **3** in cyclohexane at 140°C for 2 h. The regions highlighted in red correspond to the geminal, remote CF_3 groups, serving as an internal standard since their chemical shift remains relatively constant regardless of the connectivity at the periphery of the molecule. The region highlighted in blue corresponds to CF_3 groups α to the reactive diazirine moieties, and this signal is absent in the spectrum of the crude reaction product, indicating complete conversion of starting material. The region highlighted in orange corresponds to CF_3 groups that are located α to a C–H insertion site, and are used to estimate the overall C–H insertion yield.

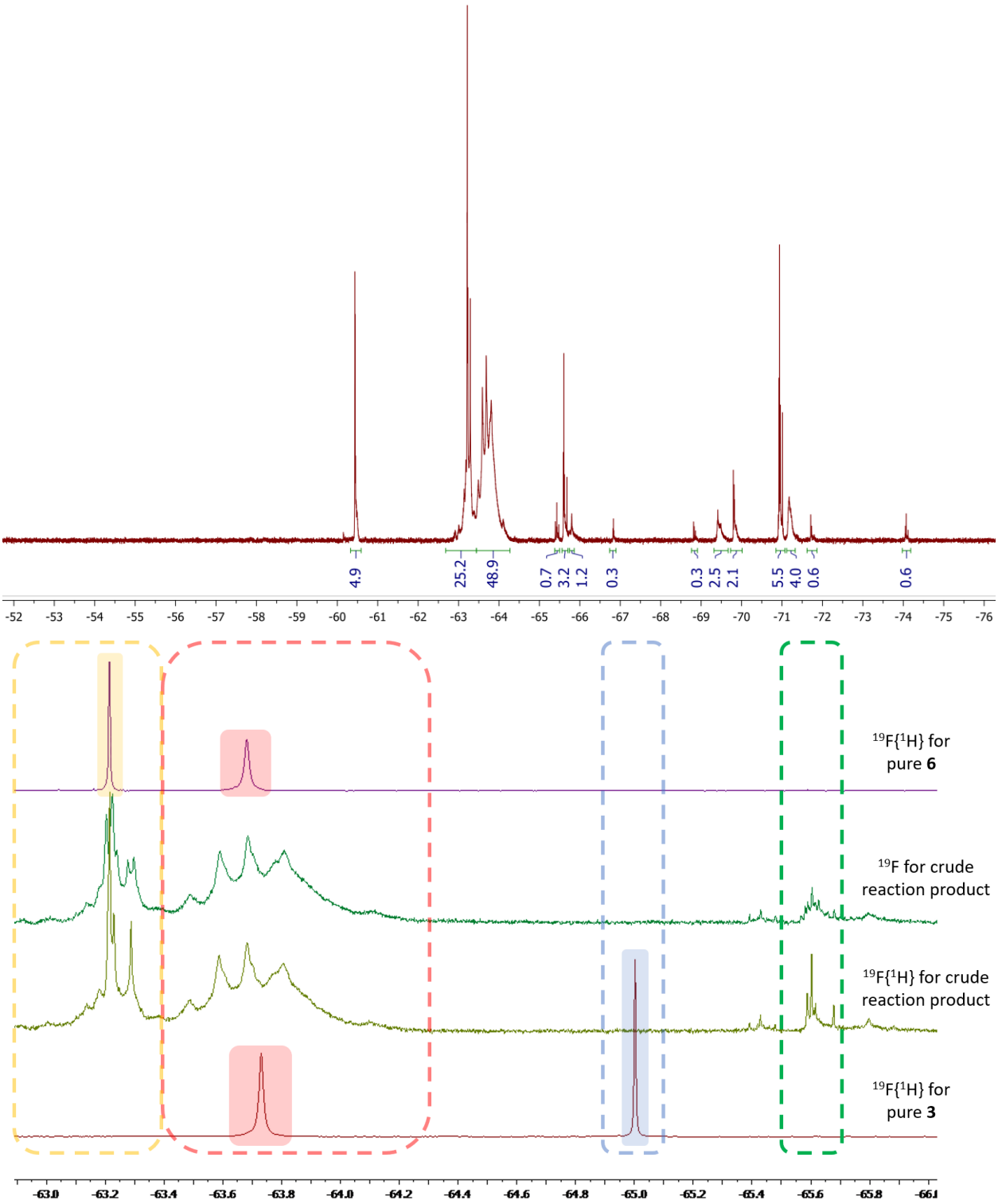


Figure S13. Crude NMR spectrum for C–H insertion reaction of 3 in cyclohexane. *Top:* Full-range $^{19}F\{^{1}H\}$ NMR spectrum of crude residue obtained from the reaction of **3** in cyclohexane at 140°C for 2 h. A variety of signals are observed, indicating the presence of oligomers and other species, in addition to the canonical crosslinked product **6**. *Bottom:* Comparison of ^{1}H-coupled and ^{1}H-decoupled ^{19}F NMR spectra for the crude reaction mixture, showing that signals found in the regions outlined in orange and green undergo splitting when ^{1}H coupling is enabled, but

signals found in the region outlined in red do not. By analogy to the known starting material and product, signals from the region outlined in red are assigned to the perfluroisopropyl group, while signals from the region outlined in orange are assigned to CF_3 groups adjacent to C–H insertion sites. In addition to simple isomerization to the diazoisomer, non-productive pathways for **3** could include a variety of homodimerizations including Buchner ring expansions, C–H insertions into the aromatic protons of the crosslinker, azine formation, and a variety of related transformations.

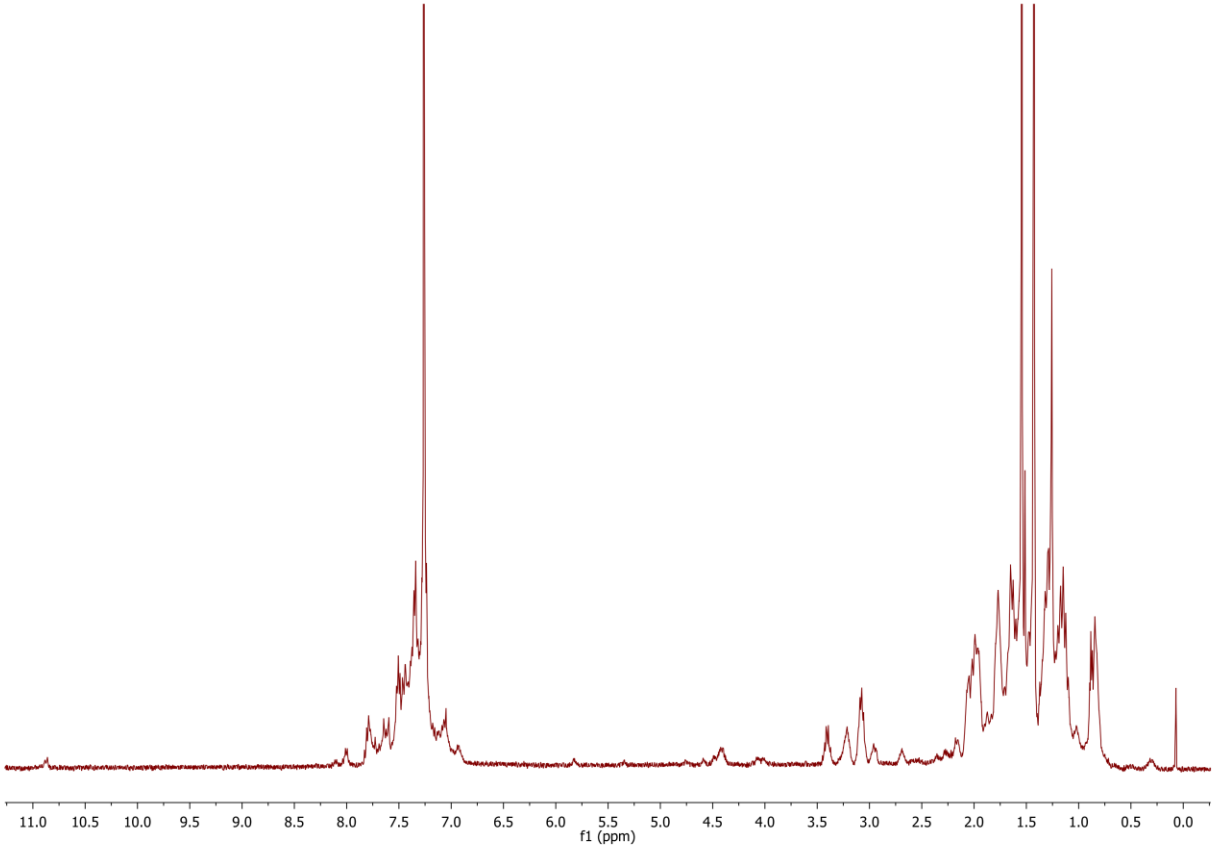


Figure S14. Full-range ^{1}H NMR spectrum of crude residue obtained from the reaction of 3 in cyclohexane at 140°C for 2 h.

Complete procedure for the crosslinking of paraffin wax

Material used: paraffin wax from Sigma-Aldrich (ref 327212, m.p. = 58–62 °C, CAS 8002-74-2)

Procedure: 8 samples were prepared by mixing molten wax (above 60°C) with **3** in various ratios. For each sample, the two products were added to the same vial and then melted together by using a mild heating from a heat gun, or a water bath set up slightly above 60°C. The following mixtures were prepared:

Table S2. Composition of paraffin wax samples doped with 3.

Sample	Loading (wt%)	Mass wax (mg)	Mass 3 (mg)	Total mass (mg)
A	0	200	0	200
B	0	200	0	200
C	1	200	2	202
D	5	200	10	210
E	20	100	20	120
F	50	50	25	75
G	100	50	50	100
H	200	25	50	75

All samples were opaque, white and solid at room temperature. Samples B-H were placed in an oven at 110°C for 16 h. Sample A was kept at room temperature as a control. A portion of each of the samples (10 mg) was covered with THF (1.0 mL). After shaking for ca. 1 h, all samples but sample H dissolved completely. The latter (highest crosslinker loading) did not fully dissolve, leaving a swollen material. The dissolved samples were analyzed by gel permeation chromatography (GPC) using THF as mobile phase.

Results:

- All samples placed in the oven melted.
- The activation of crosslinker caused the doped samples to turn yellow, and more so with higher loadings.
- When allowed to cool down to room temperature, all samples returned to opaque solids, with a yellow coloration increasing with the crosslinker loading.
- Sample H, loaded with 200 wt% **3** remained partially soluble and produced a swollen, insoluble fraction.
- GPC analysis of the dissolved samples shows several key features supporting the crosslinking mechanism at play.
- GPC analysis also confirms insolubility of sample H (loaded with 200 wt% **3**), as the intensity of the signal is significantly lower in all three channels.

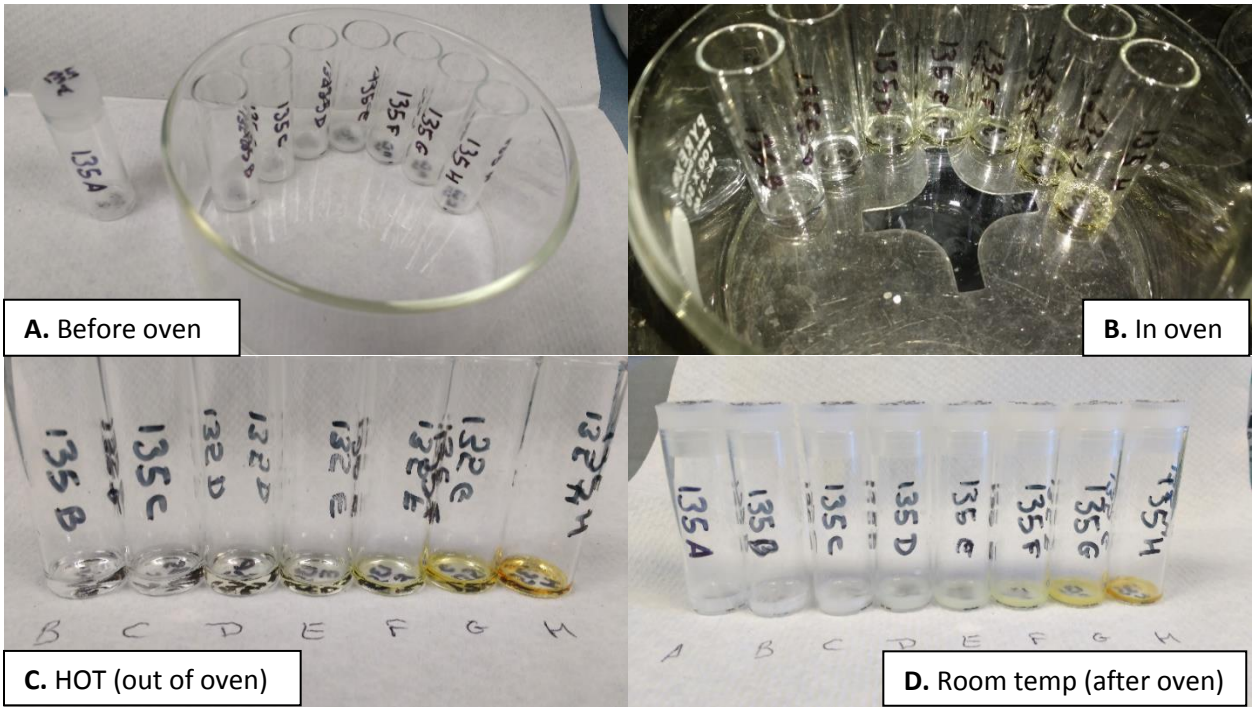


Figure S15. Samples of paraffin wax at various stages of the crosslinking process. (**A**) After mixing, before crosslinking; (**B**) Crosslinking in the oven at 110°C; (**C**) After crosslinking, just out of the oven; (**D**) After crosslinking, cooled down to room temperature.

Figure S16. Insoluble fraction from paraffin wax crosslinked with 200 wt% 3. The picture was taken several days after swelling: the solvent had evaporated, and the resin had de-swollen.

Complete procedure and GPC traces for the crosslinking of PDMS

Material used: 3 grades of hydroxyl-terminated PDMS (CAS 70131-67-8) were used:

- Sigma 481939: 25 cSt (Mn = 550 g/mol)
- Sigma 432989: 2550-3570 cSt, later called “3000 cSt”
- Sigma 432997: 18000–22000 cSt, later called “20000 cSt”

Procedure: 1.00 g of each grade was thoroughly mixed with 50 mg (96 µmol) of **3** (i.e. 5 wt% doping). Those mixtures were placed in an oven at 110°C for 16 h. After cooling down to room temperature, a sample of each mixture (10 mg*) was dissolved in THF (1 mL) for a nominal concentration of 10 g/L and analyzed by gel permeation chromatography (GPC) using THF as mobile phase. Control samples were prepared in an analogous manner without adding the crosslinker.

*NB: for 3000 cSt and 20000 cSt, 40 mg of the mixture was covered in THF (1 mL) for a nominal concentration of 40 g/L; the intensity of the signals has been divided by 4 to account for this excess.

Results:

- the sample based on 25 cSt PDMS remained a viscous liquid, whereas the 3000 and 20000 cSt samples underwent thermosetting.
- the 3000 and 20000 cSt samples were mostly insoluble in THF and swelled.
- GPC traces (viscosimeter and refractive index) show chain elongation for 25 cSt and insolubility for 3000 cSt and 20000 cSt when compared to the control samples.
- the good correlation of those signals with signals in the UV detector supports the grafting of the UV-active crosslinker onto UV-inactive PDMS.

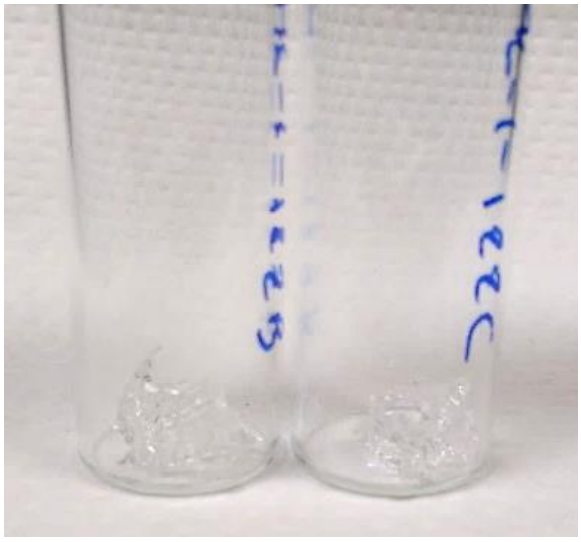


Figure S17. Swelled samples of PDMS 3000 cSt (left) and 20000 cSt (right) after crosslinking with 5wt% of bis-diazirine 3.

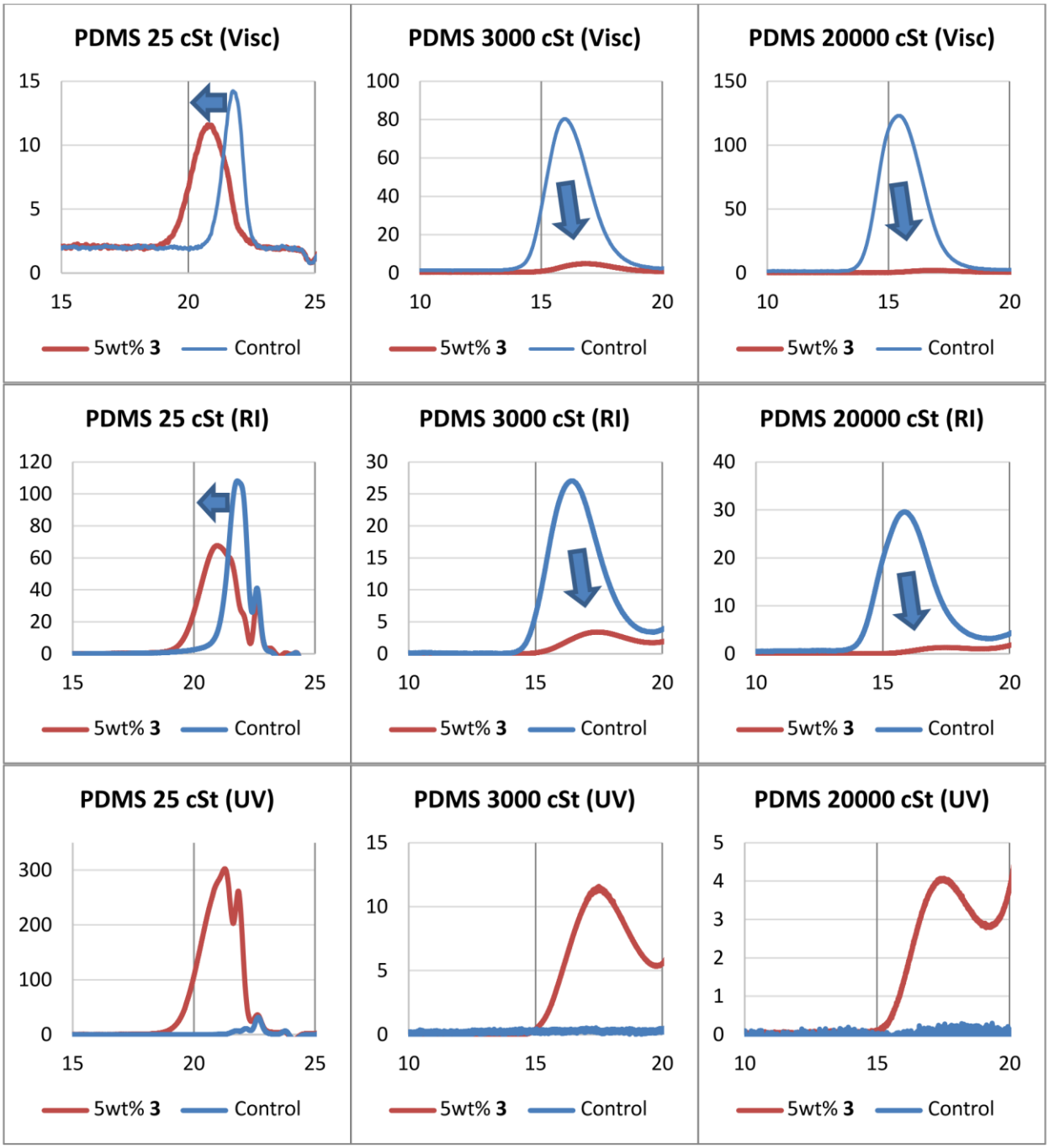


Figure S18. Gel Permeation Chromatography traces for PDMS samples (10 mg/L, see procedure) showing chain elongation or insolubility after crosslinking with 5wt% of bis-diazirine 3. *Top*: Viscosimeter; *Middle*: refractive index; *Bottom*: UV at 254 nm. Horizontal axis: retention time (min); Vertical axis (mV): viscosity, refractive index and absorbance at 254 nm, respectively.

Complete procedure and GPC traces for the crosslinking of PCL

Material used: 3 grades of polycaprolactone (CAS 24980-41-4) were used:

- Sigma 440752: average Mn = 10000 g/mol (average Mw = 14000 g/mol), later called 10K
- Sigma 704105: average Mn = 45000 g/mol, later called 45K
- Sigma 440744: average Mn = 80000 g/mol, later called 80K

Procedure: 1.00 g of each grade was melted (60°C) and thoroughly mixed with 50 mg (96 µmol) of **3** (*i.e.* 5 wt% doping). Those mixtures were placed in an oven at 110°C for 16 h. After cooling down to room temperature, a sample of each mixture (20 mg) was dissolved in THF (1 mL). This solution was diluted 10-fold with THF for a nominal concentration of 2 g/L and analyzed by gel permeation chromatography (GPC) using THF as mobile phase. Control samples were prepared in an analogous manner without adding the crosslinker.

Results:

- All samples were partly insoluble in THF and swelled.
- GPC traces (refractive index) show chain elongation for 10K and insolubility for 45K and 80K when compared to the control samples.
- the strong correlation of new, higher-MW, signals observed by refractive index with signals observed by UV detection supports the grafting of the UV-active crosslinker onto UV-inactive PCL.

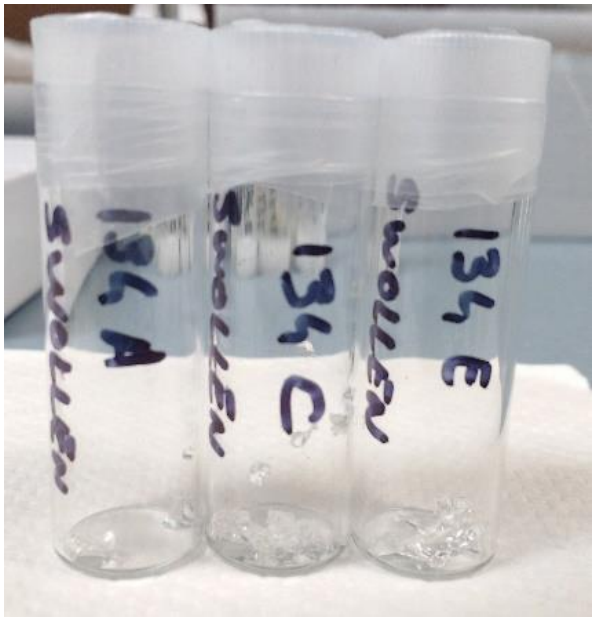


Figure S19. Swelled samples of PCL 10K (left), 45K (middle) and 80K (right) after crosslinking with 5wt% of bis-diazirine 3.

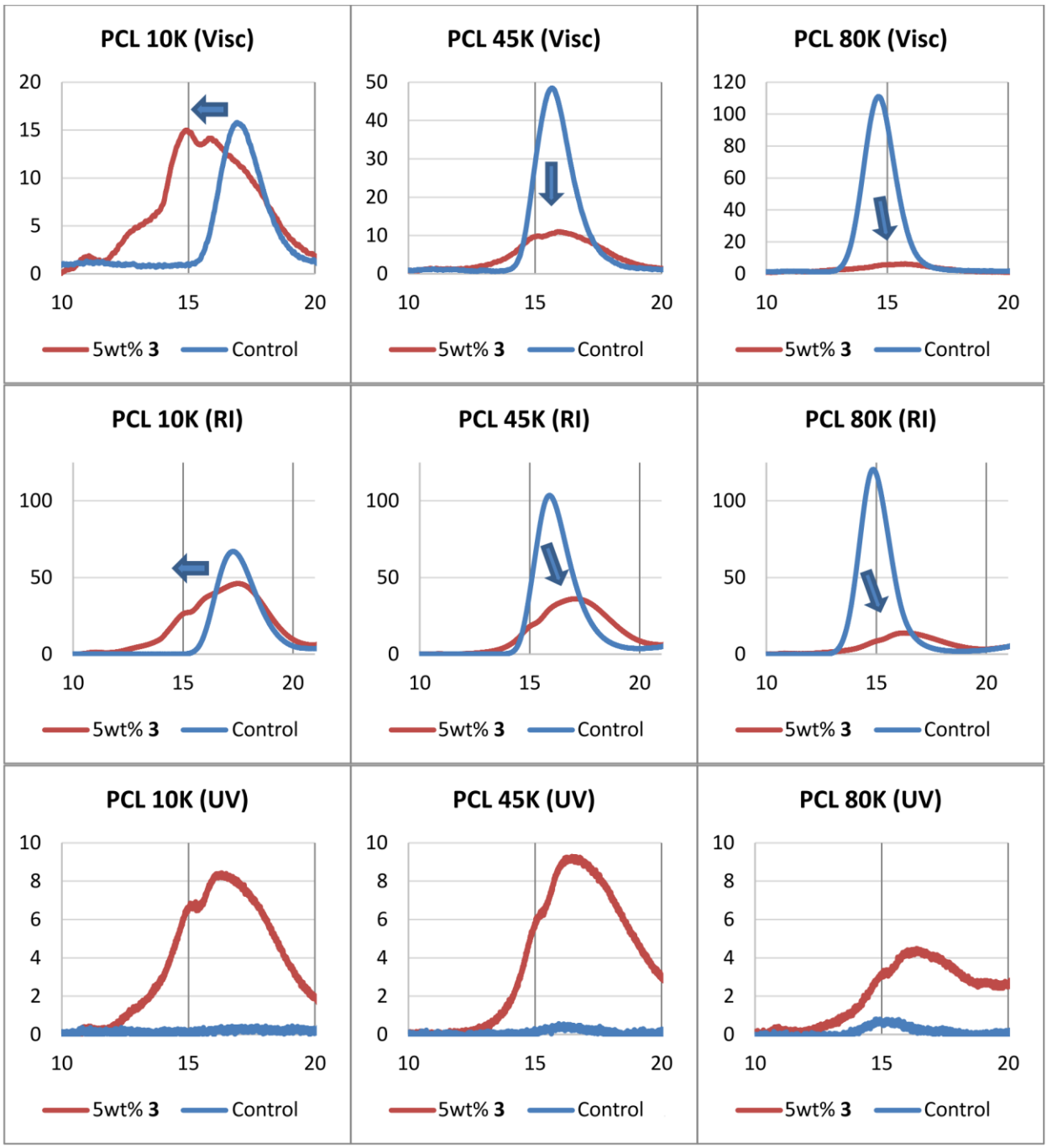


Figure S20. Gel Permeation Chromatography traces for PCL samples (2 mg/L, see procedure) showing chain elongation or insolubility after crosslinking with 5wt% of bis-diazirine 3. *Top*: viscosimeter; *Middle*: refractive index; *Bottom*: UV at 254 nm. Horizontal axis: retention time (min); Vertical axis (mV): viscosity, refractive index and absorbance at 254 nm, respectively.

Complete procedure for the photochemical crosslinking of PDMS

Material used: hydroxyl-terminated PDMS (CAS 70131-67-8) from Sigma-Aldrich, ref 432997 with a viscosity of 18000-22000 cSt.

To a vial containing the colorless liquid PDMS (500 mg) was added **3** (5 wt%, 25 mg, 48 µmol). After gently melting the crosslinker (slightly above 34°C), the mixture was manually stirred with a very thin needle to disperse the crosslinker. Sonication for 1 h removed bubbles created during the manual stirring. The resulting mixture remained a colorless liquid (Sample A).

Another vial containing the same PDMS (500 mg) was prepared (Sample B) as a control.

Both vials were placed in a Rayonet UV reactor and irradiated at 350 nm for 24 h.

Within 10 min of UV irradiation, sample A turned intense yellow, most likely because of diazoisomer formation. At the end of the irradiation process, the color had faded to provide an almost colorless product. The sample was slightly opaque and no longer liquid. In contrast to the analogous thermal crosslinking experiment, no bubbles were formed during the irradiation process.

The appearance of sample B did not change.

Samples A and B were flipped (see Movie S3) and were observed for 24 h (the movie covers the first ca. 10 min). The contents of sample B flowed downwards. The contents of sample A did not flow at all in 24 h (see below), confirming the crosslinked state of the substance.

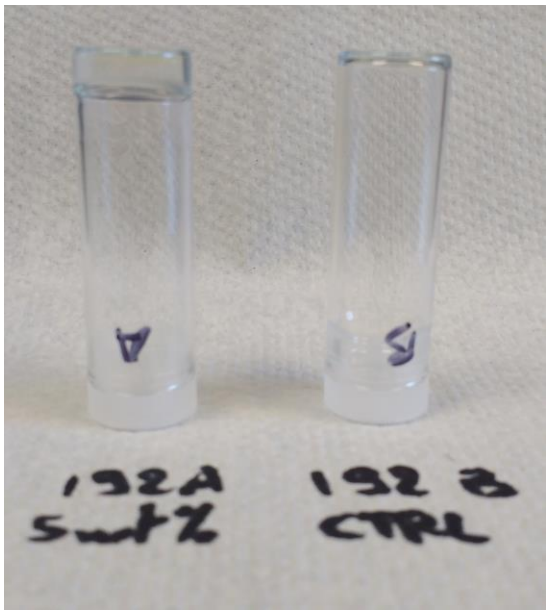


Figure S21. Vials containing either crosslinked or regular PDMS, 24 h after being flipped. Left: vial containing PDMS crosslinked with 5wt% **3**; Right: vial containing regular, non-crosslinked PDMS.

Procedure for the photochemical and thermal crosslinking of aqueous polyolefin dispersion

Discs of cured polyolefin containing increasing amounts of crosslinker **3** were prepared by slow, room-temperature curing of a water-based polyolefin dispersion (HYPOD 8501). Those discs were photochemically crosslinked under 350 nm UV light for 48 h. Alternatively, thermal crosslinking was performed by placing an identical set of discs in an oven at 110°C for 18 h.

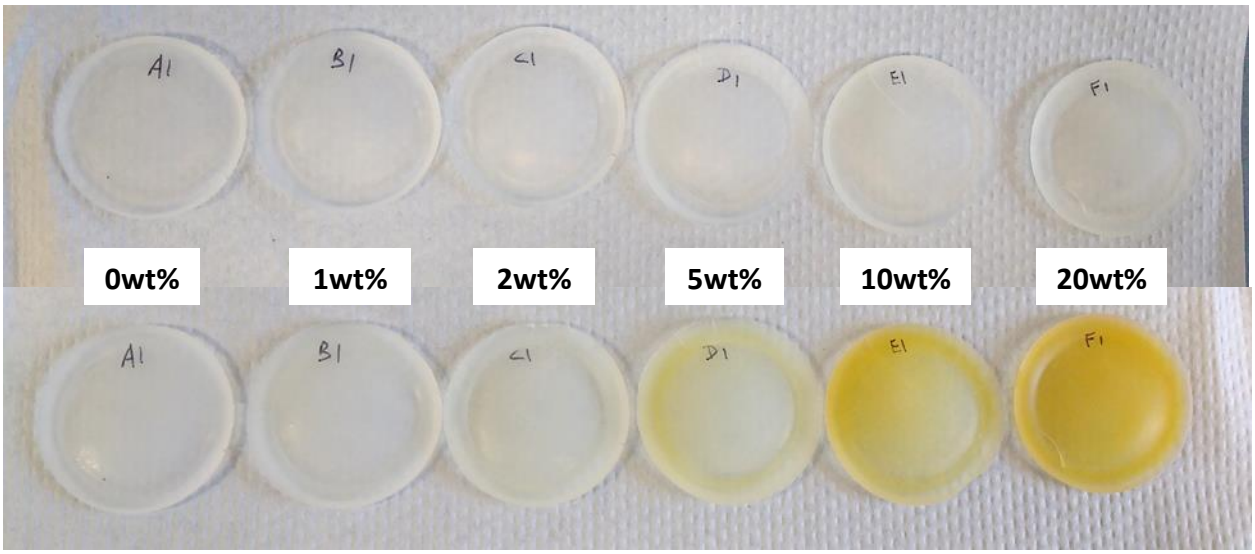


Figure S22. Photochemical crosslinking of polyolefin HYPOD 8501. Top: Cured HYPOD 8501 discs, doped with increasing amounts of **3**; Bottom: Photochemically crosslinked HYPOD 8501 discs.

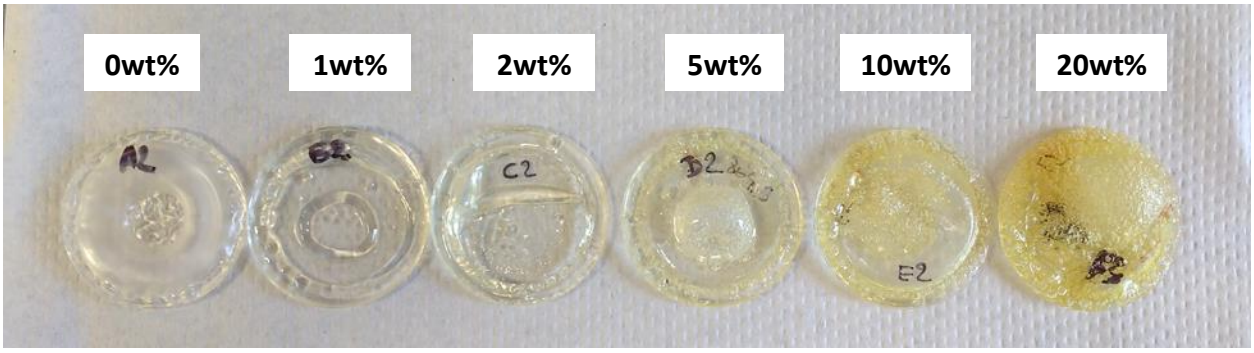


Figure S23. Thermal crosslinking of polyolefin HYPOD 8501.

Extensive bubble formation was observed for the thermally cured samples, but not for the photochemically cured samples.

In general, bubble formation was not observed during thermal crosslinking of substrates that were solid at the temperature employed for the crosslinking reaction.

Complete procedure and absorbance measurements for the crosslinking of PVA

Polyvinyl alcohol (PVA, CAS 9002-89-5, Mw = 89,000 to 98,000 g/mol) was mixed with increasing amounts of bis-diazirine **3** (1wt% to 100wt%). This was done by suspending powdered PVA in an appropriate volume of a 12 mg/mL solution of **3** in pentane and letting the solvent evaporate. The dried mixtures, along with a pure PVA sample used as a control, were baked in an oven at 115°C for 14 h. A sample of each mixture (100 mg) was placed in a vial containing 10 mL of water. The contents of the vials were then stirred at 75°C for 16 h to allow dissolution of the soluble fractions. Optical density of the resulting dispersions was then measured between 400-800 nm.

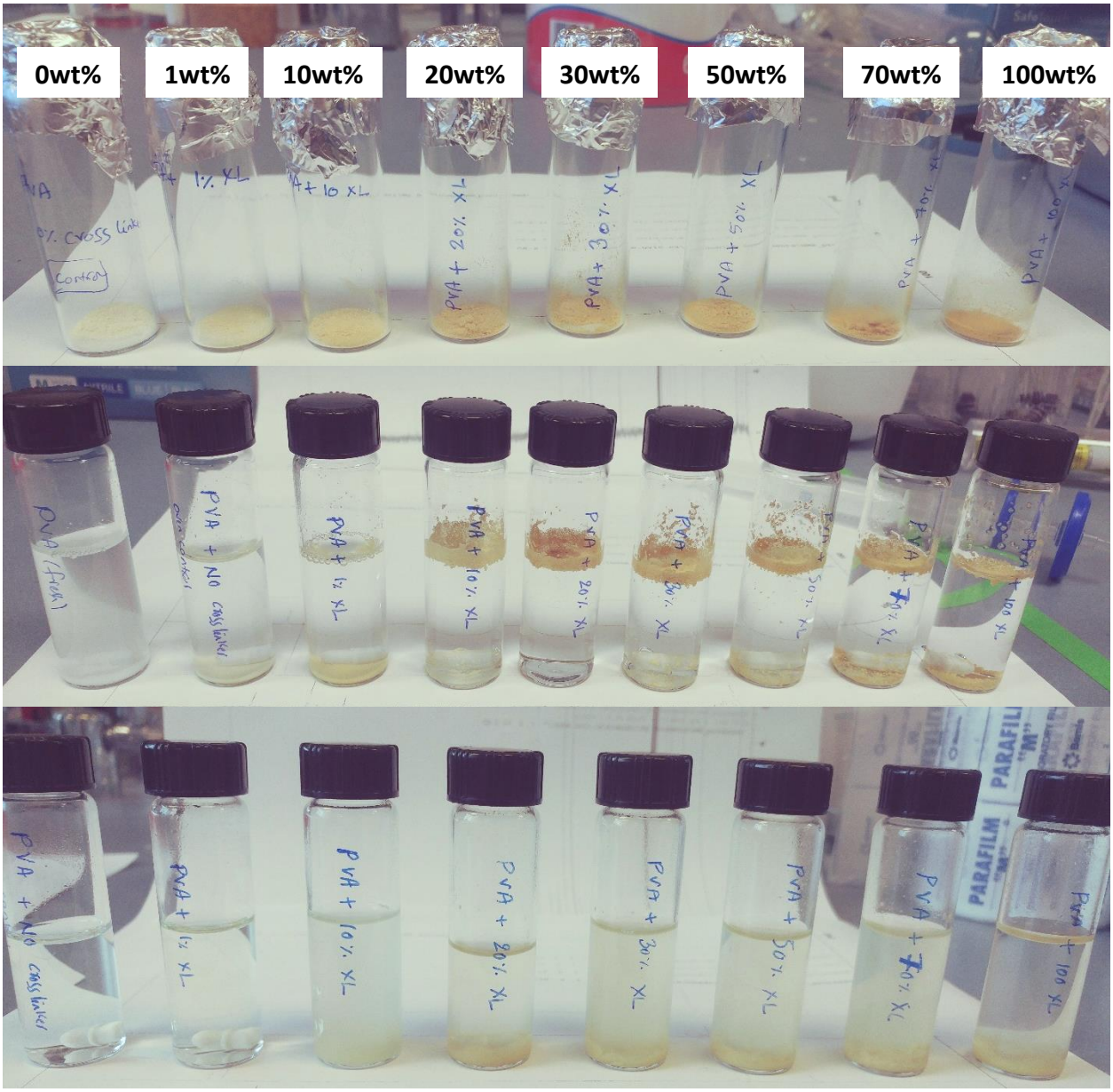


Figure S24. Crosslinking of PVA with increasing amounts of 3. *Top*: After crosslinking; *Middle*: After addition of the powders to water, no stirring; *Bottom*: After stirring for 16 h at 75°C.

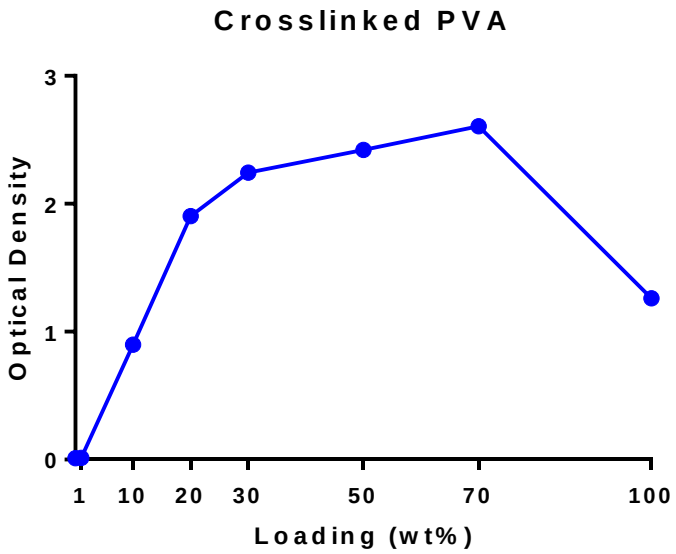


Figure S25. Optical density at 600 nm of aqueous dispersions of PVA crosslinked with 3.

Complete procedure for the crosslinking of low molecular weight polypropylene

Material used: fine grain low-melting point polypropylene (Licocene® PP 6102 from Clariant)

Procedure: 5 glass vials (samples A-E) containing polypropylene (PP) (100 mg) covered with toluene (300 µL) were capped and heated at 85°C until near- or complete dissolution of PP. Solutions of **3** in toluene (0, 25, 100, 250 and 500 g/L, 200 µL each) were added to samples A-E, which were then briefly and gently mixed before being placed in an ice bath. Upon cooling, the solutions congealed into PP/toluene gels doped with increasing amounts of crosslinker **3** (none, 5 mg, 20 mg, 50 mg and 100 mg, respectively). The vials were then capped with septa and placed under high vacuum to remove toluene. Upon drying, the gels turned into white solids. Overall, this procedure allowed the homogeneous dispersion of **3** into PP matrices.

Table S3. Composition of polypropylene samples doped with increasing amounts of 3.

Sample	Loading (wt%)	Mass PP (mg)	Mass 3 (mg)	Total mass (mg)
A	0	100	0	100
B	5	100	5	105
C	20	100	20	120
D	50	100	50	150
E	100	100	100	200

All 5 samples were placed in a heat block and crosslinked at 115°C for 1 h. After cooling, a small portion (4-8 mg) was taken from each vial for DSC analysis.

Solubility test: The remaining sample was covered with toluene (1 mL) and heated at 85°C for 1 h. Samples A-C dissolved, but samples D-E were insoluble and afforded swollen gels (see pictures).

DSC analysis: Samples were placed in Tzero hermetic aluminum pans and analyzed on the following cycle under a flow of nitrogen (50 mL/min) at 5°C/min: –90°C → 250°C → –90°C → 250°C. The values for T_g, T_m and fusion enthalpy were recorded from the second heating phase.

Table S4. Evolution of thermal properties of low molecular weight polypropylene crosslinked at increasing degrees.

Sample	Loading	T_g (°C)	T_m (°C)	Fusion enthalpy (J/g)
A	0wt%	–26°C	130°C	49.3
B	5wt%	–24°C	127°C	45.2
C	20wt%	–15°C	128°C	36.5
D	50wt%	–8°C	130°C	24.1
E	100wt%	–1°C	132°C	14.7

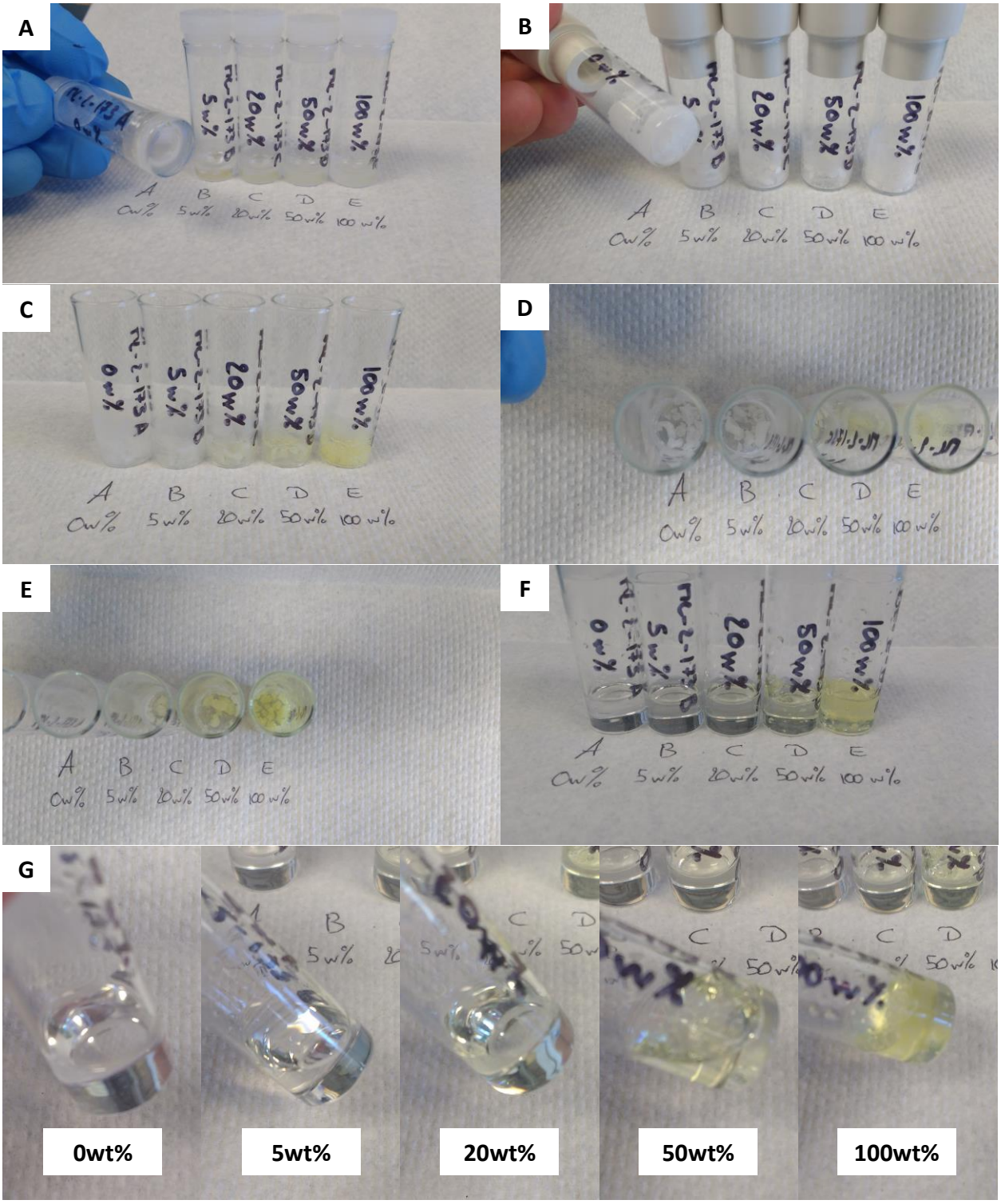


Figure S26. Samples of polypropylene at various stages of the crosslinking process. (**A**) Loaded gels; (**B**) After drying under high vacuum; (**C**)-(**E**) After crosslinking; (**F**)-(**G**) Solubility test: samples were covered with toluene (1 mL) and heated at 85°C; samples with higher crosslinking density (50-100 wt%) were not soluble anymore.

Complete procedure for the crosslinking of higher molecular weight polypropylene

Material used: polypropylene (Sigma-Aldrich, ref 428116, isotactic, average M_w ~12000, average M_n ~5000, m.p. = 157 °C, CAS 9003-07-0)

Procedure: 5 glass vials (samples A-E) containing polypropylene (PP) (100 mg) covered with toluene (1 mL) were heated to provide the PP in gel form. After allowing them to cool down by ca. 10°C, solutions of **3** in toluene (0, 50, 200, 500 and 1000 g/L, around 200 µL each) were added to samples A-E. All the samples were briefly and gently mixed before being capped with septa and placed under high vacuum to remove toluene. Upon drying, the gels turned into white solids. Overall, this procedure allowed the homogenous dispersion of **3** into PP matrices.

Table S5. Composition of polypropylene samples doped with increasing amounts of 3.

Sample	Loading (wt%)	Mass PP (mg)	Mass 3 (mg)	Total mass (mg)
A	0	100	0	100
B	5	100	5	105
C	20	100	20	120
D	50	100	50	150
E	100	100	100	200

All 5 samples were crosslinked at 105°C for 1 h. After cooling, a small portion (3-6 mg) was taken from each vial for DSC analysis.

DSC analysis: Samples were placed in Tzero hermetic aluminum pans and analyzed on the following cycle under a flow of nitrogen (50 mL/min) at 5°C/min: 40°C → 250°C → -90°C → 250°C. The values for T_g, T_m and fusion enthalpy were recorded from the second heating phase.

Table S6. Evolution of thermal properties of polypropylene crosslinked at increasing degrees.

Sample	Loading (wt%)	T_g (°C)	T_m (°C)	Fusion enthalpy (J/g)
A	0	-23.4	154.9	91.7
B	5	-12.9	153.6	87.8
C	20	-11.0	151.9	79.3
D	50	16.5	144.2	62.8
E	100	-1.69*	n/a*	0*

* at 100 wt% loading, no melting point was detected. It is also unclear if the reported T_g value for this sample is still relevant.

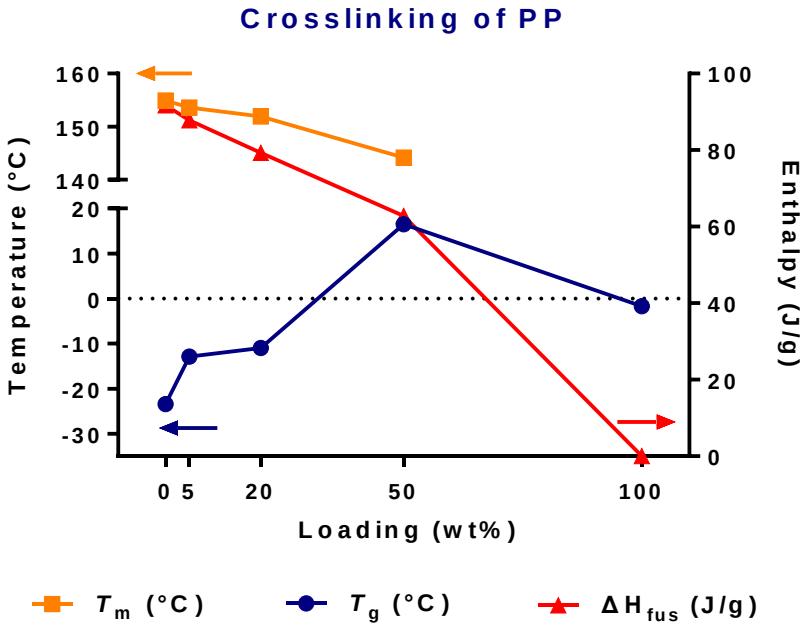


Figure S27. Crosslinking of polypropylene increases the glass transition temperature (T_g) and decreases the fusion enthalpy (ΔH_{fus}).

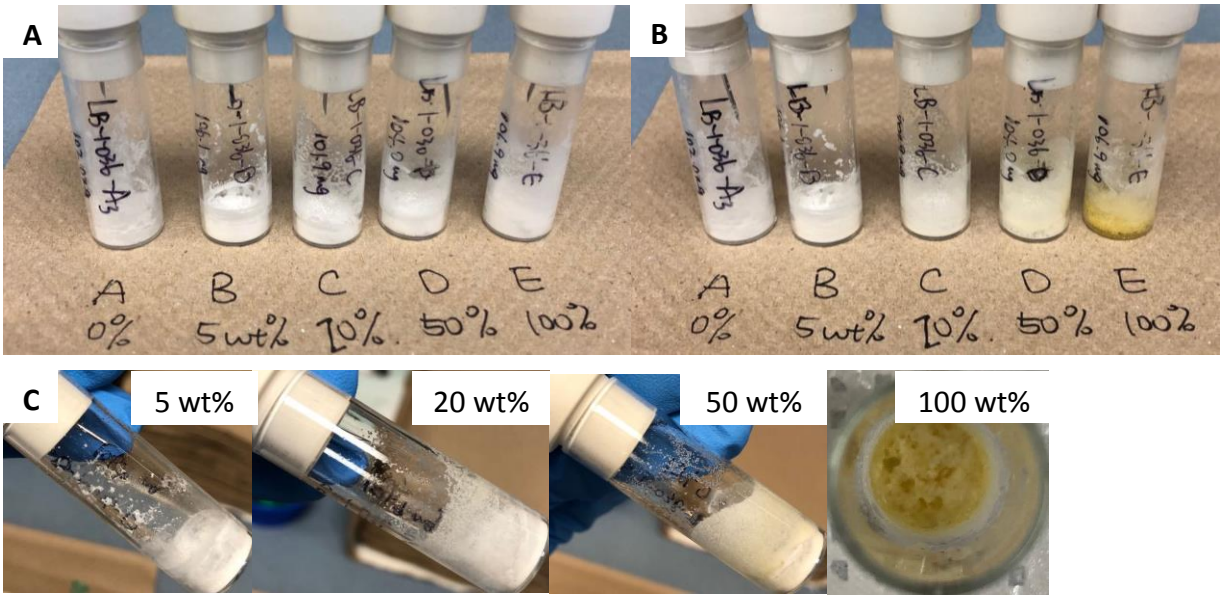


Figure S28. Samples of polypropylene at various stages of crosslinking process. (**A**) After drying under high vacuum; (**B**)-(**C**) After crosslinking.

Complete procedure for the crosslinking of polyethylene

Material used: polyethylene (Sigma-Aldrich, ref 427772, average M_w ~4000, average M_n ~1700, m.p. = 92 °C, CAS 9002-88-4).

Procedure: 5 glass vials (samples A-E) containing polyethylene (PE) (100 mg) covered with toluene (200 µL) were capped and heated at 90°C until near- or complete dissolution of PE. Solutions of **3** in toluene (0, 50, 200, 500 and 1000 g/L, 100 µL each) were added to samples A-E, which were then briefly and gently mixed before capped with septa and placed under high vacuum to remove toluene. Upon drying, the gels turned into white solids. Overall, this procedure allowed the homogenous dispersion of **3** into PE matrices.

Table S7. Composition of polyethylene samples doped with increasing amounts of 3.

Sample	Loading (wt%)	Mass PE (mg)	Mass 3 (mg)	Total mass (mg)
A	0	100	0	100
B	5	100	5	105
C	20	100	20	120
D	50	100	50	150
E	100	100	100	200

All 5 samples were placed in a heat block and crosslinked at 110°C for 1 h. After cooling, a small portion (3-6 mg) was taken from each vial for DSC analysis.

DSC analysis: Samples were placed in Tzero hermetic aluminum pans and analyzed on the following cycle under a flow of nitrogen (50 mL/min) at 5°C/min: –90°C → 250°C → –90°C → 250°C. The values for T_m and fusion enthalpy were recorded from the second heating phase.

Table S8. Evolution of thermal properties of polyethylene crosslinked at increasing degrees.

Sample	Loading (wt%)	T_m (°C)	Fusion enthalpy (J/g)
A	0	105.00	139.82
B	5	102.96	125.31
C	20	87.85	99.86
D	50	87.06	87.57
E	100	85.45	76.28

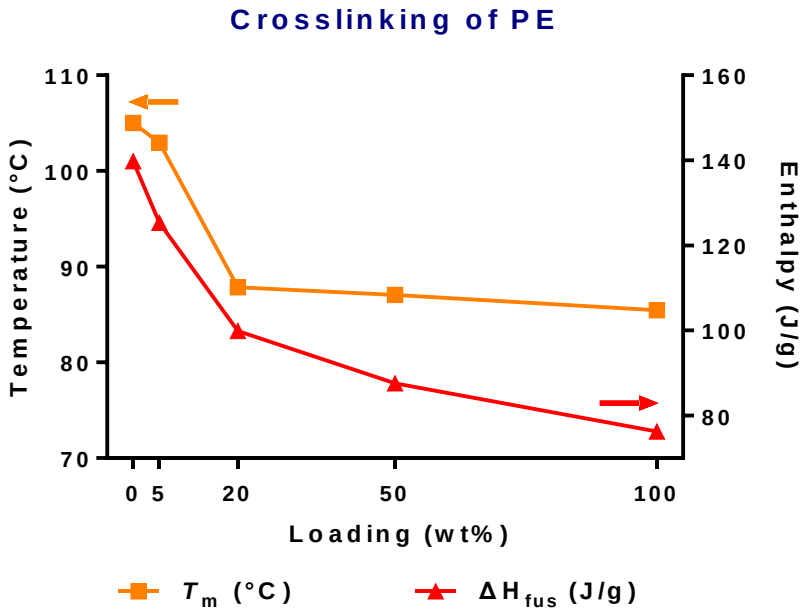


Figure S29. Crosslinking of polyethylene decreases the fusion enthalpy (ΔH_{fus}).

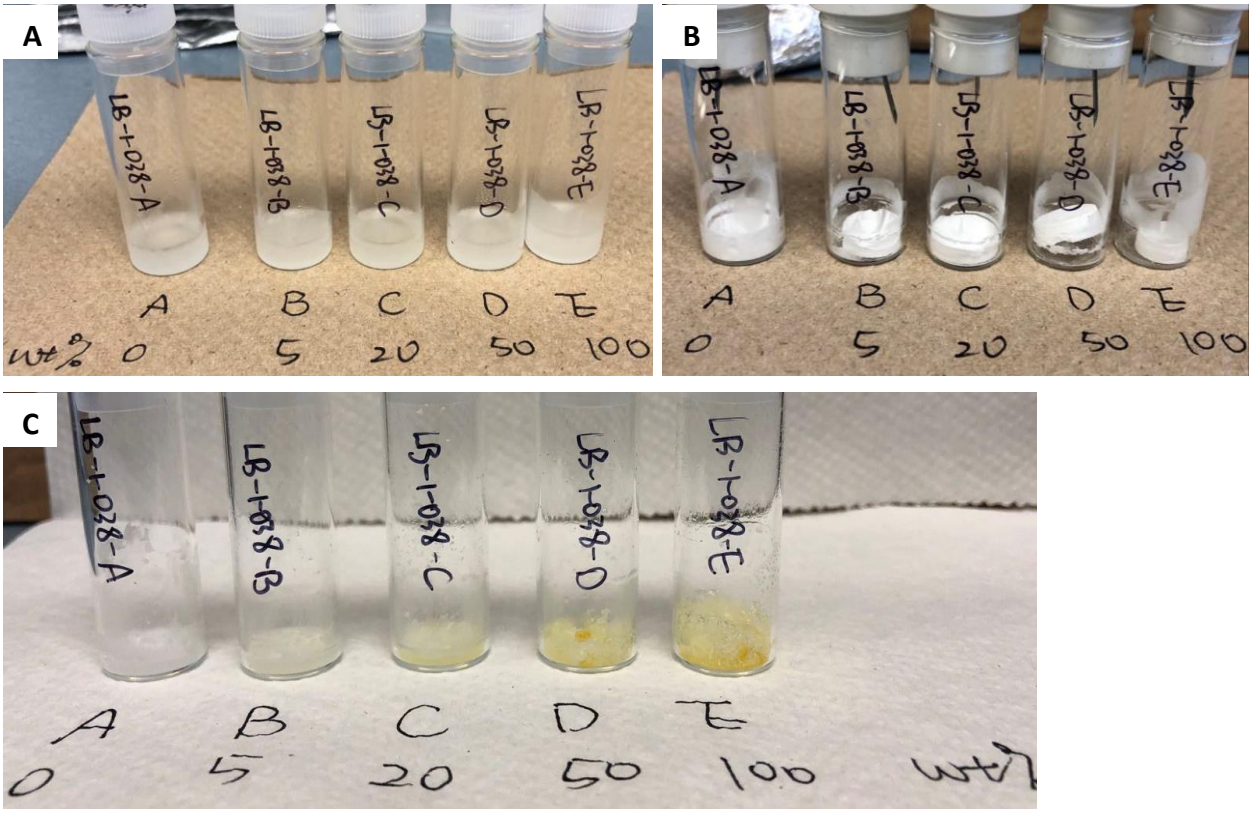


Figure S30. Samples of polyethylene at various stages of crosslinking process. (**A**) Loaded gels; (**B**) After drying under high vacuum; (**C**) After crosslinking.

Complete procedure for the crosslinking of polystyrene

Material used: polystyrene (Sigma-Aldrich, ref 331651, average M_w 35000, CAS 9003-53-6)

Procedure: 5 glass vials (samples A-E) containing polystyrene (PS) (50 mg) and crosslinker **3** (0, 2.5, 10, 25, 50 mg) covered with tetrahydrofuran (THF) (100 µL) were capped and sonicated until the mixture was a clear solution. All samples were left overnight to naturally evaporate THF first. Then the five vials were capped with septa and placed under high vacuum to remove residual THF. Overall, this procedure allowed the homogenous dispersion of **3** into PS matrices.

Table S9. Composition of polystyrene samples doped with increasing amounts of 3.

Sample	Loading (wt%)	Mass PS (mg)	Mass 3 (mg)	Total mass (mg)
A2	0	50	0	50
B2	5	50	2.5	52.5
C2	20	50	10	60
D2	50	50	25	75
E2	100	50	50	100

All 5 samples were placed in a heat block and crosslinked at 115°C for 3 h. After cooling, a small portion (3-6 mg) was taken from each vial for DSC analysis. Another sample of each mixture (5 mg) was dissolved in THF (1 mL) for a nominal concentration of 5 g/L and analyzed by gel permeation chromatography (GPC) using THF with 0.1 % (v/v) triethylamine as mobile phase. A control sample was prepared in an analogue manner without adding the crosslinker.

DSC analysis: The samples were placed in Tzero hermetic aluminum pans and analyzed on the following cycle under a flow of nitrogen (50 mL/min) at 5°C/min: 0°C → 150°C → 0°C → 150°C. The values for T_g were recorded from the second heating phase.

GPC analysis results:

- The sample D2 and E2 were not fully dissolved in THF.
- GPC traces (refractive index, viscometer and right-angle light scattering detectors) show decreased solubility for D2 and E2 samples when compared to the control samples.

Table S10. Evolution of glass transition temperature of polystyrene crosslinked at increasing degrees.

Sample	Loading (wt%)	T_g (°C)
A2	0	56.23
B2	5	52.23
C2	20	62.01
D2	50	68.32
E2	100	67.95

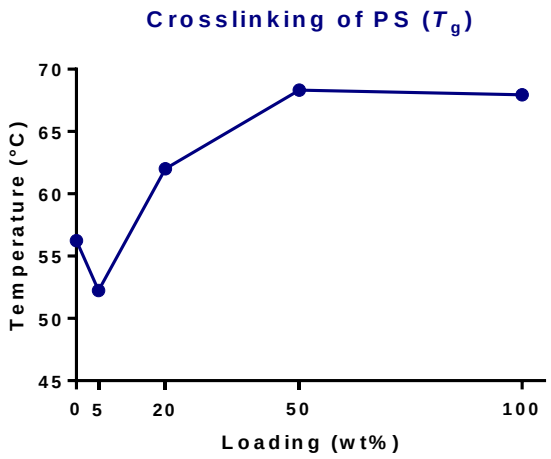


Figure S31. Crosslinking of polystyrene increases the glass transition temperature (T_g).

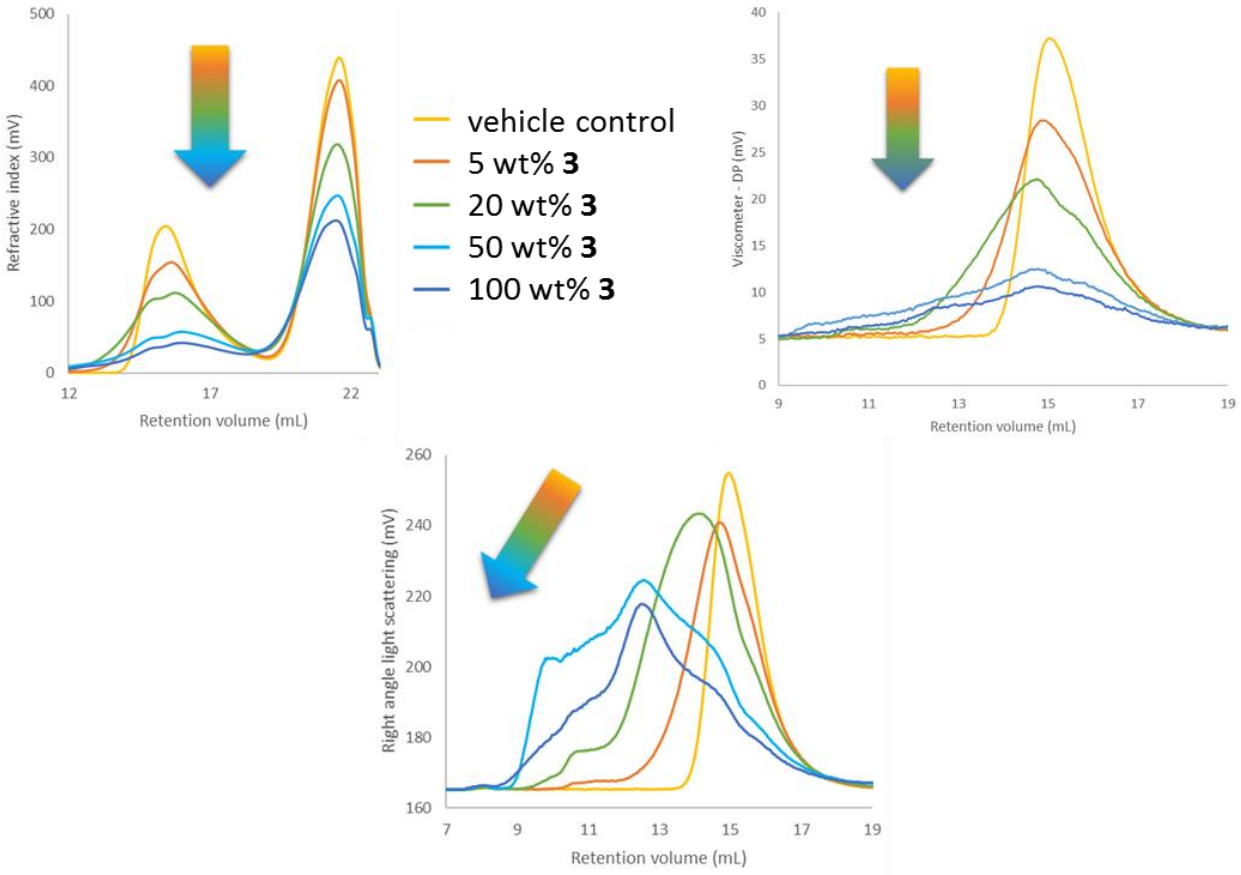


Figure S32. GPC analysis of polystyrene crosslinked to various degrees. Three detectors were used. Top left: refractive index; Top right: Viscometer; Bottom: right-angle light scattering (RALS). All three show decreased intensity of the signal at higher crosslinker loading. The viscometer and RALS also show broadening of the peaks toward higher molecular weights (*i.e.* smaller retention volume).

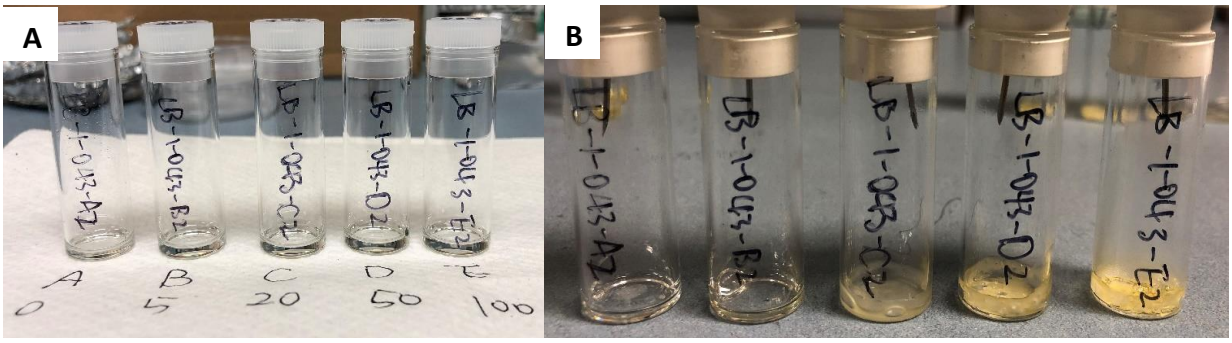


Figure S33. Samples of polystyrene at various stages of the crosslinking process. (**A**) Loaded gels; (**B**) After crosslinking.

Complete procedure for the crosslinking of cis-polyisoprene

Material used: cis-polyisoprene (Sigma-Aldrich, ref 431265, average M_w ~35000, CAS 104389-31-3)

Procedure: 5 glass vials (samples A-E) containing polyisoprene (PI) (50 mg) and crosslinker **3** (0, 2.5, 10, 25, 50 mg) covered with THF (200 µL) were capped and sonicated until the mixture was a clear solution. All samples were capped with septa and placed under high vacuum to remove THF. Overall, this procedure allowed the homogenous dispersion of **3** into PI matrices.

Table S11. Composition of polyisoprene samples doped with increasing amounts of 3.

Sample	Loading (wt%)	Mass PI (mg)	Mass 3 (mg)	Total mass (mg)
A	0	50	0	50
B	5	50	2.5	52.5
C	20	50	10	60
D	50	50	25	75
E	100	50	50	100

All 5 samples were placed in a heat block and crosslinked at 115°C for 3 h. After cooling, a small portion (3-6 mg) was taken from each vial for DSC analysis. Another sample of each mixture (5 mg) was dissolved in THF (1 mL) for a nominal concentration of 5 g/L and analyzed by gel permeation chromatography (GPC) using THF with 0.1 % (v/v) triethylamine as mobile phase. A control sample was prepared in an analogue manner without adding the crosslinker.

DSC analysis: The samples were placed in Tzero hermetic aluminum pans and analyzed on the following cycle under a flow of nitrogen (50 mL/min) at 5°C/min: –90°C → 50°C → –90°C → 50°C. The values for T_g were recorded from the second heating phase.

GPC analysis results:

- The samples B, C, D and E were mostly insoluble in THF and swelled.
- GPC traces (refractive index, viscometer, right angle light scattering detectors and low angle light scattering detectors) show decreased solubility for B-E samples when compared to the control samples.

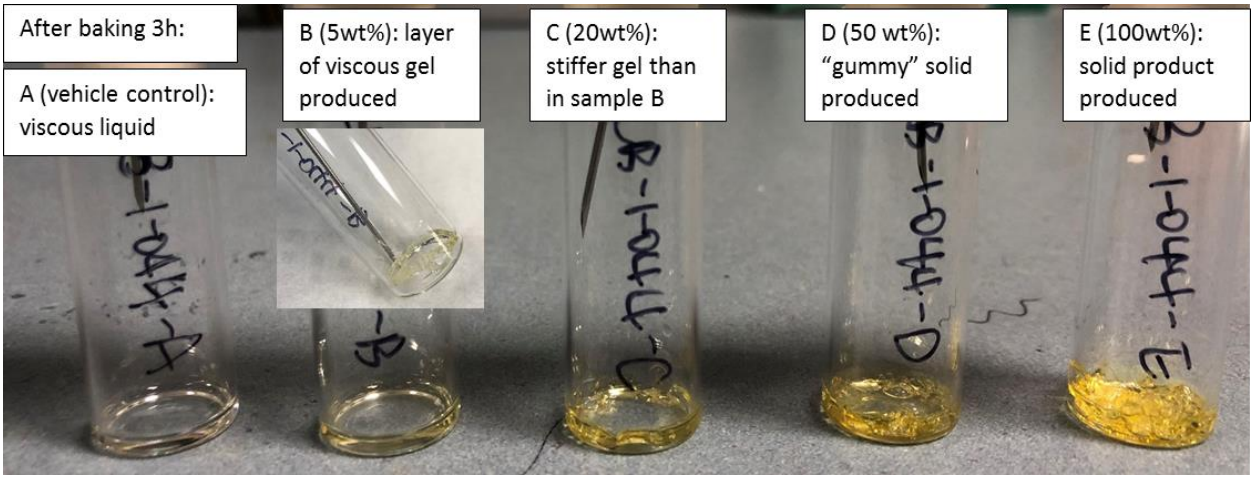


Figure S34. Physical changes induced in polyisoprene upon crosslinking with various concentrations of crosslinker 3.

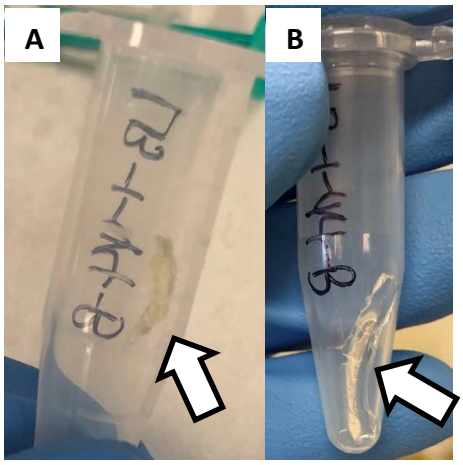


Figure S35. Sample of polyisoprene (ca. 5 mg) crosslinked with 5 wt% 3 to produce an insoluble gel that swells in THF. (**A**) before adding THF; (**B**) After suspension in THF and removal of supernatant**.**

Table S12. Evolution of glass transition temperature for polystyrene crosslinked with varying concentrations of crosslinker 3.

Sample	Loading (wt%)	T_g (°C)
A	0	-61.90
B	5	-58.71
C	20	-54.40
D	50	-52.82
E	100	-54.90

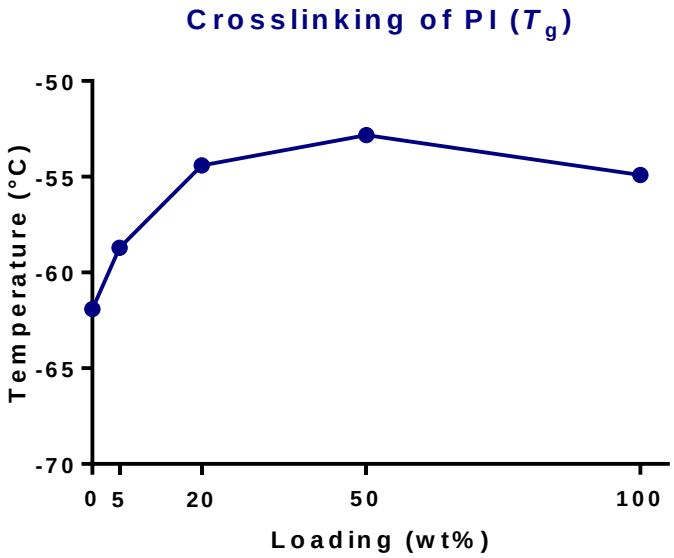


Figure S36. Crosslinking of polyisoprene increases the glass transition temperature (T_g).

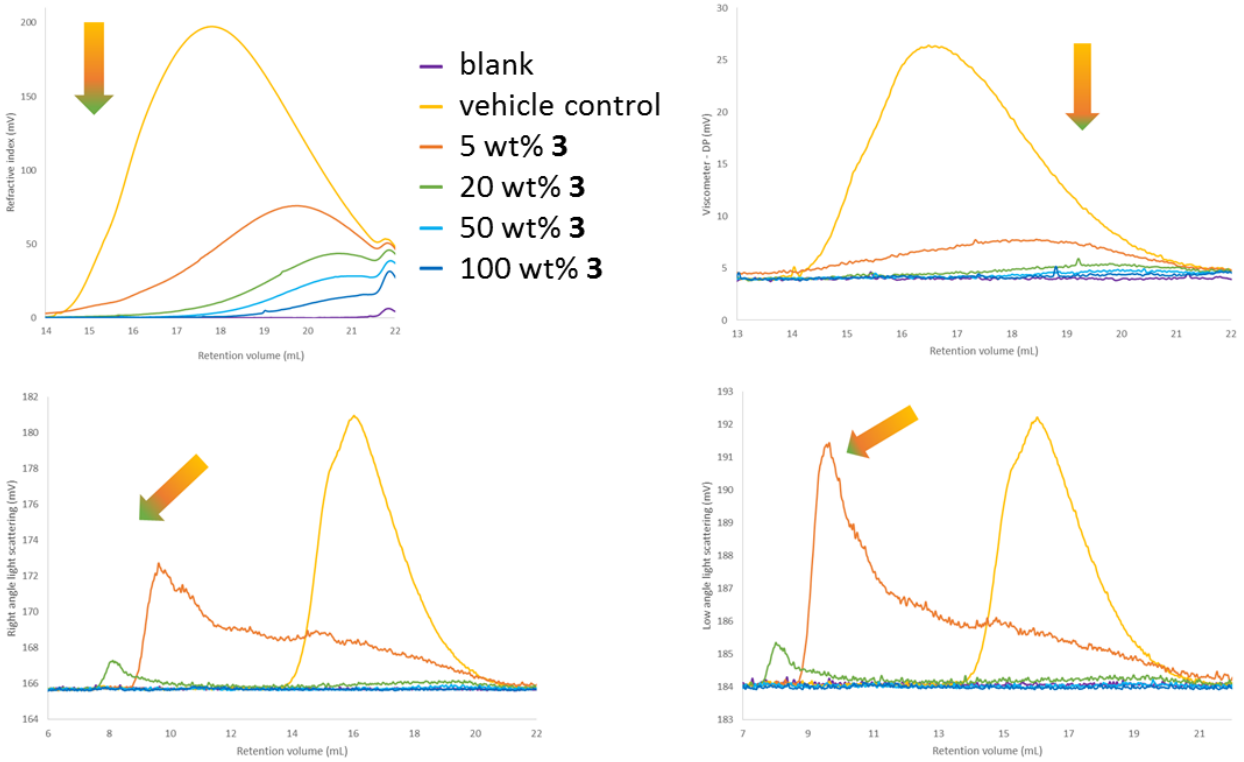


Figure S37. GPC analysis of polyisoprene crosslinked to various degrees. Four detectors were used. Top left: refractive index; Top right: Viscometer; Bottom left: right-angle light scattering (RALS); Bottom right: low-angle light scattering (LALS). All four show decreased intensity of the signal at higher crosslinker loading. The RALS and LALS also show shifting of the peak toward higher molecular weights (*i.e.* smaller retention volume).

Mode of failure for adhered HDPE bars during lap-shear experiment

After performing the lap-shear experiment on adhered bars of HDPE, the surface of the samples retained a yellow substance (presumably crosslinked **3** and decomposition products thereof) on both sides of the adhesion surface; more material was visible close to the edges. For the most part of the glued surfaces, the yellow layer was not visible, so an optical profilometer was used to characterize surface roughness in different regions of the two pieces of a lap shear sample. Control profiles were measured at untreated regions.

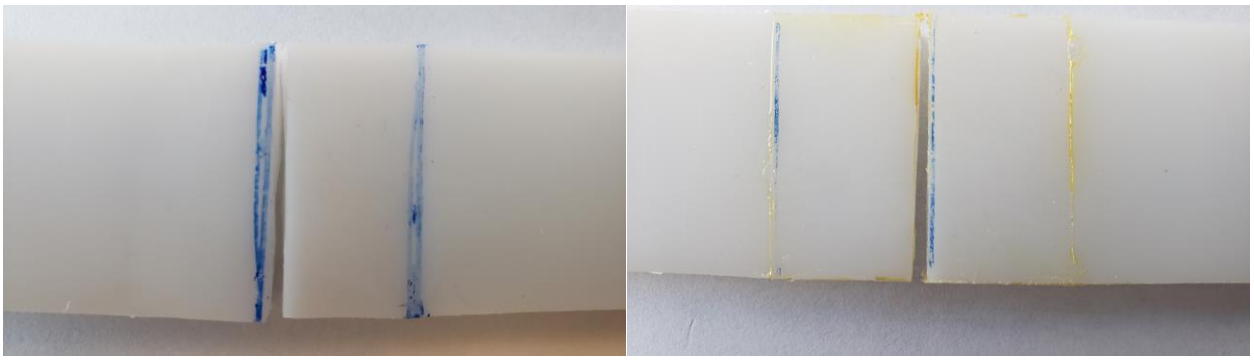


Figure S38. HDPE samples after lap-shear test. Left: control sample; right: adhered sample (with 10 mg **3**) showing residual yellow substance on both adhesion surfaces.

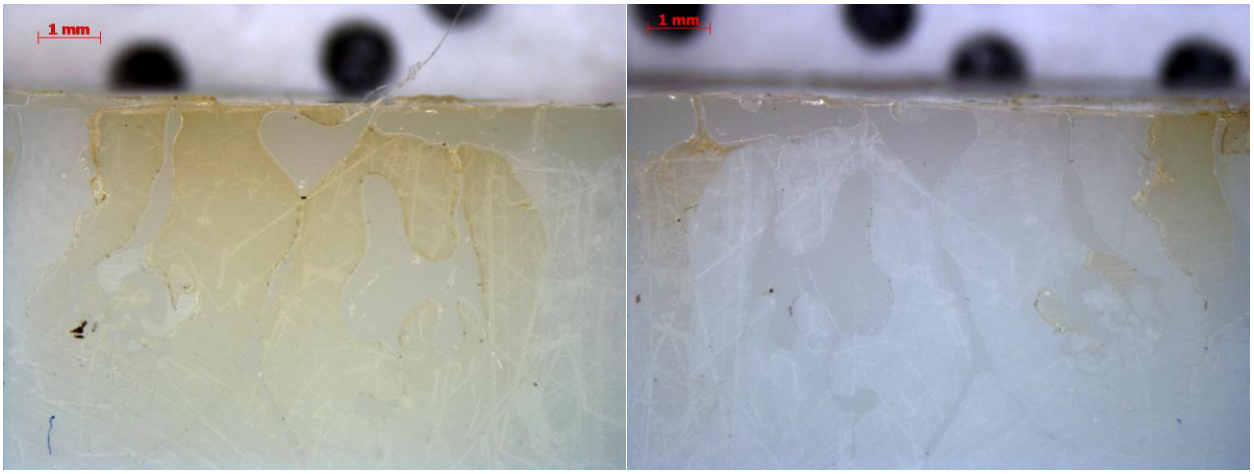


Figure S39. Optical microscope images of both adhesion surface of on sample.

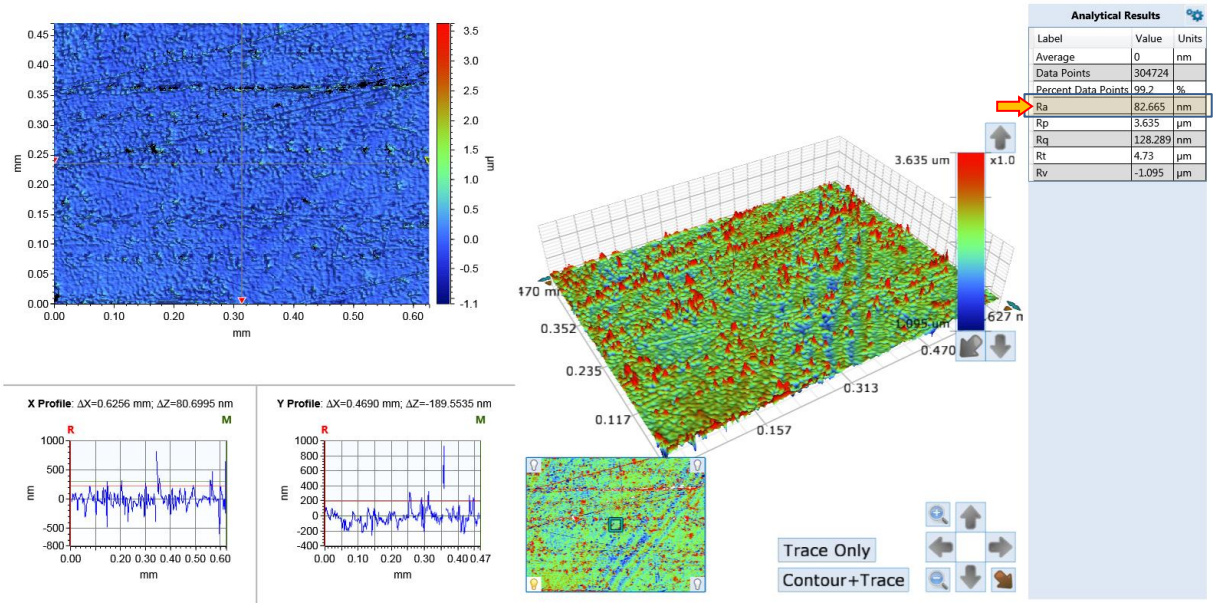


Figure S40. Optical profilometer characterization of the surface of a control lap-shear sample. The R_a value in the table indicates the average surface roughness (in nm).

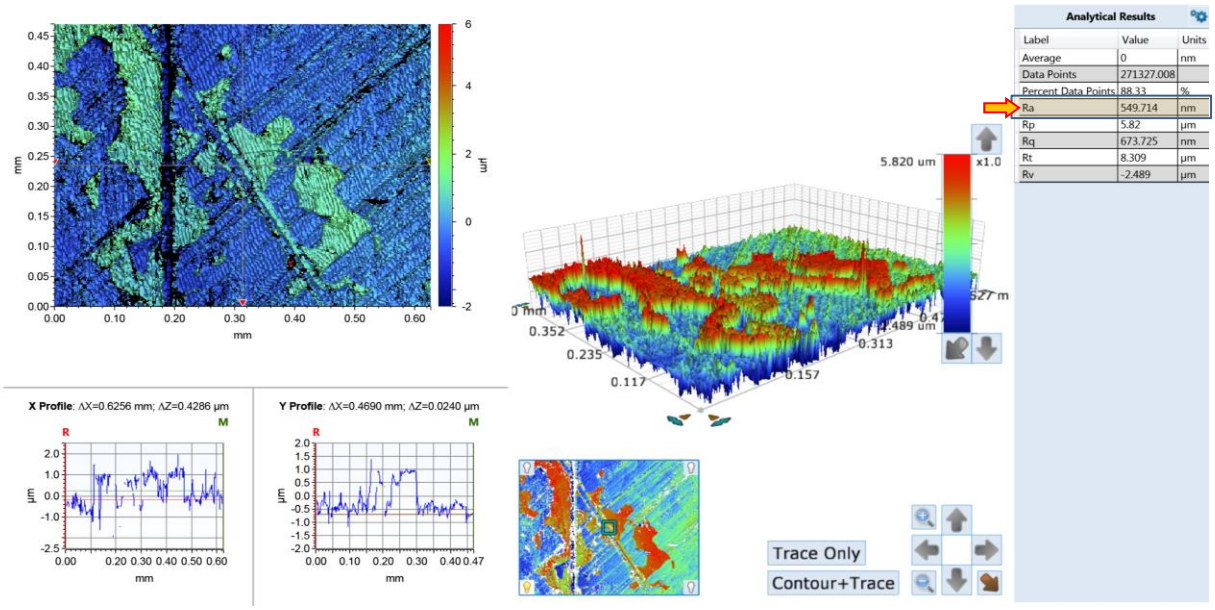


Figure S41. Optical profilometer characterization of the surface of an adhered lap-shear sample. The R_a value in the table indicates the average surface roughness (in nm).

The roughness on adhered surfaces are different from non-adhered regions (control) and traces of bonding can be found on both surfaces. This is consistent with a cohesive failure mode.

Strengthening of UHMWPE fabric

Material used: two grades of fabric made of woven fibers of ultra-high molecular weight polyethylene (UHMWPE), characterized by their area density: 75 g/m² and 90 g/m².

Procedure: the fabric was impregnated with **3** by placing a piece of desired dimensions into a close-fitting aluminum pan filled with a solution of the crosslinker in pentane at the appropriate concentration. This concentration was calculated to impregnate the fabric with 1 wt% or 10 wt% of crosslinker, but in order to compensate for crosslinker deposited on the sides and bottom of the aluminum pan, an extra 0.25 wt% and 2.5 wt% (resp.) was added: for a given piece of fabric, the amount of crosslinker in the solution was 1.25 wt% or 12.5 wt% (resp.) of its mass. For instance, a 10cm x 10cm piece of 75 g/m² fabric (weight = 750 mg) was impregnated using a solution containing 93.7 mg (12.5 wt%) crosslinker, in order to provide a 10 wt%-impregnated sheet. The bath was covered with aluminum foil and left to sit at room temperature for 1 h. Then the cover was removed to allow the pentane to evaporate in a well-ventilated fume hood. This generally occurred within 20 min. After evaporation, the impregnated sheets of fabric were wrapped in aluminum foil and placed in an oven at 110°C for 4 h. If not covered by aluminum, the crosslinker could evaporate (loss of the impregnated mass) before reacting at high temperature, most likely due to increased surface exposure.

To study the impact of the pentane bath and oven baking, “vehicle control” samples were prepared following the same procedure, but without adding crosslinker in the pentane bath.

To distinguish the impact of added weight versus actual crosslinking, a set of “molecular control” samples (based on the 90 g/m² fabric) was prepared following the same procedure but with the crosslinker replaced by the corresponding molecular control (**7**) bearing only one diazirine moiety.

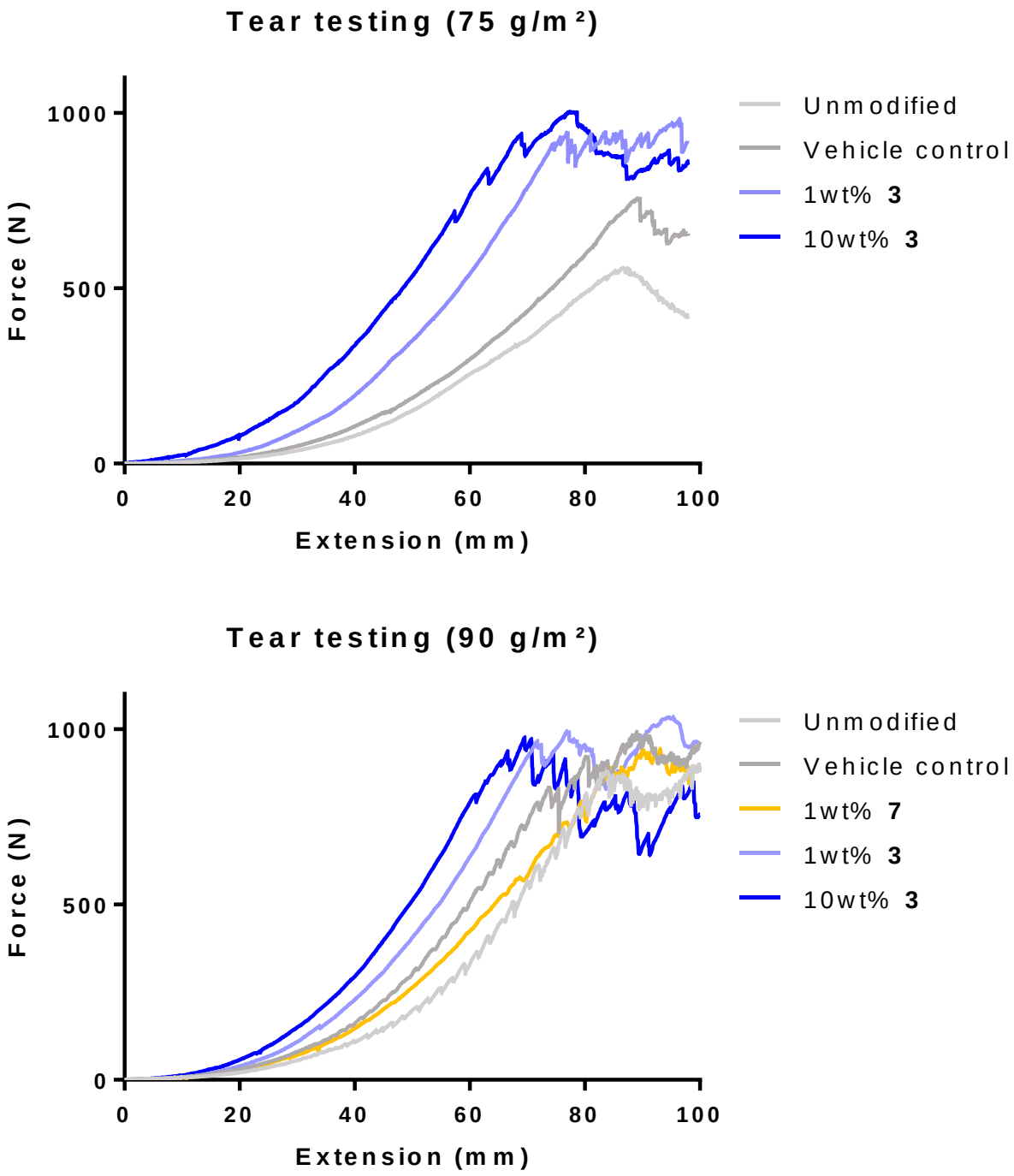


Figure S42. Representative set of curves for tear testing analysis of two deniers of UHMWPE fabric (unmodified, vehicle control (VC), 1 wt% crosslinked, 10 wt% crosslinked). Top: 75 g/m² fabric; bottom: 90 g/m² fabric.

The integration of the tear testing curves from 0 to 50 mm extension (*i.e.* on the continuous portion before yielding point) provided a value of energy (N·m = J) quantifying the strengthening of the fabric upon crosslinking.

Table S13. Integration of tear testing curves up to 50 mm extension.

Fabric	Treatment	Average (J)		St. Dev.	# of replicates
75 g/m²	Unmodified	2.40	±	0.53	2
	Vehicle control	1.99	±	0.56	7
	1wt% **3**	4.72	±	0.39	6
	10wt% **3**	7.45	±	0.91	4*
90 g/m²	Unmodified	2.59	±	0.21	3
	Vehicle control	4.61	±	1.31	5
	1wt% **7**	3.18	±	0.44	4
	1wt% **3**	6.25	±	0.85	5*
	10wt% **3**	10.82	±	2.55	4

*One sample in each indicated series was removed as statistical outlier (1.5 x IQR method).

Strengthening of aramid fabric

Material used: 204 g/m² aramid fabric made of woven fibers of polyaramid.

Procedure: the fabric was impregnated with **3** following a procedure similar to the one used for UHMWPE fabric, described above. A 11”x11” piece of fabric was impregnated with 10wt% **3** using a 9.95 g/L pentane solution (200 mL).

Crosslinking: the fabric was placed between two sheets of aluminum foil and then heated on a 12”x12” Carver press under 2000 kg load (*i.e.* 211 kPa) at 130°C for 1 h.

A “vehicle control” sample was prepared following the same procedure, but without adding crosslinker in the pentane bath.

The crosslinked sample became very stiff and rigid, contrary to the control sample which remained soft.

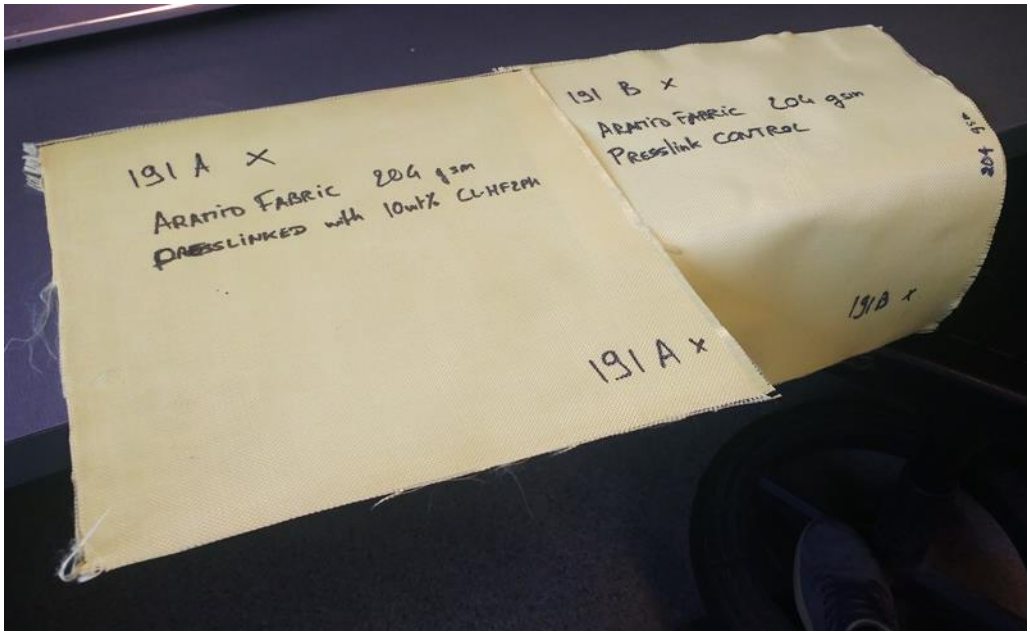


Figure S43. Aramid fabric. Left: crosslinked sample, which became stiff and rigid; Right: control sample, which remained soft and bends normally from the edge of a table.

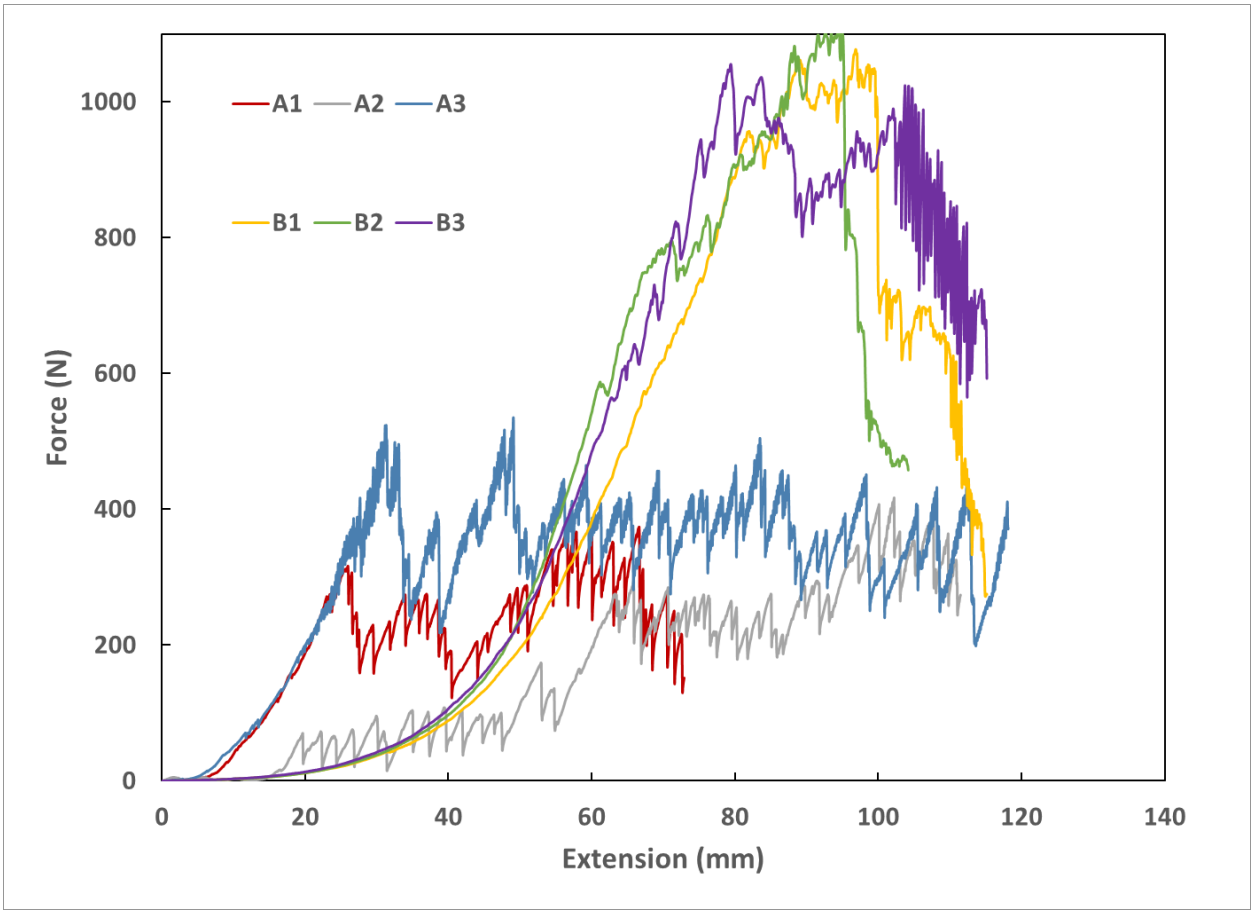


Figure S44. Tear testing curves for tear testing analysis of aramid fabric. A1-A3: crosslinked fabric, which is harder to extend but ruptures earlier; B1-B3: control fabric.

Figure S45. Aramid fabric (crosslinked or vehicle control) after tear test. Left: crosslinked sample; Right: control sample.

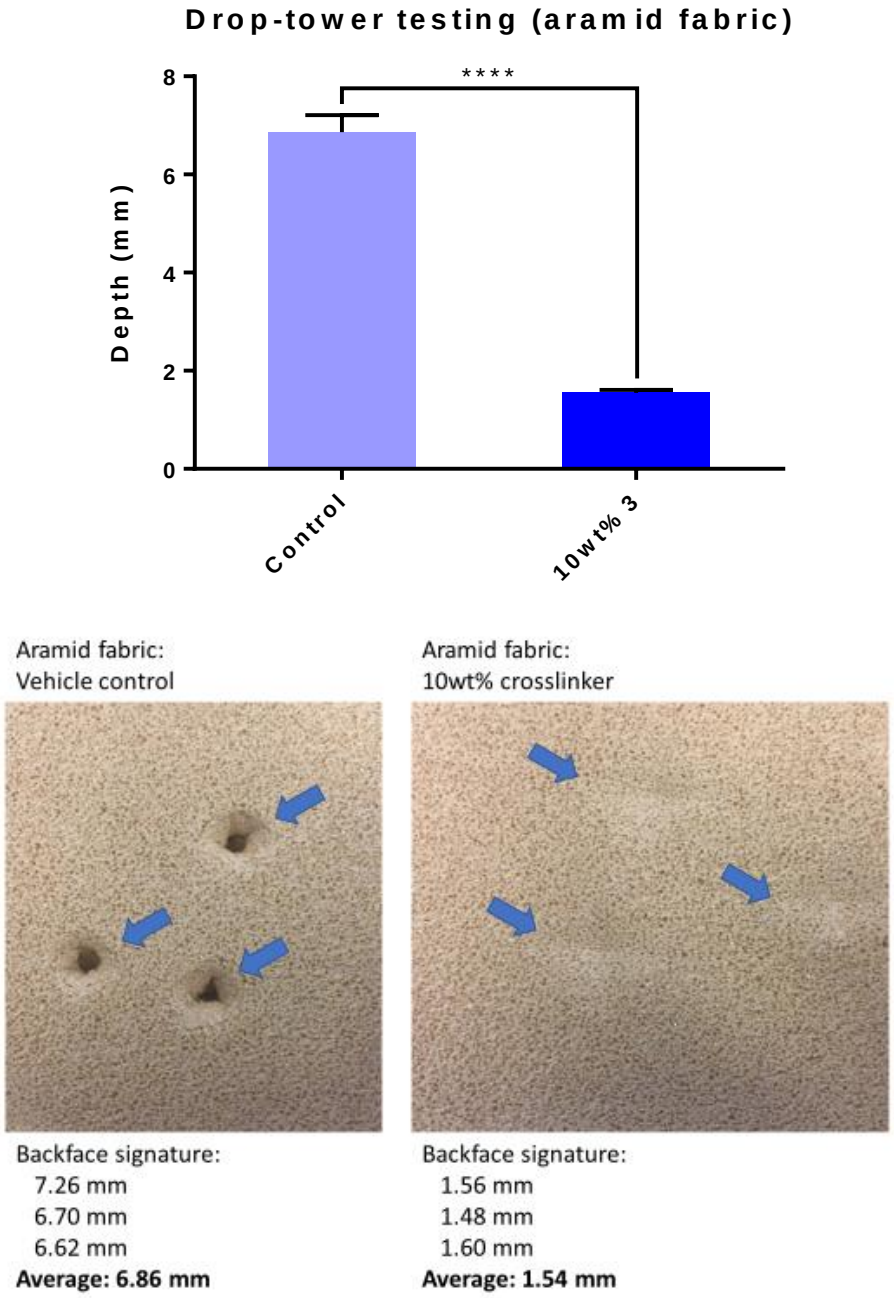


Figure S46. Depth of indentation in drop-tower test on 5-ply stacks of aramid fabric (regular or crosslinked). Crosslinking the fabric with 10wt% **3** greatly reduces indentation. **** indicates a *p*-value < 0.0001. Number of replicates = 3 for each fabric (regular or crosslinked).

Movie S1

Compound **3** (10 mg) was placed in a 10-mL round-bottom flask and heated with a heat gun. As the material reaches its activation temperature, one can successively observe: (i) bubbles indicating the beginning of nitrogen gas evolution; (ii) yellow coloration resulting from transient and/or conjugated species; (iii) rapid gas evolution without detonation, spark, flame or breakage of the glassware.

Movie S2

Compound **3** (10 mg) in its liquid form was adsorbed on a piece of filter paper. The material was hit by a hammer without causing detonation, spark, flame or fumes.

Movie S3

Two vials containing either photochemically crosslinked PDMS (A) or regular PDMS (B) were flipped to demonstrate the gel state of the crosslinked PDMS by comparison with regular liquid PDMS.