Electronic Supplementary Information for:

Electronically optimized diazirine-based polymer crosslinkers

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Materials and Methods

General considerations

All commercial materials were used as received. THF was freshly dried over Na/benzophenone. Anhydrous cyclohexane was used in crosslinking experiments. Spectranalyzed™ pentane was used for purification of diazirines.

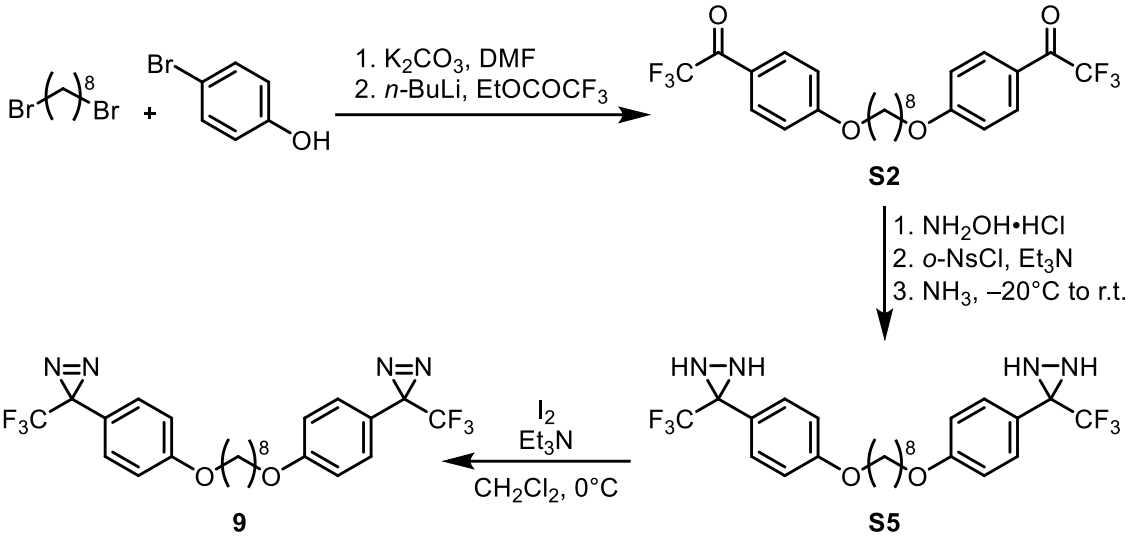
NMR spectra were acquired on either a Bruker AVANCE 300 (300.27 MHz for ^{1}H, 282.54 MHz for ^{19}F, 75.5 MHz for ^{13}C) or a Bruker AVANCE Neo 500 (500.27 MHz for ^{1}H, 470.72 MHz for ^{19}F, 125.7 MHz for ^{13}C) spectrometer. Chemical shifts were reported in parts per million (ppm) and were calibrated to the central peak of residual NMR solvent (central peak of chloroform-d: ^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm; dichloromethane-d_2: ^{1}H NMR δ = 5.32 ppm, ^{13}C NMR δ = 53.84 ppm; acetone-d_6: ^{1}H NMR δ = 2.04 ppm, ^{13}C NMR δ = 29.8 ppm; methanol-d_4: ^{1}H NMR δ = 3.31 ppm). ^{13}C spectra and ^{19}F spectra were ^{1}H decoupled. Data is reported as follows: chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, qd = quartet of doublet, p = pentet, dt = doublet of triplet, tt = triplet of triplet, td = triplet of doublet, br-s = broad singlet, m = multiplet], coupling constant in Hz, integration). Chemical shifts in ^{19}F spectra are reported in ppm and reported as obtained. Melting points were measured using a Gallenkamp melting point apparatus and are uncorrected.

High resolution mass spectrometry (HRMS) data were acquired using field desorption (FD) ionization on a JEOL AccuTOF GCx mass spectrometer. IR spectra were recorded using a Perkin-Elmer ATR spectrometer. IR wave numbers (ν) are reported in cm^{-1}. UV spotlight 365 nm (ThorLabs, 3685 lux, 38 W/m^2) and LED Strip Lights 395 nm (Waveform Lighting, 5129 lux, 53 W/m^2) were used for photochemical C–H insertion experiments. Illuminance readings were made using a wireless light sensor from PASCO (PS-3213). Differential Scanning Calorimetry analysis was performed using a DSC 25 TA instrument.

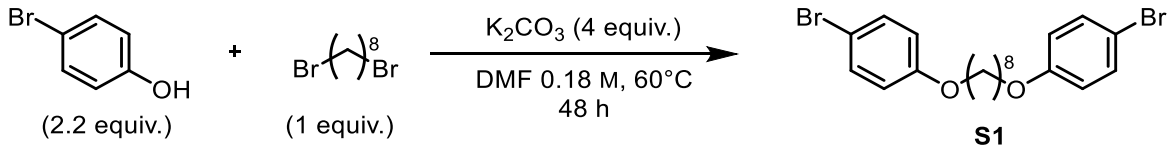
All diazirine-forming reactions were performed in the dark. Removal of solvent was done at 25 °C, avoiding the use of excessive vacuum.

Synthesis of aryl ether crosslinker **9** with a flexible aliphatic linker

Synthetic scheme for compound 9



Synthesis of 1,8-bis(4-bromophenoxy)octane (S1)



In a 1 L round bottom flask equipped with a magnetic stir bar and a condenser, to a stirring mixture of 4-bromophenol (14.8 g, 85.8 mmol, 2.2 equiv.) and potassium carbonate (21.5 g, 155.9 mmol, 4 equiv.) in DMF (200 mL), 1,8-dibromooctane (10.6 g, 38.9 mmol, 1 equiv.) was added. The mixture was heated to 60 °C for two days. The reaction mixture was cooled to room temperature, diluted with Et_2O followed by water, the aqueous layer was extracted with Et_2O (3 times) and EtOAc (1 time). The organic layers were combined, washed subsequently with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude compound **S1** was obtained as colourless crystals (17.6 g, 38.6 mmol, 99%). Melting point = 39–40 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.9 Hz, 4H), 6.77 (d, *J* = 8.9 Hz, 4H), 3.91 (t, *J* = 6.5 Hz, 4H), 1.77 (p, *J* = 6.6 Hz, 4H), 1.46 (qt, *J* = 6.8, 2.9 Hz, 4H), 1.42 – 1.34 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.36, 132.33, 116.43, 112.72, 68.32, 29.40, 29.28, 26.07. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{20}H_{24}Br_2O_2$: 454.0138, found: 454.0142.

Fig. S1. ^{1}H NMR spectrum of S1 in $CDCl_3$.

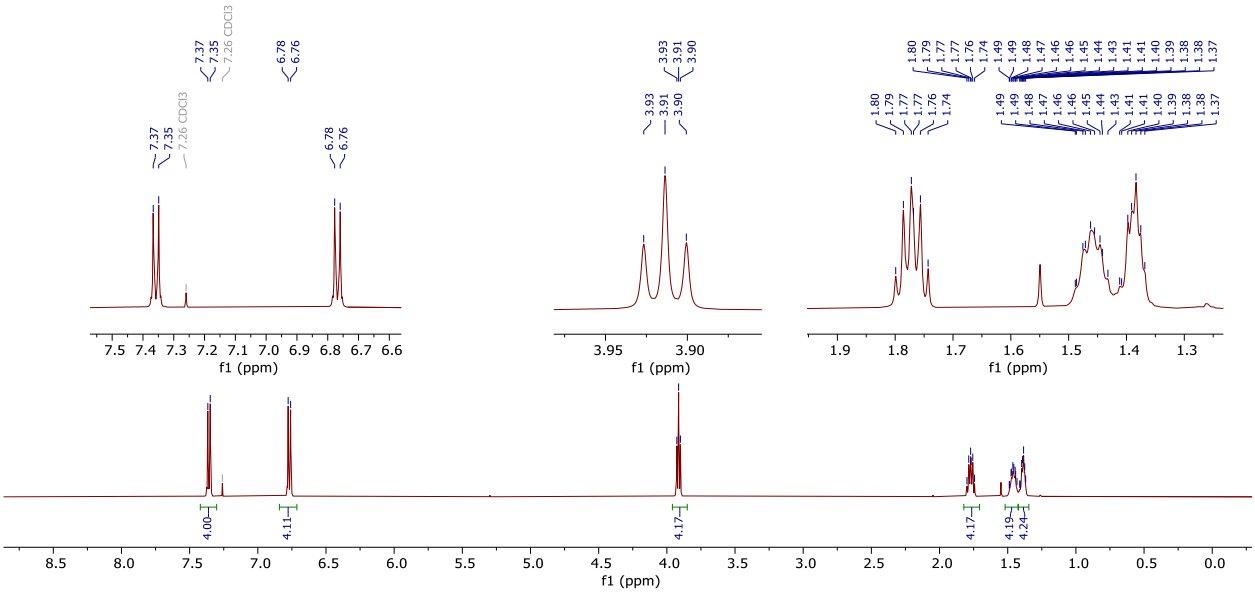
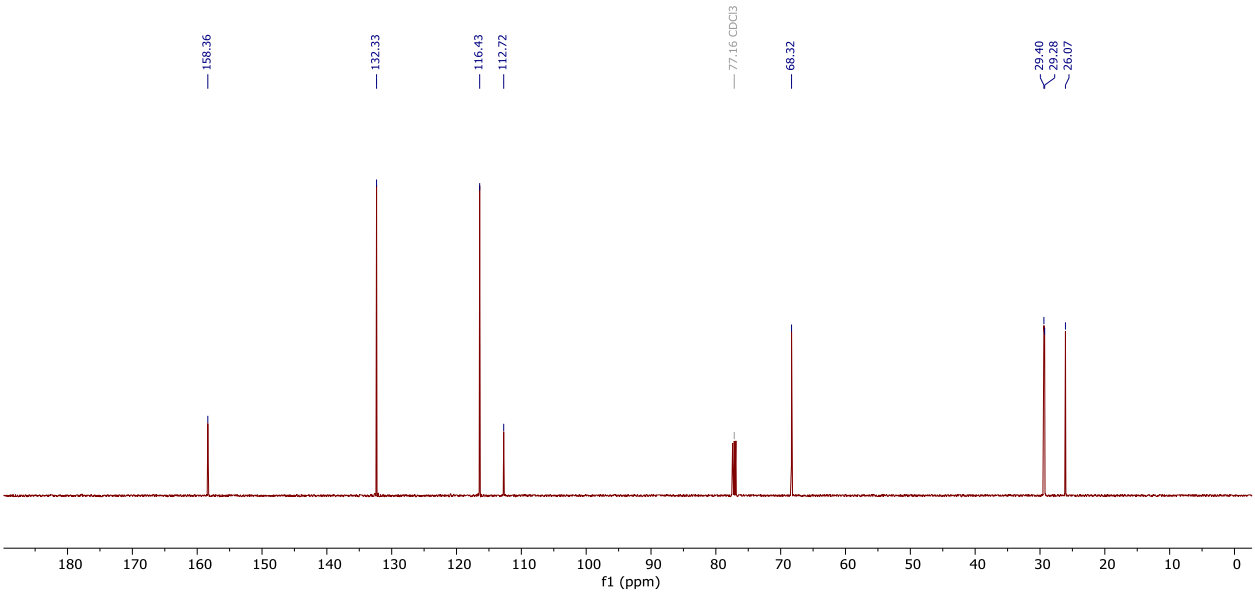
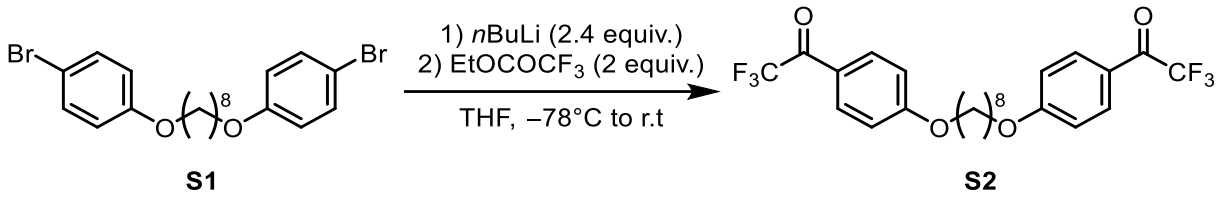


Fig. S2. ^{13}C NMR spectrum of S1 in $CDCl_3$.



Synthesis of 1,1'-((octane-1,8-diylbis(oxy))bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) (S2)



S1 **S2**

To a stirring solution of compound **S1** (1.2 g, 2.6 mmol, 1 equiv.) in dry THF (15 mL) under argon atmosphere at –78 °C, *n*-butyllithium (2.5 ml, 6.3 mmol, 2.4 equiv.) was slowly added and stirring was maintained at –78 °C for 1 h. Then ethyl trifluoroacetate (0.6 mL, 5.3 mmol, 2 equiv.) was added dropwise, and the mixture was stirred for a further 1 h at –78 °C and then allowed to warm to room temperature with continued stirring. After 6 h the reaction was quenched with sat. aq. NH_4Cl, and the aqueous layer was extracted with diethyl ether (3 times) and dried over $MgSO_4$. The dried organic layer was filtered and concentrated under reduced pressure. Flash-column chromatography over silica gel using petroleum ether:Et_2O (8:2) as eluent yielded pure compound **S2** as a white solid (1.2 g, , 2.4 mmol, 92%). Melting point = 64–65 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 4H), 6.98 (d, *J* = 9.0 Hz, 4H), 4.07 (t, *J* = 6.5 Hz, 4H), 1.88 – 1.79 (m, 4H), 1.56 – 1.46 (m, 4H), 1.44 – 1.40 (m, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.15, 132.91, 122.77, 114.98, 68.67, 29.36, 29.11, 26.03. ^{19}F NMR (283 MHz, $CDCl_3$) δ –70.97. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{24}H_{24}F_6O_4$: 490.1573, found: 490.1557.

Fig. S3. ^{1}H NMR spectrum of S2 in $CDCl_3$.

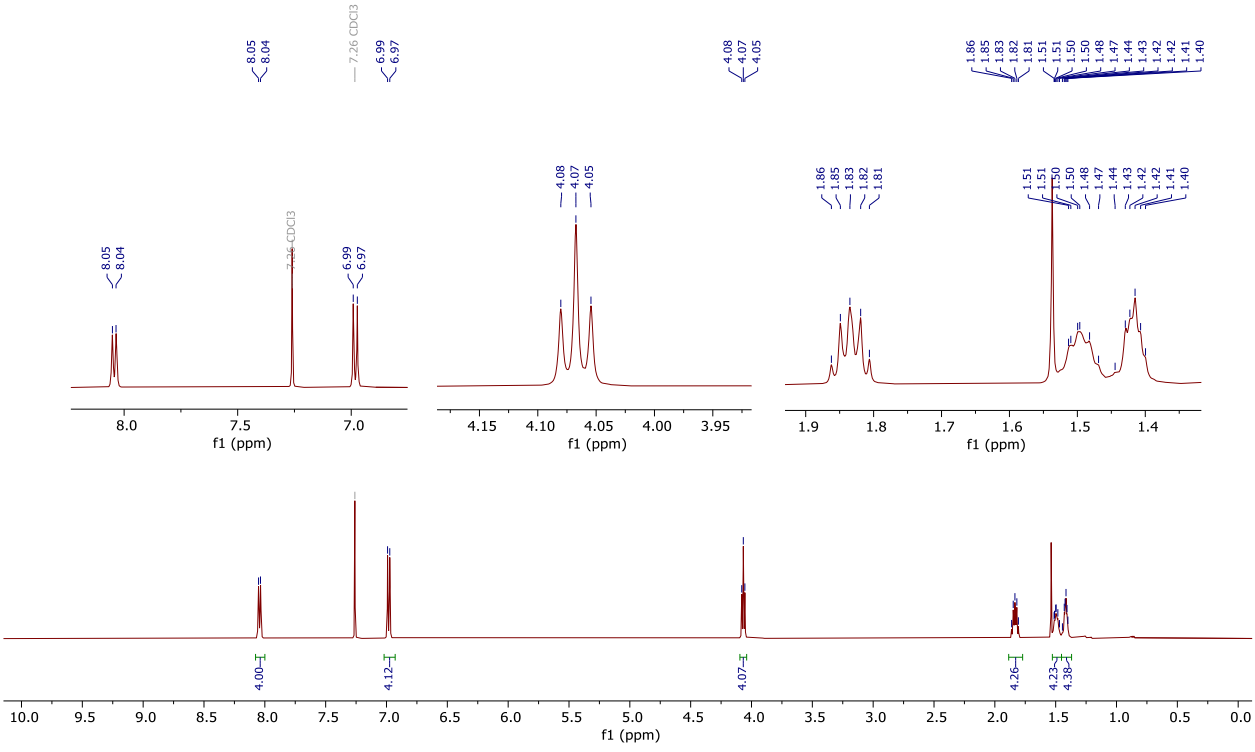


Fig. S4. ^{13}C NMR spectrum of S2 in $CDCl_3$.

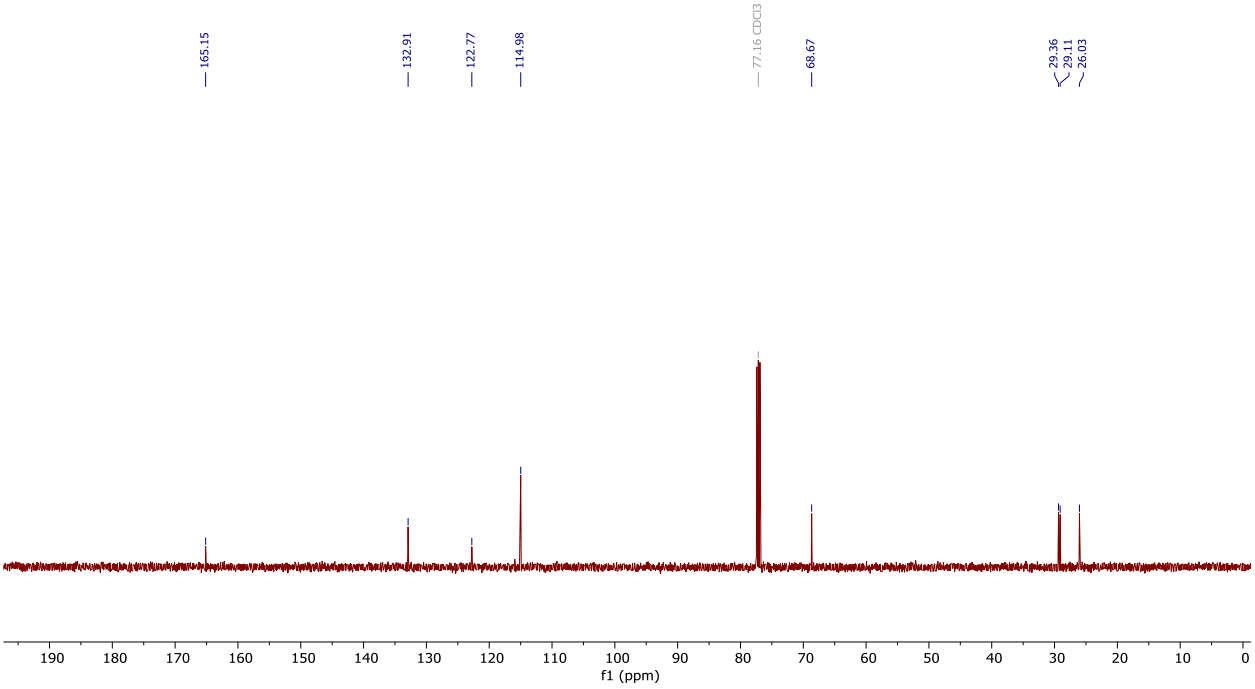
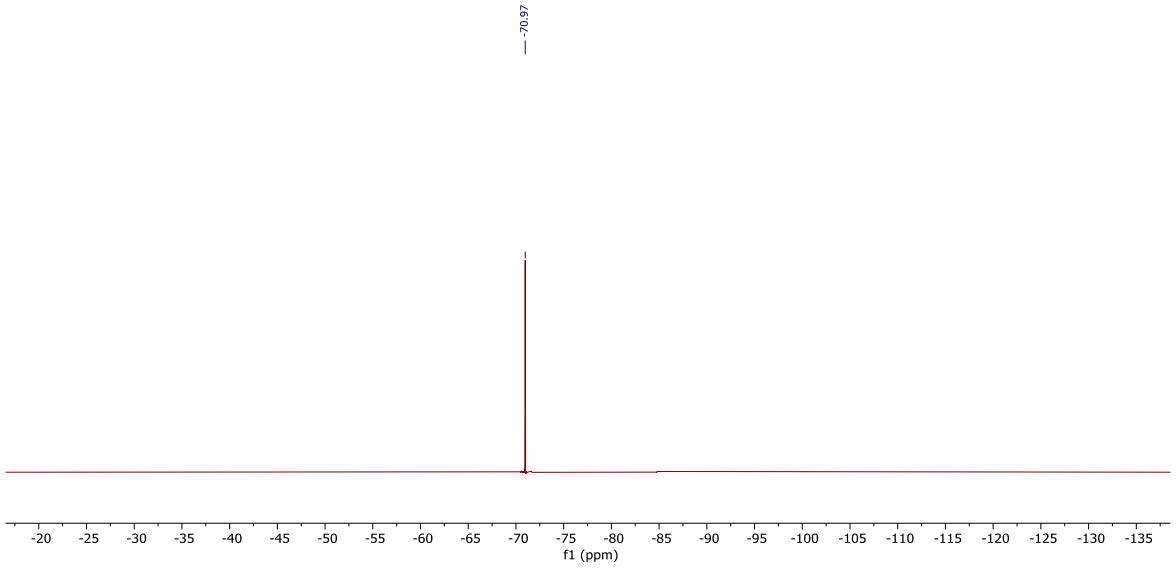
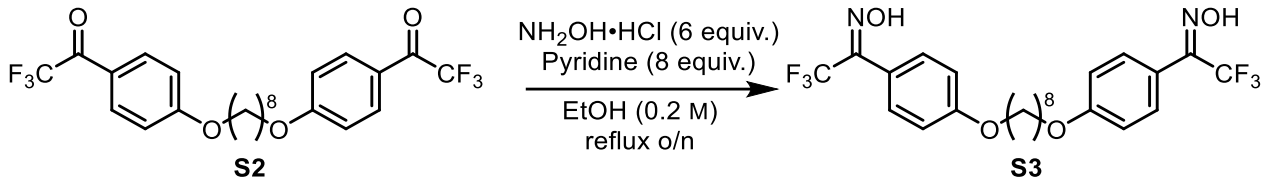


Fig. S5. ^{19}F NMR spectrum of S2 in $CDCl_3$.



Synthesis of 1,1'-((octane-1,8-diylbis(oxy))bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime (S3)



To a stirred solution of compound **S2** (4.4 g, 8.97 mmol, 1 equiv.) in ethanol (0.2 M), hydroxylamine hydrochloride (3.7 g, 53.83 mmol, 6 equiv.) and pyridine (5.8 mL, 71.77 mmol, 8 equiv.) were added and the reaction mixture was heated to reflux for 16 h. The mixture was then cooled to room temperature and the mixture was treated with 2M HCl and extracted with Et_2O (3 times). The combined organic layers were washed with distilled water until the pH of the washing layer became neutral, and then dried with sodium sulfate, filtered and concentrated. The residue was dried under high vacuum for a prolonged time to afford the desired crude *bis*-oxime **S3** (as a mixture of geometric isomers) as a white solid (4.6 g, 8.84 mmol, 99%). The compound was submitted to the next step without further purification. ^{19}F NMR (283 MHz, $CDCl_3$) δ –62.32, –66.26 (major isomer).

On one occasion, for the purpose of NMR characterization, the residue was purified by flash-column chromatography over silica gel using pentane:EtOAc (7:3) to afford the pure *bis*-oxime (major isomer). Melting point = 127–131 °C. ^1H NMR (500 MHz, Acetone) δ 7.53 (d, *J* = 8.8 Hz, 4H), 7.05 (d, *J* = 8.9 Hz, 4H), 4.08 (t, *J* = 6.4 Hz, 4H), 1.86 – 1.76 (m, 4H), 1.56 – 1.48 (m, 4H), 1.44 (p, *J* = 3.3 Hz, 4H). ^{19}F NMR (471 MHz, Acetone) δ –66.40. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{24}H_{26}F_6N_2O_4$: 520.1791, found: 520.1773.

Fig. S6. ^1H NMR spectrum of S3 in $(CD_3)_2CO$.

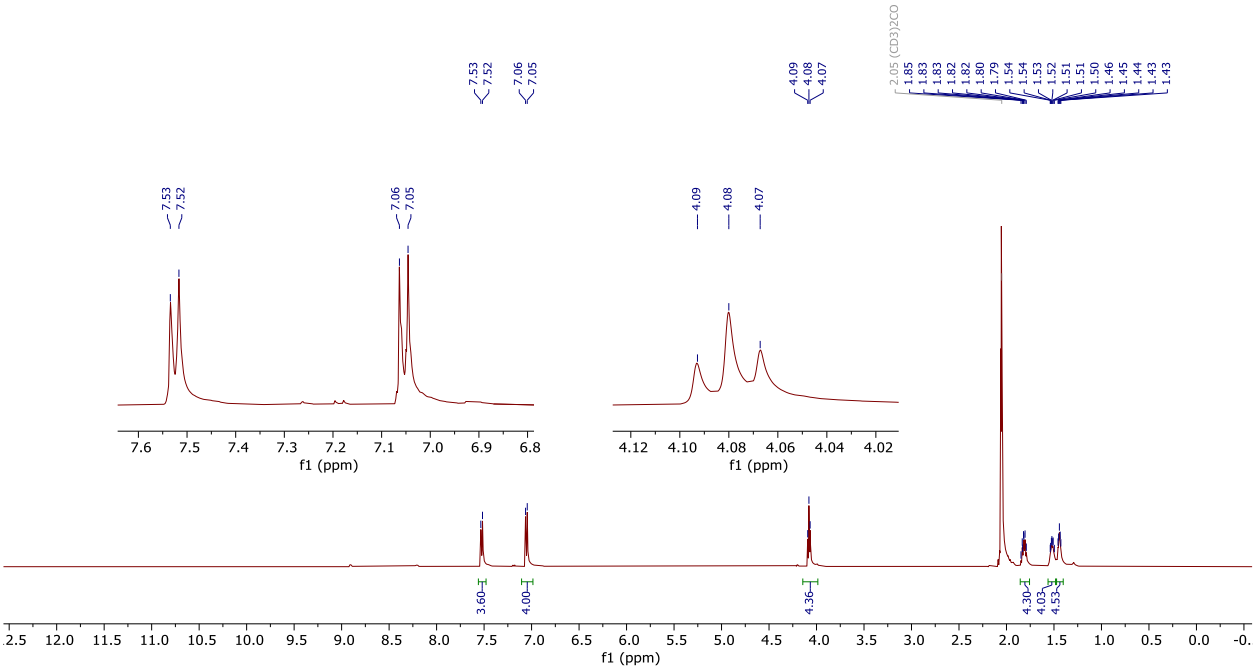
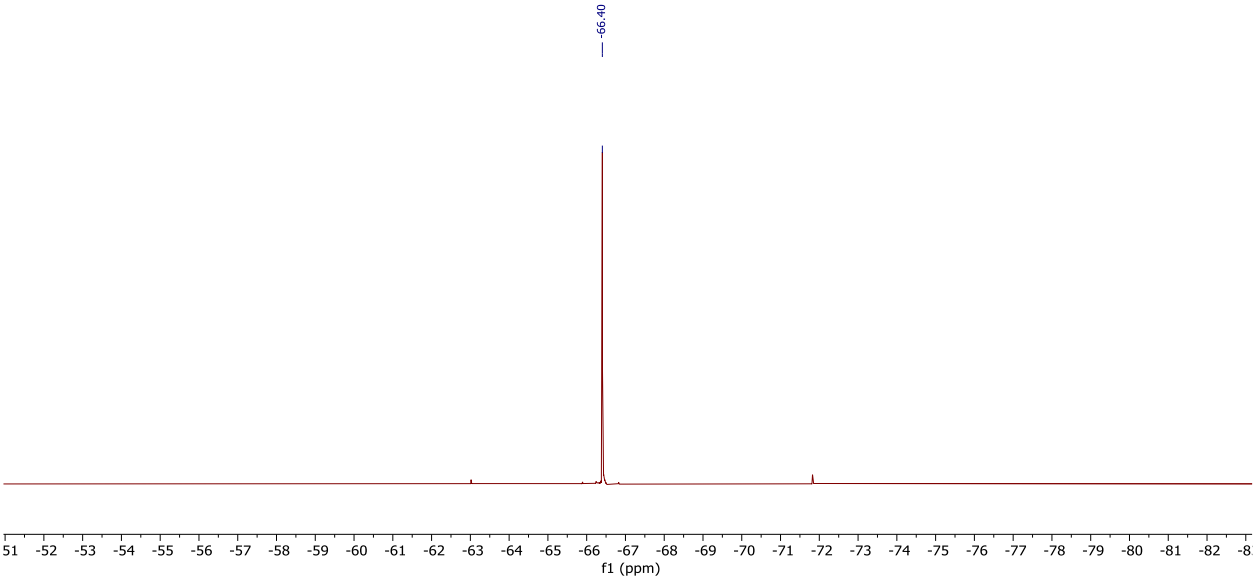
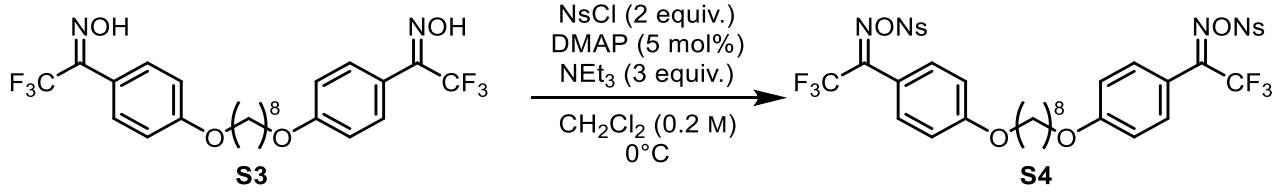


Fig. S7. ^{19}F NMR spectrum of S3 in $(CD_3)_2CO$.



Synthesis of 1,1'-((octane-1,8-diylbis(oxy))bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-di((2-nitrophenyl)sulfonyl) dioxime (S4)



Compound **S3** (5.2 g, 10.0 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (50 mL), and triethylamine (4.2 mL, 30.18 mmol, 3 equiv.), DMAP (61 mg, 0.50 mmol, 5 mol%) and 2-nitrobenzenesulfonyl chloride (4.5 g, 20.0 mmol, 2 equiv.) 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 and extracted with CH_2Cl_2. The combined organic extracts were dried with magnesium sulfate, filtered, and concentrated to afford the desired crude *bis*-nosyloxime **S4**, which was submitted to the next step without further purification.

On one occasion, for the purpose of NMR characterization, the residue was purified by flash-column chromatography over silica gel using pentane:EtOAc (7:3) to afford the pure *bis*-nosyloxime as an off-white solid (7.48 g, 8.39 mmol, 84%). Melting point = 114–117 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.8 Hz, 2H), 7.94 – 7.74 (m, 6H), 7.60 (d, *J* = 8.6 Hz, 4H), 7.00 (d, *J* = 8.9 Hz, 4H), 4.03 (t, *J* = 6.4 Hz, 4H), 1.88 – 1.76 (m, 4H), 1.49 (q, *J* = 6.4, 5.5 Hz, 4H), 1.42 (p, *J* = 3.4 Hz, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –65.59. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{36}H_{32}F_6N_4O_{12}S_2$: 890.1357, found: 890.1341.

Fig. S8. ^{1}H NMR spectrum of S4 in $CDCl_3$.

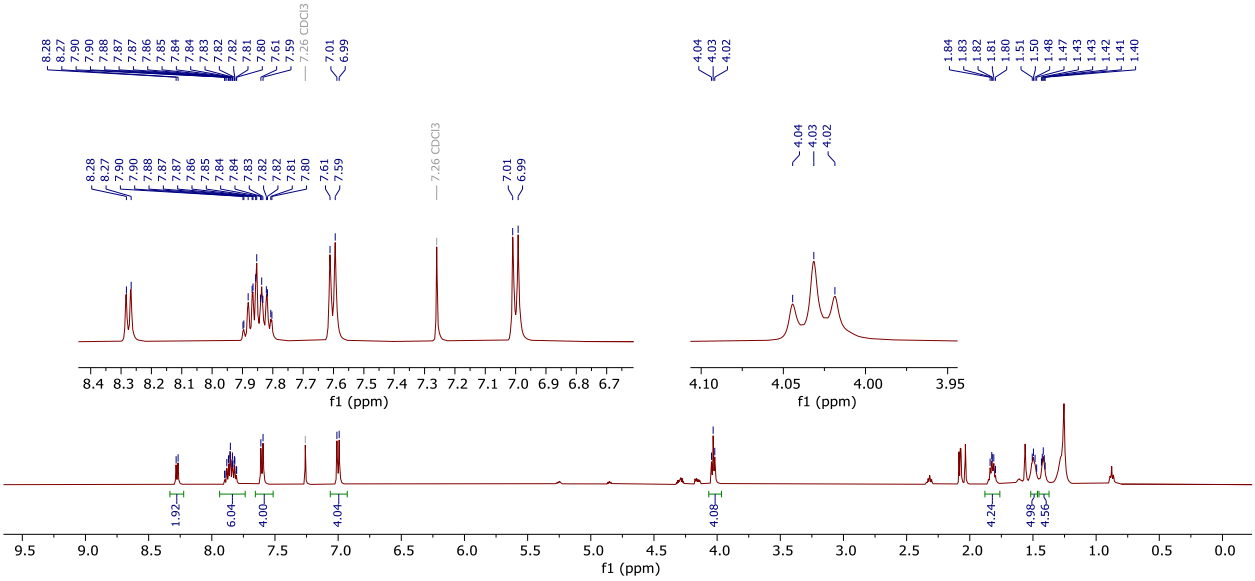
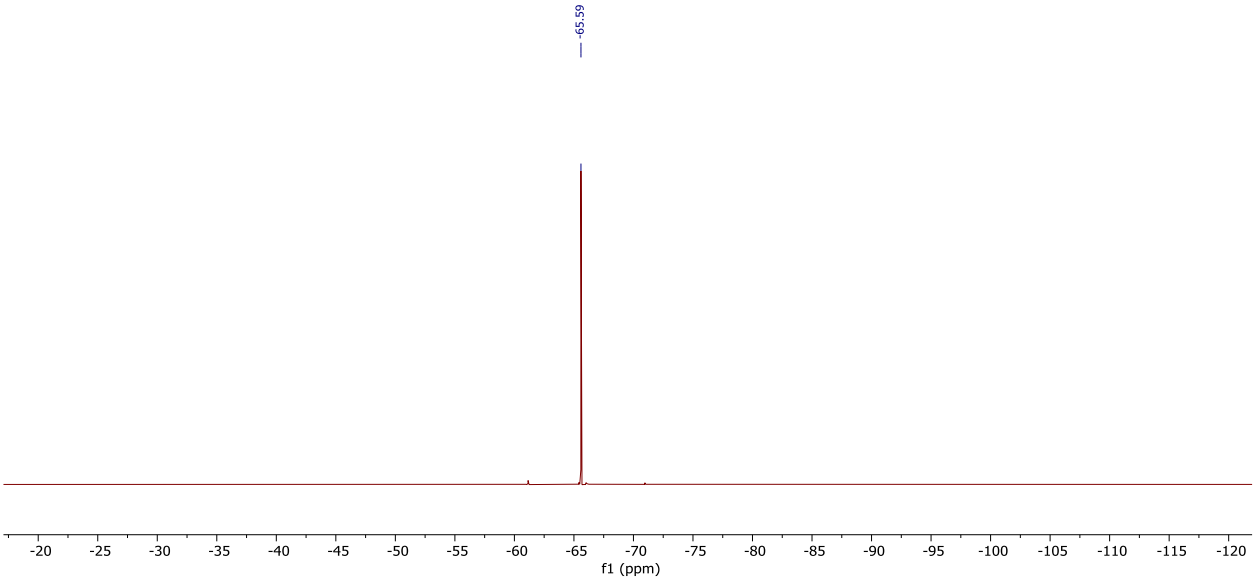
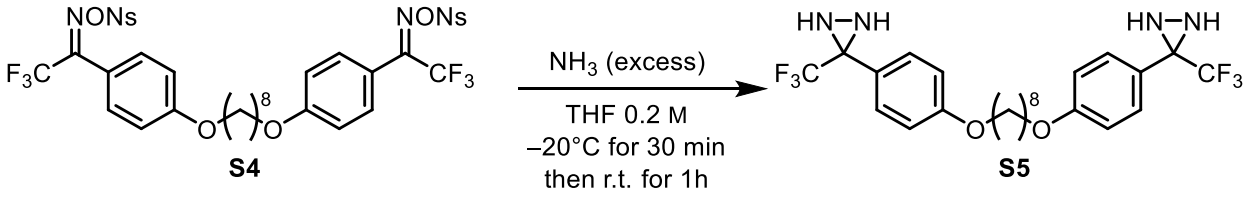


Fig. S9. ^{19}F NMR spectrum of S4 in $CDCl_3$.



Synthesis of 1,8-bis(4-(3-(trifluoromethyl)diaziridin-3-yl)phenoxy)octane (S5)



Bis-nosyloxime **S4** (7.48 g, 8.39 mmol, 1 equiv.) in anhydrous THF (42 mL) was transferred to a flame-dried 3-neck flask under argon and cooled to –20 °C. Anhydrous gaseous ammonia was bubbled into the stirred solution for 30 min. Then, the reaction was left stirring for 1 h, during which time it was allowed to warm from –20 °C to room temperature. The mixture was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 times). The combined organic layers were washed with brine and then dried with magnesium sulfate, filtered and concentrated to afford the desired crude *bis*-diaziridine **S5**, which was submitted to the next step without further purification.

On one occasion, for the purpose of NMR characterization, the residue was purified by flash-column chromatography over silica gel using pentane:EtOAc (7:3) to afford the pure *bis*-diaziridine as a white solid (4.2 g, 8.1 mmol, 96%). Melting point = 81–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 4H), 6.91 (d, *J* = 8.8 Hz, 4H), 3.97 (t, *J* = 6.5 Hz, 4H), 2.74 (d, *J* = 8.8 Hz, 2H, N-H), 2.15 (d, *J* = 8.9 Hz, 2H, N-H), 1.84 – 1.74 (m, 4H), 1.52 – 1.43 (m, 4H), 1.39 (p, *J* = 3.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.55, 129.60, 123.65, 114.76, 68.21, 29.40, 29.26, 26.09. ^{19}F NMR (471 MHz, $CDCl_3$) δ –75.78. IR (diamond-ATR) v: 3675, 3260, 2930, 2858, 1742, 1613, 1519, 1247, 1153, 1053, 939, 832, 755. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{24}H_{28}F_6N_4O_2$: 518.2111, found: 518.2091.

Fig. S10. ^{1}H NMR spectrum of S5 in $CDCl_3$.

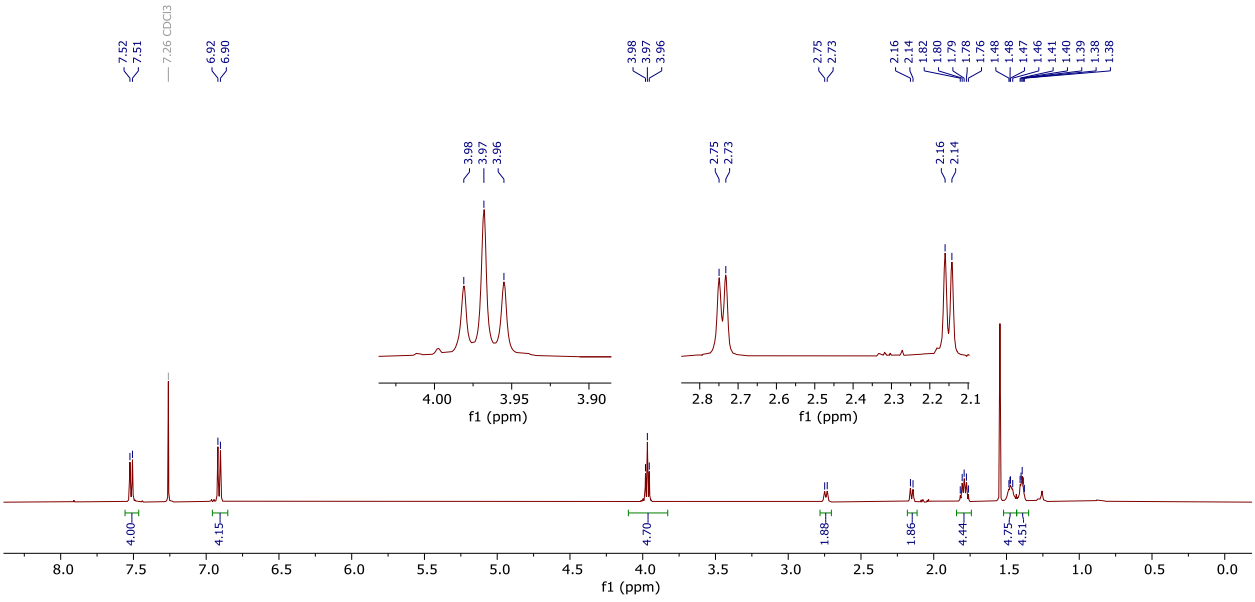


Fig. S11. ^{13}C NMR spectrum of S5 in $CDCl_3$.

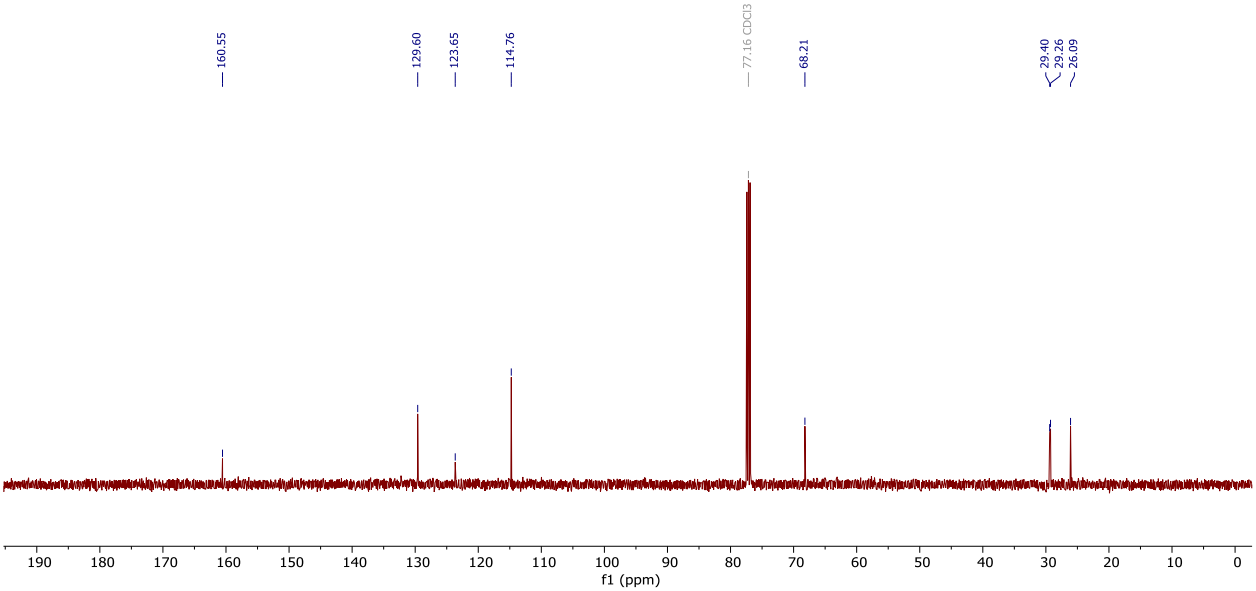
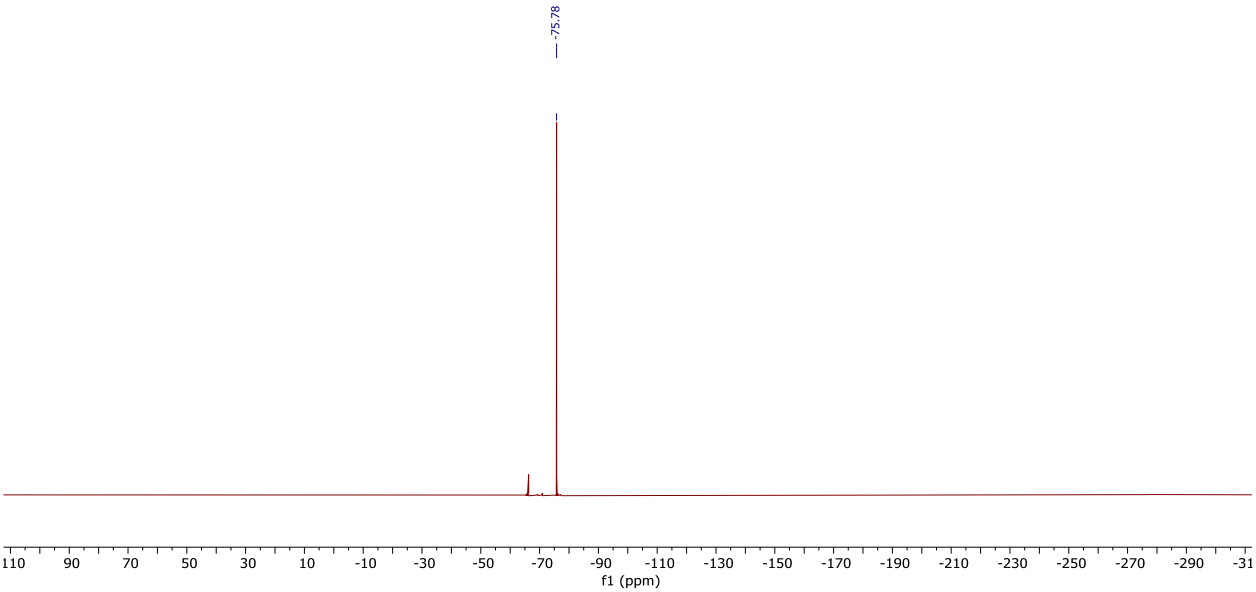
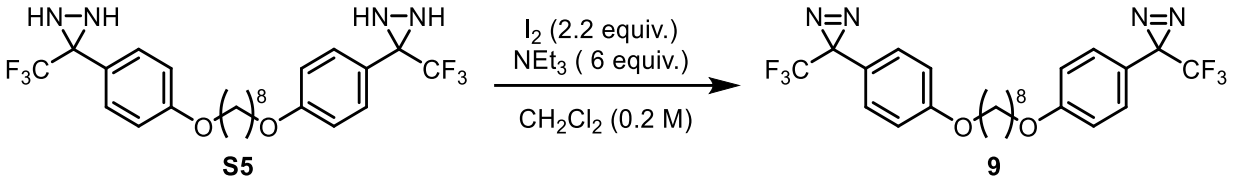


Fig. S12. ^{19}F NMR spectrum of S5 in $CDCl_3$.



Synthesis of 1,8-bis(4-(3-(trifluoromethyl)-3H-diazirin-3-yl)phenoxy)octane (9)



To a solution of *bis*-diaziridine **S5** (4.2 g, 8.1 mmol, 1 equiv.) in CH_2Cl_2 (41 mL) at 0 °C were added successively triethylamine (6.8 mL, 48.6 mmol, 6 equiv.) and iodine (4.52 g, 17.8 mmol, 2.2 equiv.). The coloured mixture was stirred at 0 °C for 1 h. The mixture was diluted with CH_2Cl_2 and washed with sat. aq. sodium thiosulfate. The aqueous layer was re-extracted with CH_2Cl_2 (3 times). Then the combined organic extracts were washed with brine and dried with magnesium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography using pentane: Et_2O (8:2) as eluent to afford the desired *bis*-diazirine **9** (3.04 g, 5.91 mmol, 73%) as a pale-yellow solid. Melting point = 48–49 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 4H), 6.88 (d, *J* = 8.9 Hz, 4H), 3.95 (t, *J* = 6.5 Hz, 4H), 1.78 (p, *J* = 6.6 Hz, 4H), 1.46 (dp, *J* = 12.4, 6.5 Hz, 4H), 1.43 – 1.35 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.32, 129.55, 128.25, 123.50, 121.32, 120.85, 114.99, 68.22, 29.38, 29.23, 26.07. ^{19}F NMR (283 MHz, $CDCl_3$) δ –65.63. IR (diamond-ATR) v: 2939, 2860, 1707, 1603, 1519, 1259, 1235, 1181, 1155, 939, 825, 626, 525. UV (*n*-hexane): λmax, diazirine = 372 nm. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{24}H_{24}F_6N_4O_2$: 514.1798, found: 514.1779.

Fig. S13. ^{1}H NMR spectrum of 9 in $CDCl_3$.

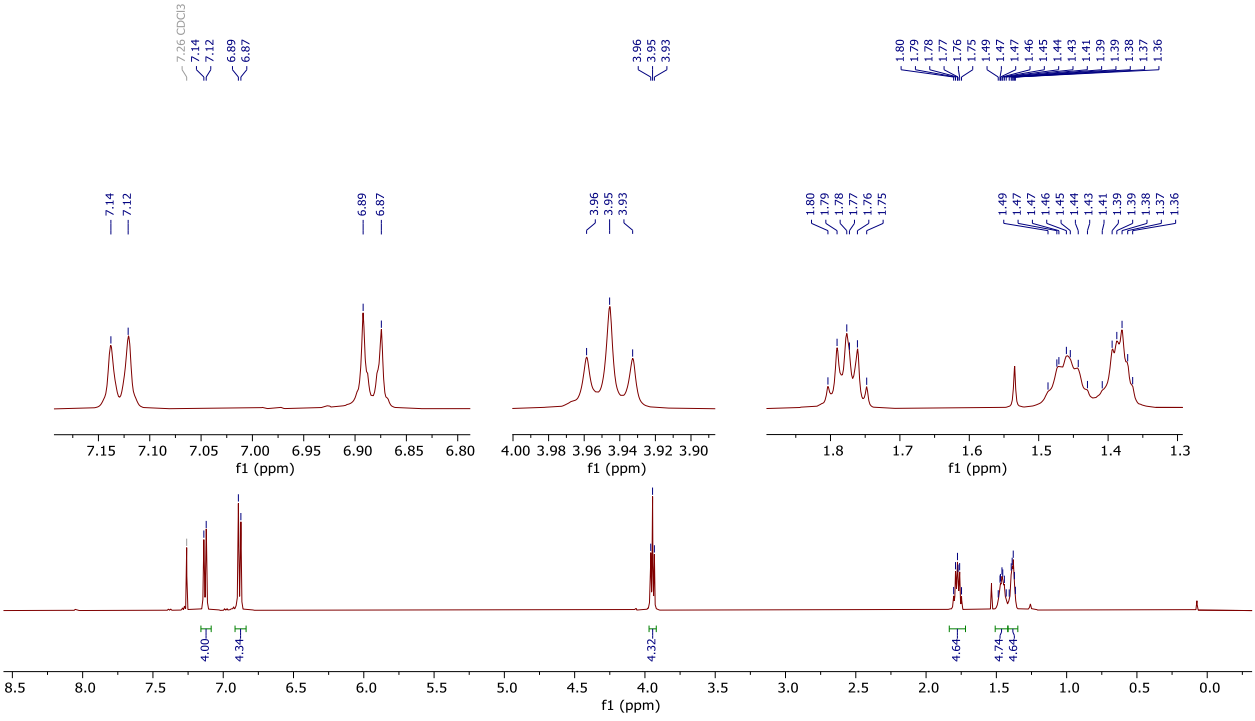


Fig. S14. ^{13}C NMR spectrum of 9 in $CDCl_3$.

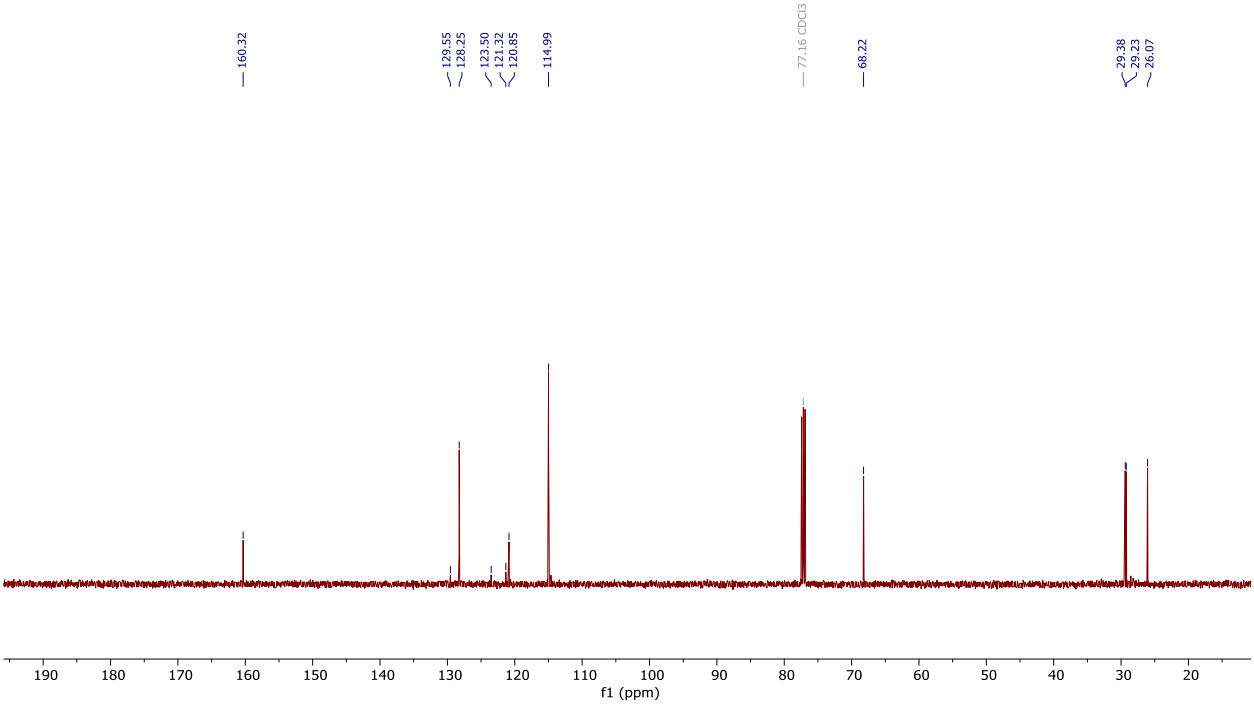
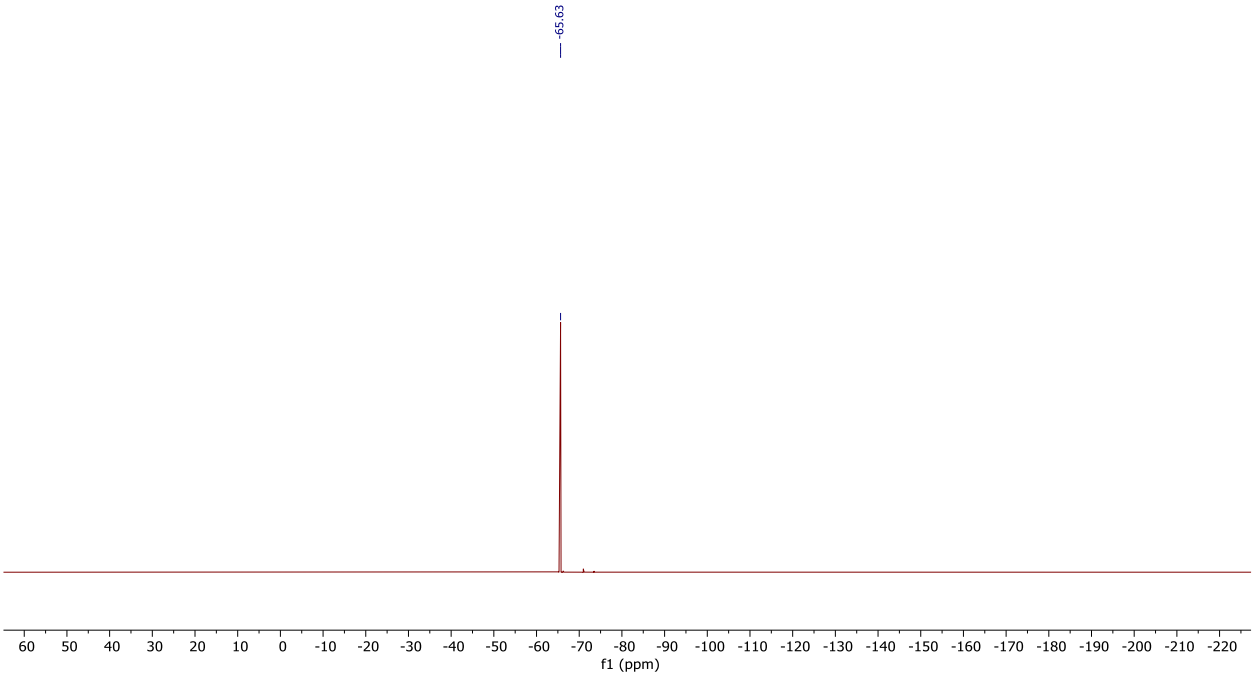
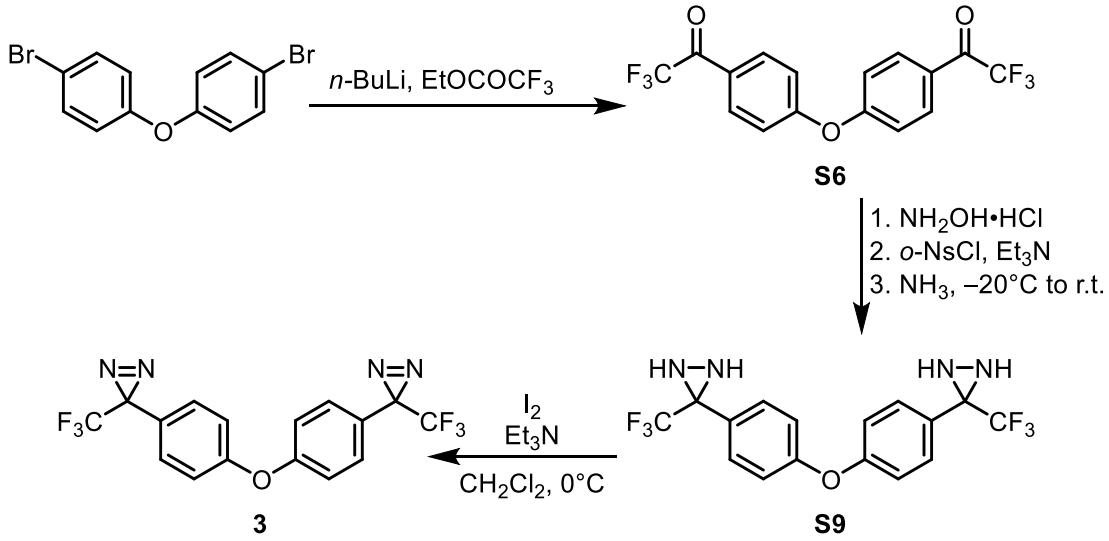


Fig. S15. ^{19}F NMR spectrum of 9 in $CDCl_3$.

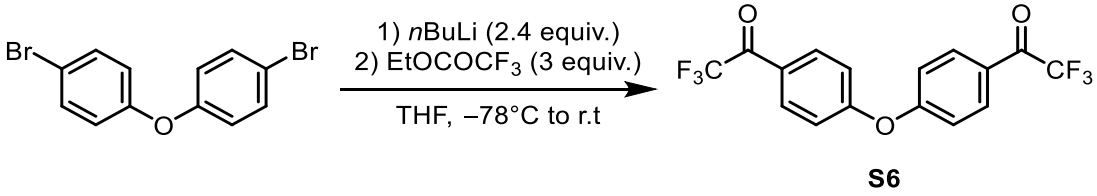


Synthesis of rigid *bis*-aryl ether crosslinker **3**

Synthetic scheme for compound 3



Synthesis of 1,1'-(oxybis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) (S6)



To a stirring solution of 4,4'-oxybis(bromobenzene) (5.12 g, 15.61 mmol, 1 equiv.) in dry THF (90 ml) under argon atmosphere at –78 °C, *n*-butyllithium (15 mL, 37.48 mmol, 2.4 equiv., 2.5 M) was slowly added and stirring was maintained at –78 °C for 1 h. Then ethyl trifluoroacetate (5.6 mL, 46.8 mmol, 3 equiv.) was added dropwise, and the mixture was stirred for a further 1 h at –78 °C and then allowed to warm to room temperature with continued stirring. After 6 h the reaction was quenched with sat. aq. NH_4Cl, and the aqueous layer was extracted with Et_2O (3 times) and dried over $MgSO_4$. The dried organic layer was filtered and concentrated under reduced pressure. Flash-column chromatography over silica gel using petroleum ether:Et_2O (8:2) as eluent yielded pure compound **S6** as a colourless oil (5.46 g, 15.07 mmol, 97%) with spectroscopic data in accordance with the literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.9 Hz, 4H). ^{19}F NMR (283 MHz, $CDCl_3$) δ –71.32.

Fig. S16. ^{1}H NMR spectrum of S6 in $CDCl_3$.

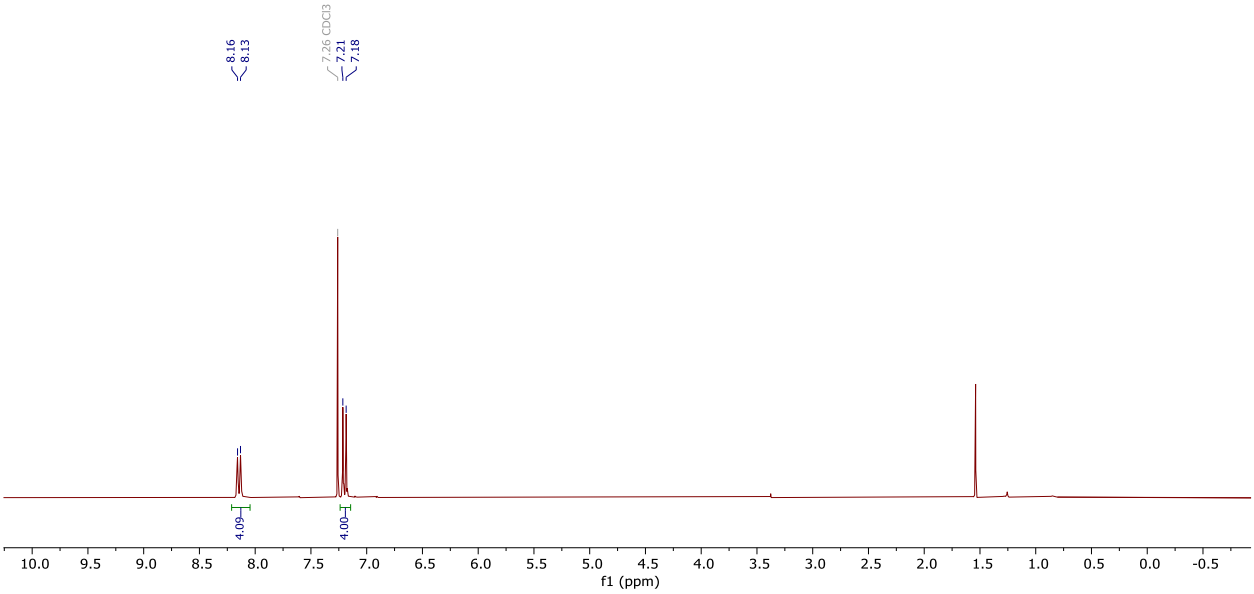
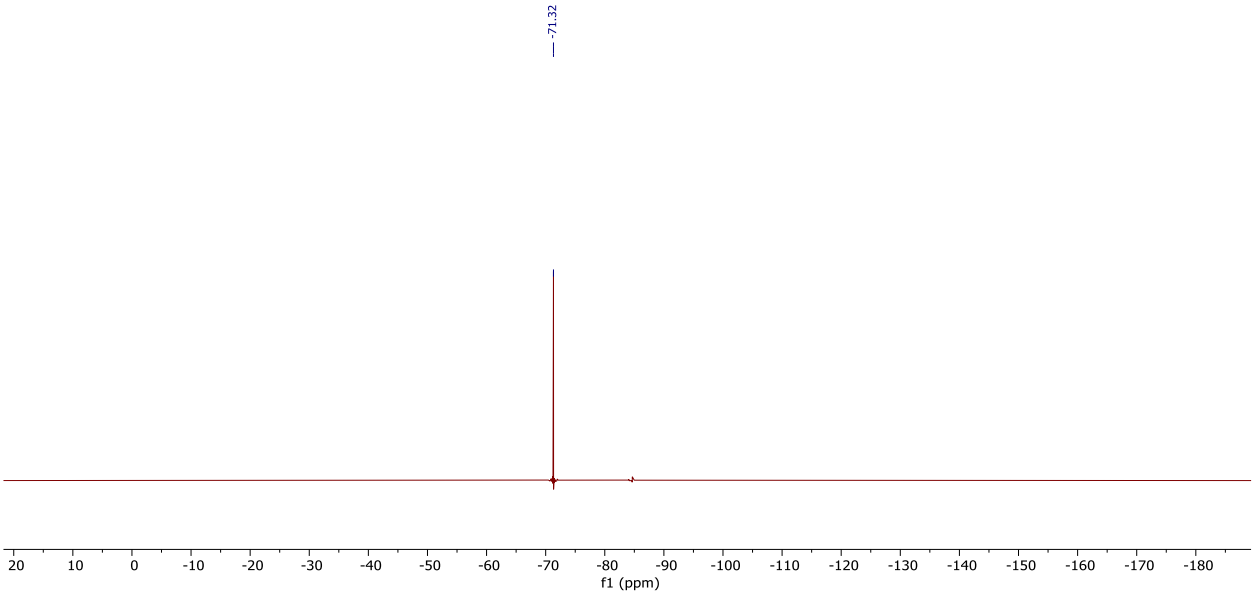
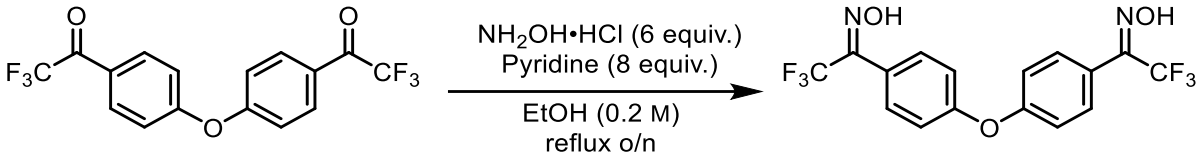


Fig. S17. ^{19}F NMR spectrum of S6 in $CDCl_3$.



Synthesis of 1,1'-(oxybis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime (S7)



S6 **S7**

To a stirred solution of compound **S6** (5.36 g, 14.8 mmol, 1 equiv.) in ethanol (0.2 M), hydroxylamine hydrochloride (6.17 g, 88.85 mmol, 6 equiv.) and pyridine (9.5 mL, 118.4 mmol, 8 equiv.) were added and the reaction mixture was heated to reflux for 16 h. The mixture was then cooled to room temperature and the mixture was treated with 2M HCl and extracted with Et_2O (3 times). The combined organic layers were washed with distilled water until the pH of the washing layer became neutral, and then dried with sodium sulfate, filtered, and concentrated. The residue was dried under high vacuum for a prolonged time to afford the desired crude *bis*-oxime **S7** (as a mixture of geometric isomers) (5.8 g, 14.78 mmol, 99%) with spectroscopic data in accordance with the literature.[1] The compound was submitted to the next step without further purification. ^{1}H NMR (300 MHz, CD_3OD) δ 7.53 (d, *J* = 8.6 Hz, 4H), 7.13 (d, *J* = 8.8 Hz, 4H).^{19}F NMR (283 MHz, $CDCl_3$) δ –62.26, –66.42.

Fig. S18. ^{1}H NMR spectrum of S7 in CD_3OD.

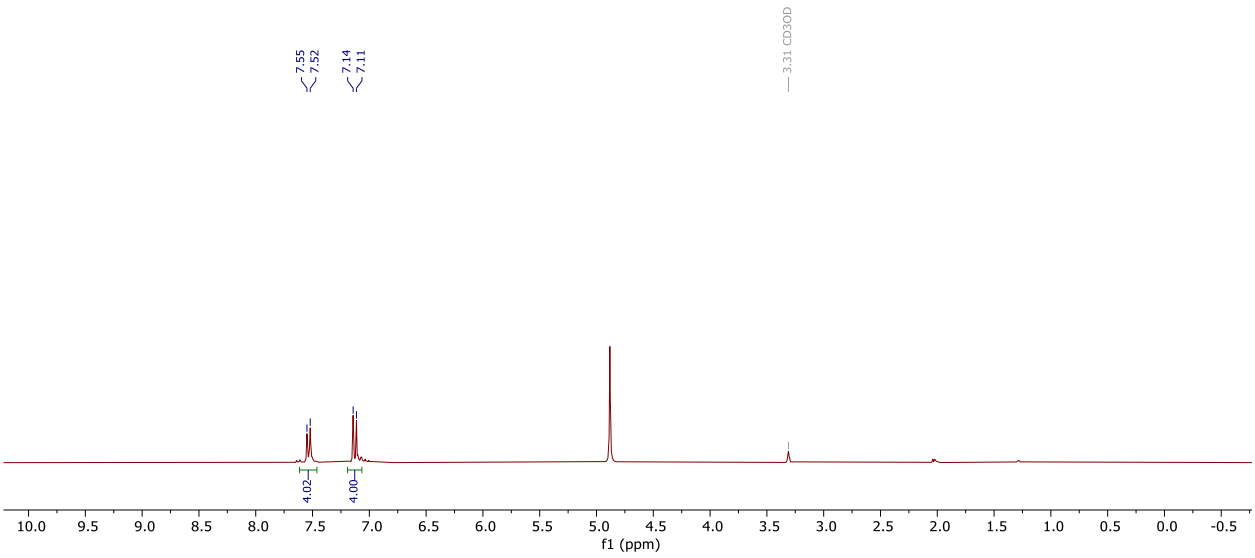
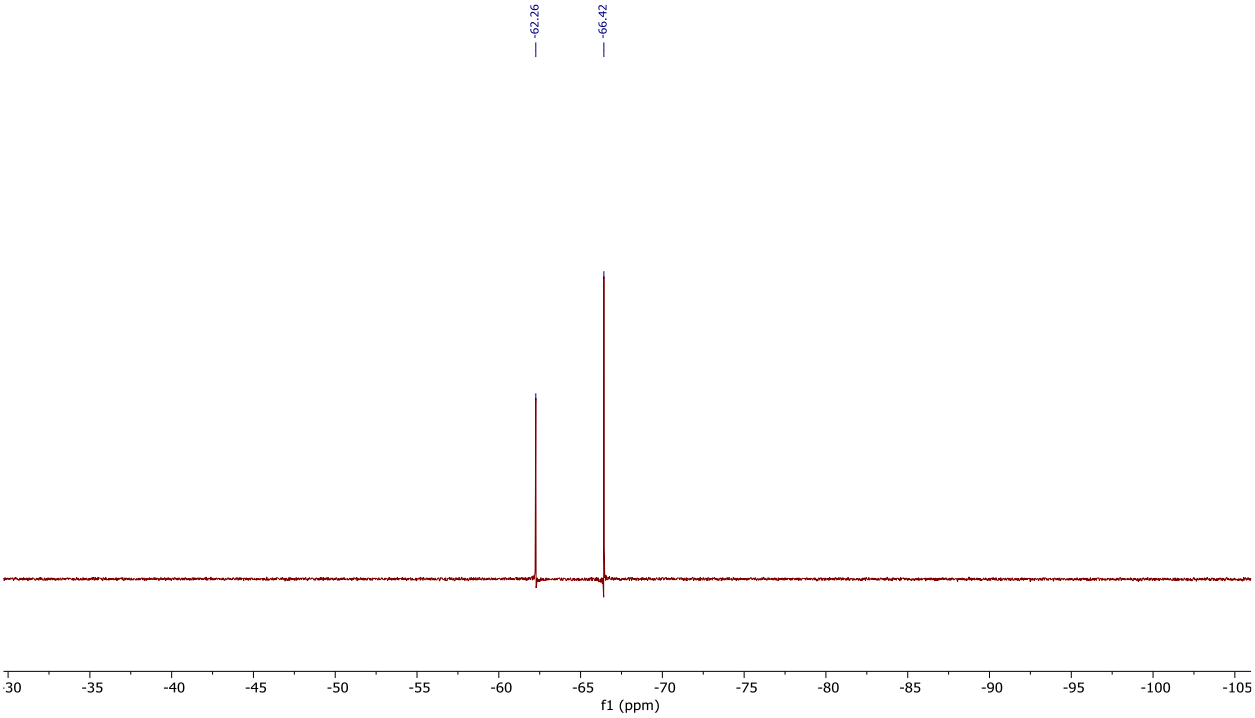
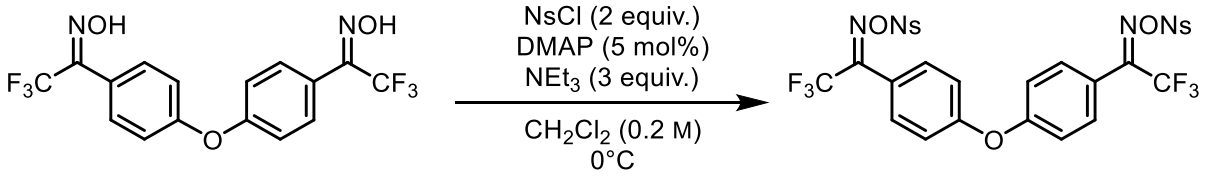


Fig. S19. ^{19}F NMR spectrum of S7 in $CDCl_3$.



Synthesis of 1,1'-(oxybis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-di((2-nitrophenyl)sulfonyl) dioxime (S8)



S7 **S8**

Compound **S7** (5.8 g, 14.8 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (74 mL), and triethylamine (6.2 mL, 44.4 mmol, 3 equiv.), DMAP (90 mg, 0.74 mmol, 5 mol%) and 2-nitrobenzenesulfonyl chloride (6.89 g, 31.8 mmol, 2.1 equiv.) 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 and extracted with CH_2Cl_2. The combined organic extracts were dried with magnesium sulfate, filtered, and concentrated to afford the desired crude *bis*-nosyloxime **S8** which was submitted to the next step without further purification.

On one occasion, for the purpose of NMR characterization, the residue was purified by flash-column chromatography over silica gel using pentane:EtOAc (7:3) to afford the pure *bis*-nosyloxime (10.91 g, 14.29 mmol, 96%) as a pale-yellow solid. Melting point = 116–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 2H), 7.96 – 7.79 (m, 6H), 7.65 (d, *J* = 8.7 Hz, 4H), 7.21 (d, *J* = 8.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.11, 136.10, 133.80, 132.38, 131.32, 127.51, 125.13, 119.59. ^{19}F NMR (471 MHz, $CDCl_3$) δ –66.09. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{28}H_{16}F_6N_4O_{11}S_2$: 762.0156, found: 762.0176.

Fig. S20. ^{1}H NMR spectrum of S8 in $CDCl_3$.

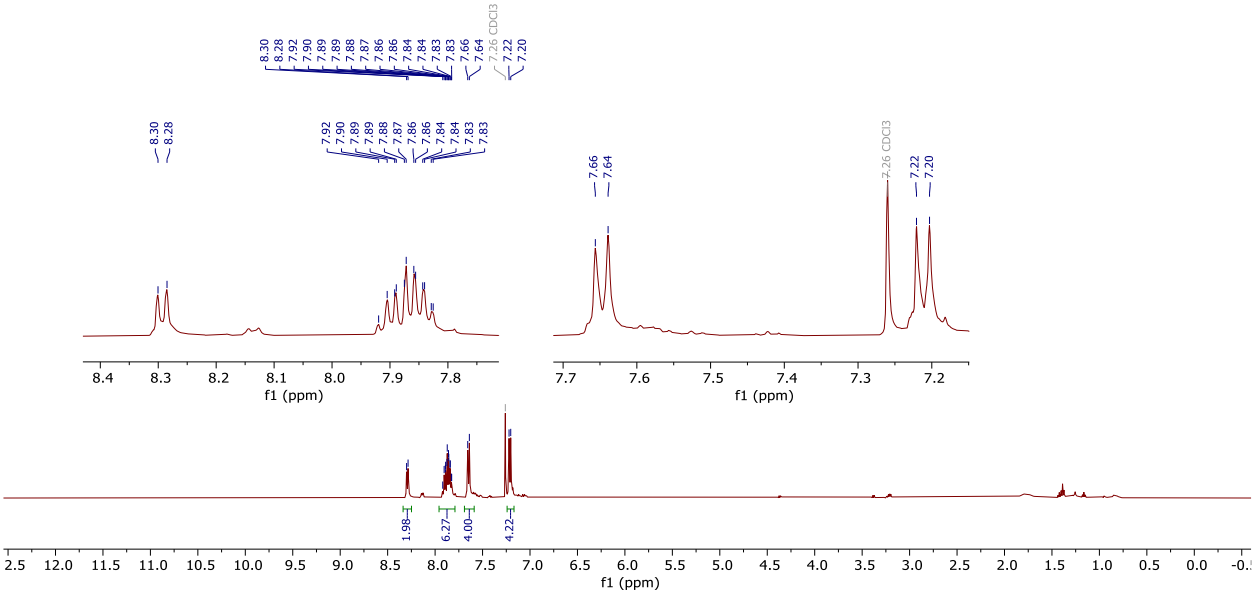


Fig. S21. ^{13}C NMR spectrum of S8 in $CDCl_3$.

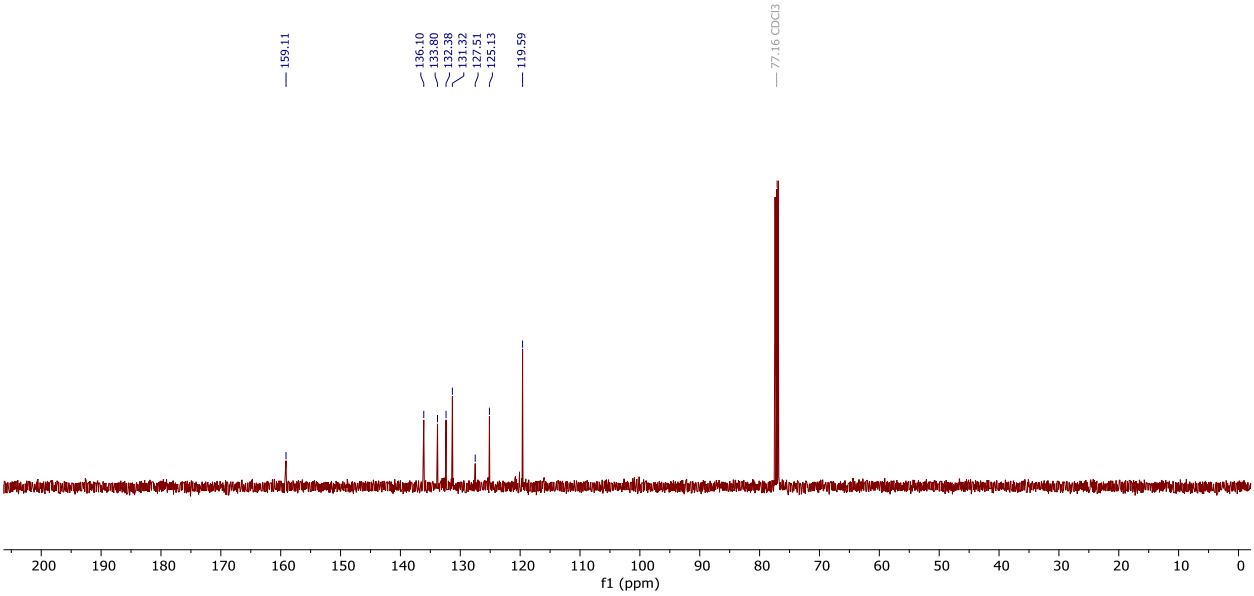
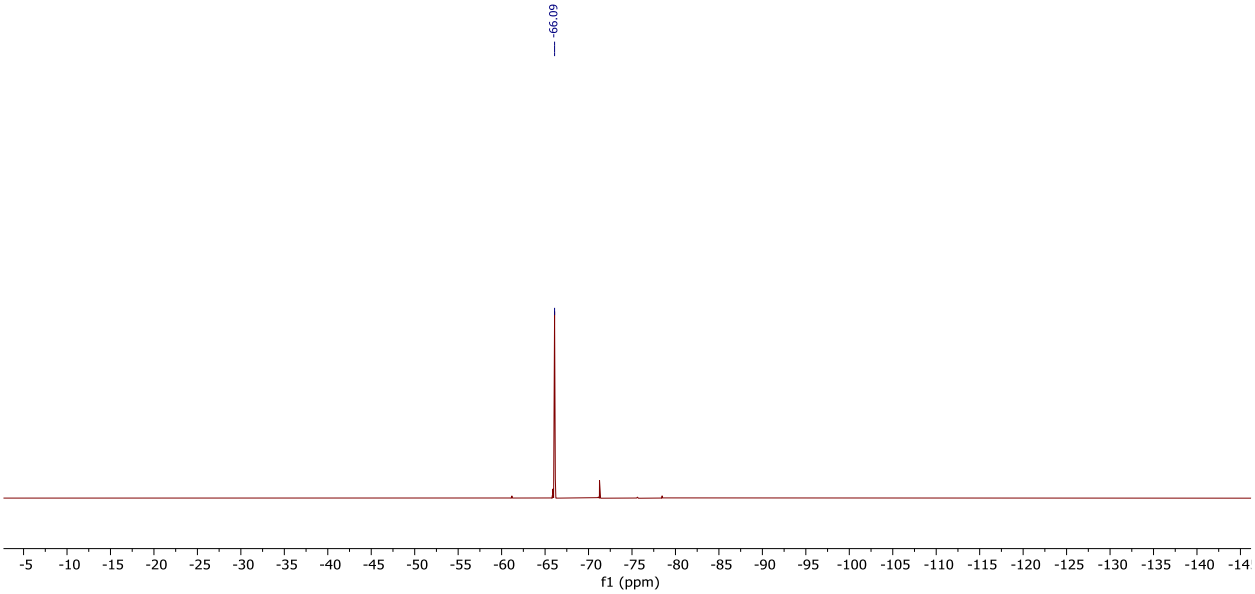
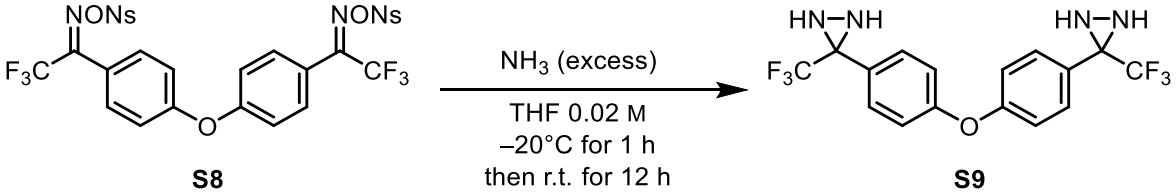


Fig. S22. ^{19}F NMR spectrum of S8 in $CDCl_3$.



Synthesis of 3,3'-(oxybis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine) (S9)



S8 **S9**

Bis-nosyloxime **S8** (10.91 g, 14.29 mmol, 1 equiv.) in anhydrous THF (70 mL) was transferred to a flame-dried 3-neck flask under argon and cooled to –20 °C. Anhydrous gaseous ammonia was bubbled into the stirred solution for 1 h. Then, the reaction was left stirring for 12 h, during which time it was allowed to warm from –20 °C to room temperature. The mixture was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 times). The combined organic layers were washed with brine and then dried with magnesium sulfate, filtered, and concentrated to afford the desired crude *bis*-diaziridine **S9** (5.4 g, 13.83 mmol, 96%) with spectroscopic data in accordance with the literature.[1] The compound was submitted to the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.7 Hz, 4H), 7.06 (d, *J* = 8.7 Hz, 4H), 2.80 (d, *J* = 9.1 Hz, 2H), 2.21 (d, *J* = 8.9 Hz, 2H).^{19}F NMR (283 MHz, $CDCl_3$) δ –75.81. IR (diamond-ATR) v: 3675, 3262, 2972, 2901, 1603, 1507, 1247, 1153, 884.

Fig. S23. ^{1}H NMR spectrum of S9 in $CDCl_3$.

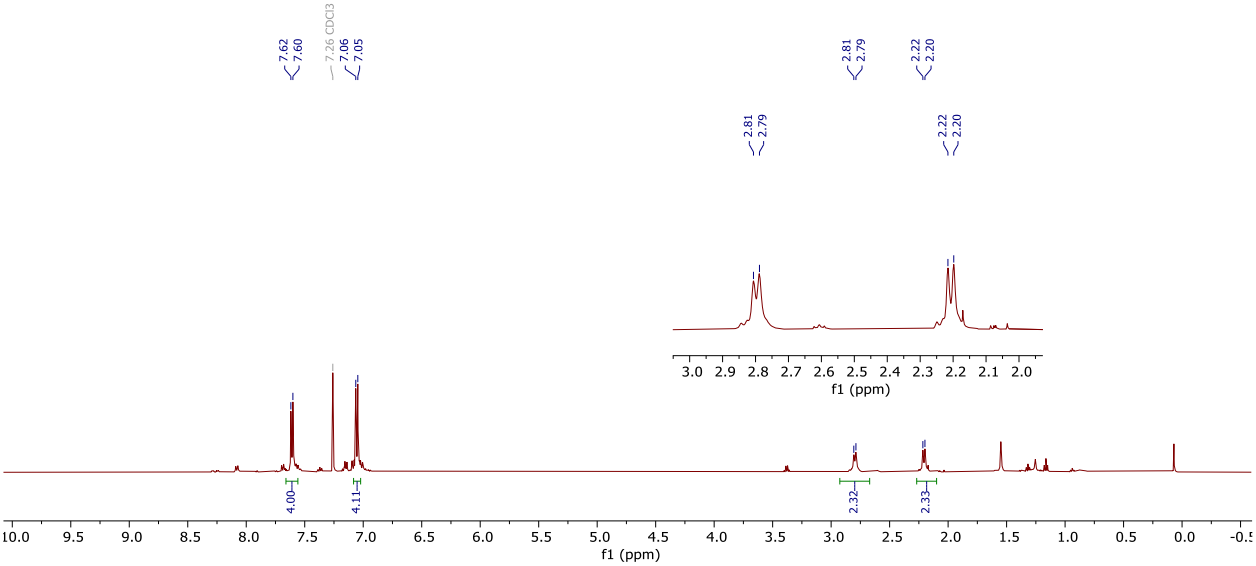
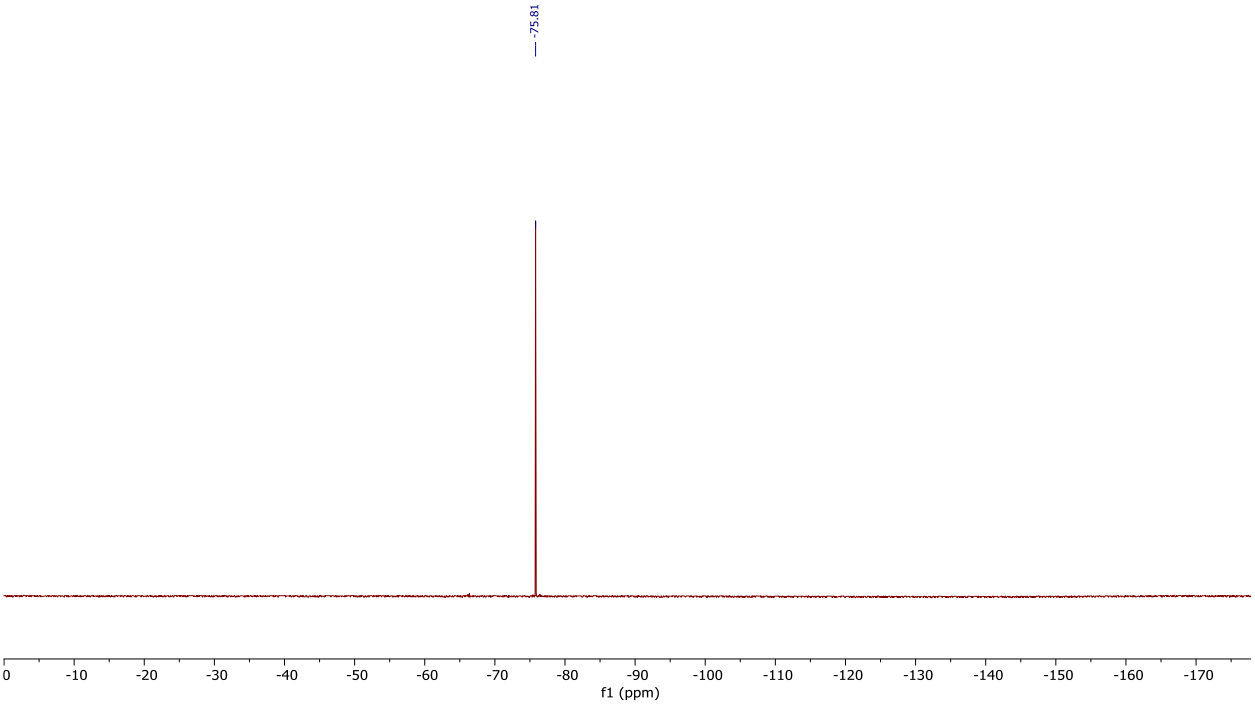
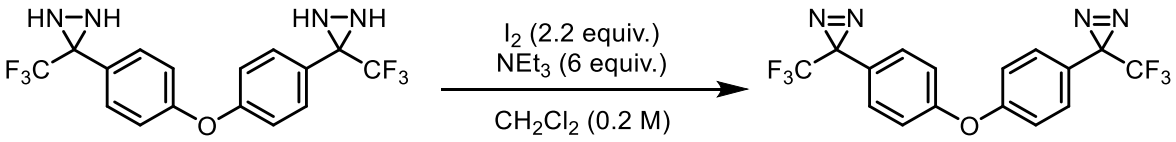


Fig. S24. ^{19}F NMR spectrum of S9 in $CDCl_3$.



Synthesis of 3,3'-(oxybis(4,1-phenylene))bis(3-(trifluoromethyl)-3H-diazirine) (3)



S9 **3**

To a solution of *bis*-diaziridine **S9** (5.77 g, 14.8 mmol, 1 equiv.) in CH_2Cl_2 (74 mL) at 0 °C were added successively triethylamine (12.4 mL, 88.8 mmol, 6 equiv.) and iodine (7.5 g, 29.6 mmol, 2 equiv.). The coloured mixture was stirred at 0 °C for 1 h. The mixture was diluted with CH_2Cl_2 and washed with sat. aq. sodium thiosulfate. The aqueous layer was re-extracted with CH_2Cl_2 (3 times). Then the combined organic extracts were washed with brine and dried with magnesium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography using pentane as eluent to afford the desired *bis*-diazirine **3** (4.66 g, 12.06 mmol, 81%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.8 Hz, 4H), 7.01 (d, *J* = 8.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.79, 128.67, 124.52, 119.45, 29.86. ^{19}F NMR (283 MHz, $CDCl_3$) δ –65.45. IR (diamond-ATR) v: 2971, 1603, 1508, 1251, 1154, 938, 827, 539. UV (*n*-hexane): λmax, diazirine = 360 nm. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{28}H_{32}F_6O$: 386.0597, found: 386.0599.

Fig. S25. ^{1}H NMR spectrum of 3 in $CDCl_3$.

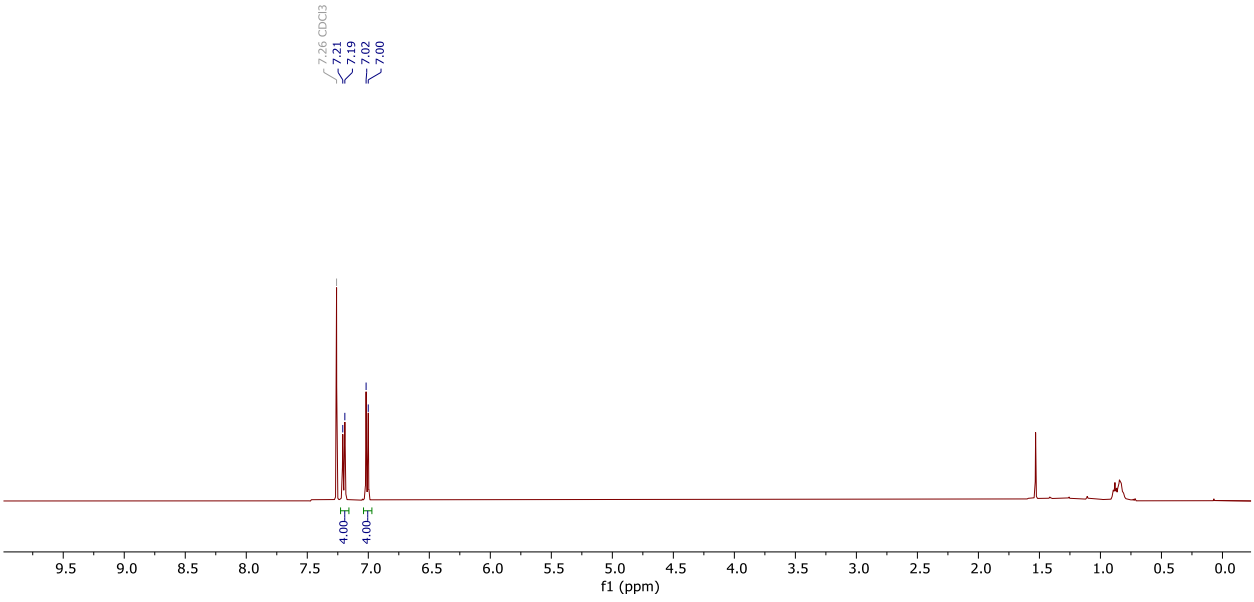


Fig. S26. ^{13}C NMR spectrum of 3 in $CDCl_3$.

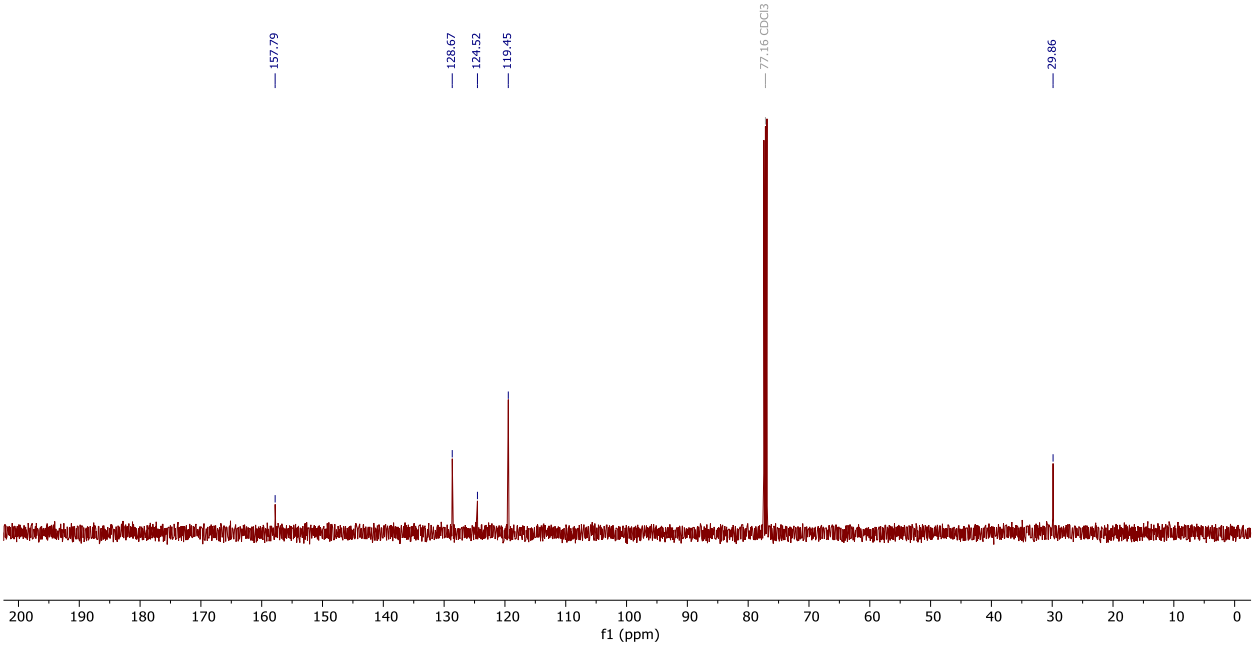
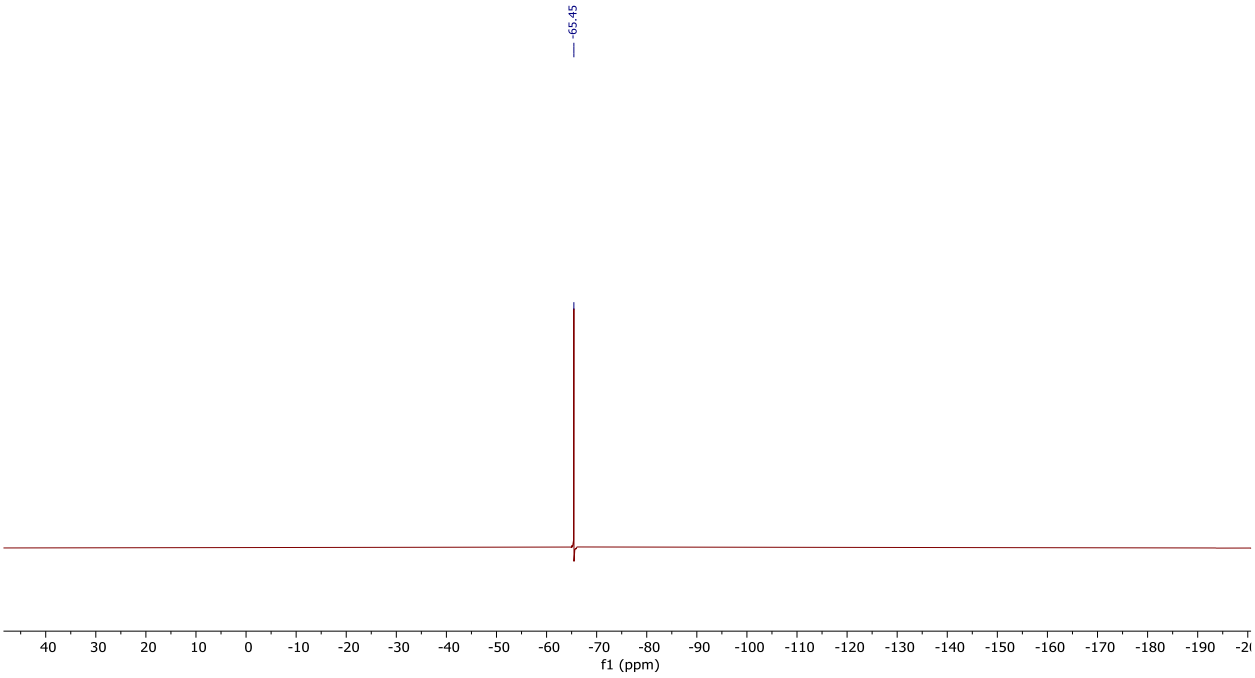
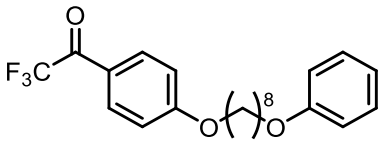


Fig. S27. ^{19}F NMR spectrum of 3 in $CDCl_3$.



Synthesis of molecular control **10**

Synthesis of 2,2,2-trifluoro-1-(4-((8-phenoxyoctyl)oxy)phenyl)ethan-1-one (S10)



S10

During the purification of 1,1'-((octane-1,8-diyl*bis*(oxy))*bis*(4,1-phenylene))*bis*(2,2,2-trifluoroethan-1-one) **S2** described above, the corresponding mono-ketone **S10**, precursor of molecular control **10**, was isolated in small amounts (260 mg, 0.6591 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.26 (tt, *J* = 7.5, 2.3 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 6.97 – 6.82 (m, 3H), 4.08 (t, *J* = 6.5 Hz, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 1.90 – 1.69 (m, 4H), 1.51 – 1.35 (m, 8H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 182.61, 165.66, 159.63, 133.05, 129.77, 122.84, 120.77, 115.31, 114.80, 69.14, 68.23, 29.68, 29.63, 29.35, 26.37, 26.23. ^{19}F NMR (283 MHz, $CDCl_3$) δ –70.95. HRMS (FD+) m/z $[M^{\bullet}]^{+}$ calculated for $C_{22}H_{25}F_3O_3$: 394.1750, found: 394.1771.

Fig. S28. ^{1}H NMR spectrum of S10 in CD_2Cl_2.

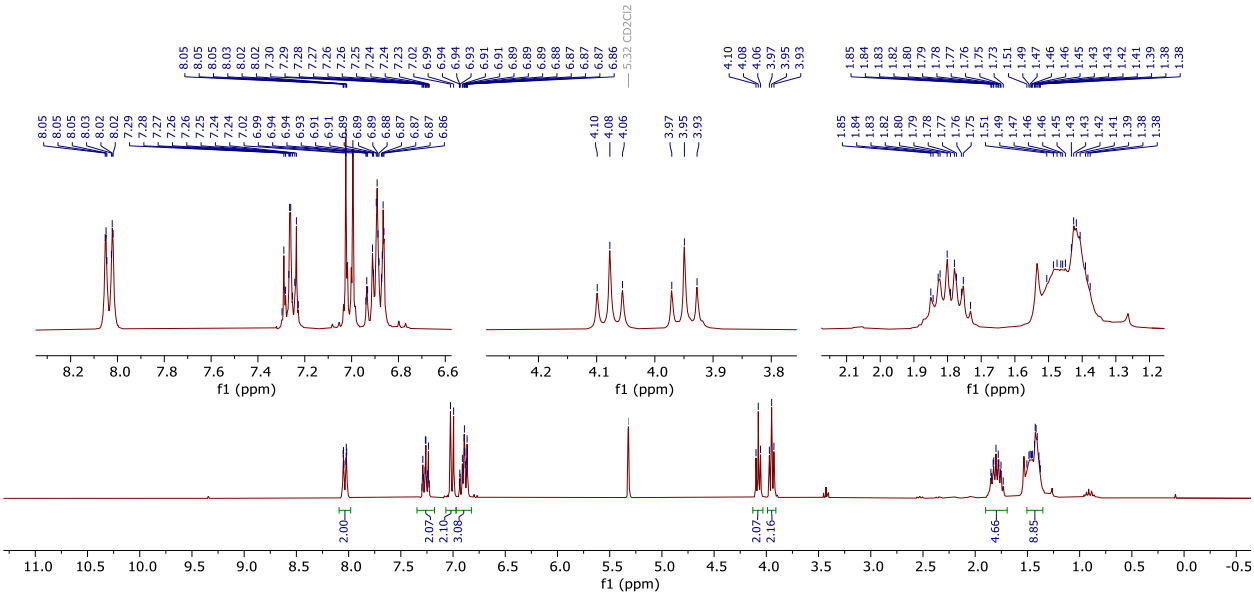


Fig. S29. ^{13}C NMR spectrum of S10 in CD_2Cl_2.

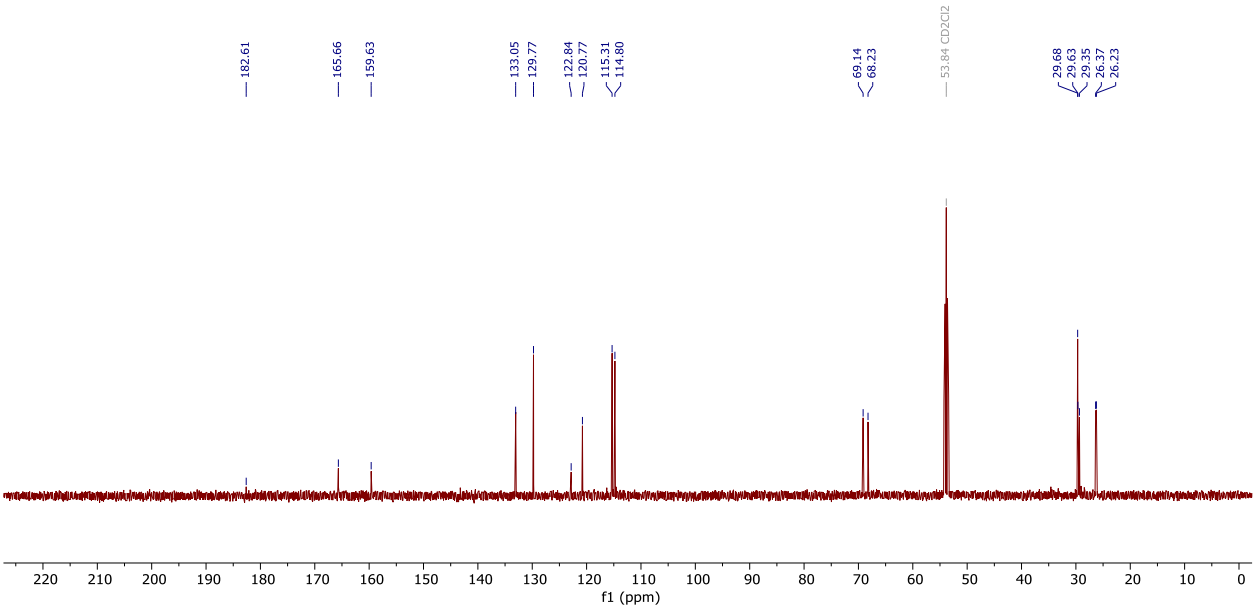
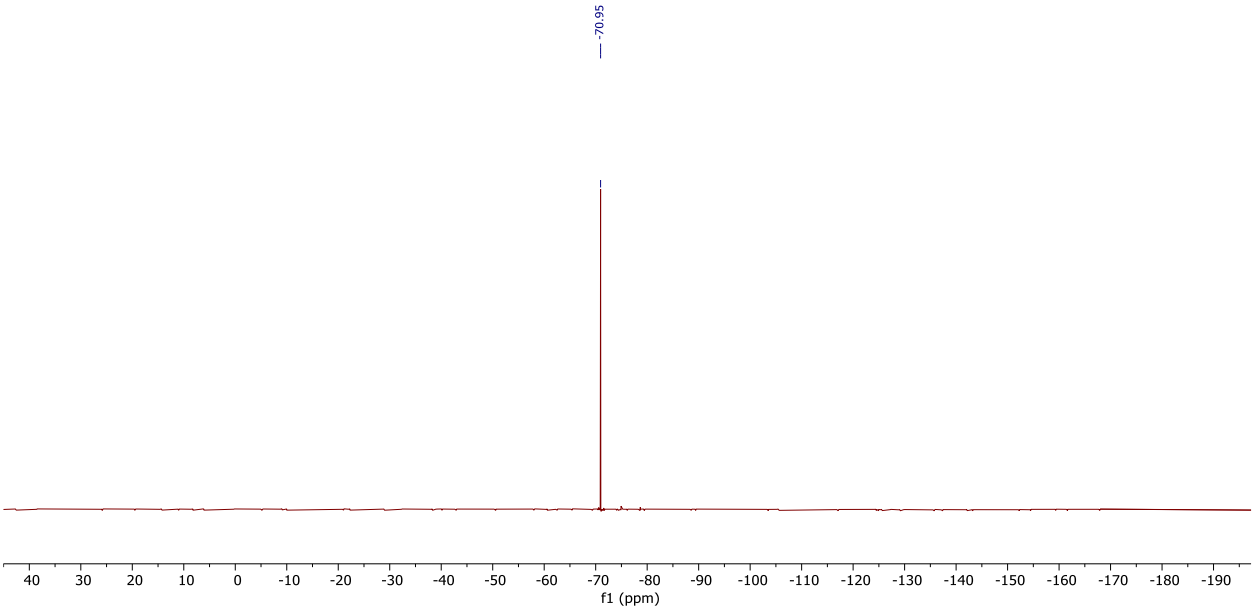
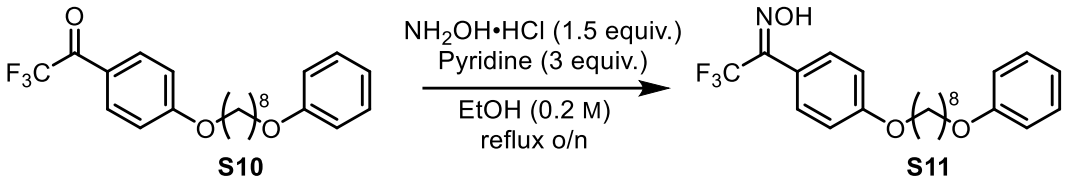


Fig. S30. ^{19}F NMR spectrum of S10 in $CDCl_3$.



Synthesis of 2,2,2-trifluoro-1-(4-((8-phenoxyoctyl)oxy)phenyl)ethan-1-one oxime (S11)



To a stirred solution of compound **S10** (260 mg, 0.6591 mmol, 1 equiv.) in ethanol (0.2 M), hydroxylamine hydrochloride (65.6 mg, 0.943 mmol, 1.5 equiv.) and pyridine (0.16 mL, 1.97 mmol, 3 equiv.) were added and the reaction mixture was heated to reflux for 16 h. The mixture was then cooled to room temperature and the mixture was treated with 2M HCl and extracted with Et_2O (3 times). The combined organic layers were washed with distilled water until the pH of the washing layer became neutral, and then dried with sodium sulfate, filtered, and concentrated. The residue was dried under high vacuum for a prolonged time to afford the desired crude oxime **S11** (as a mixture of geometric isomers) as a white solid (261.3 mg). ^{1}H NMR (500 MHz, Acetone) δ 11.63 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.93 – 6.85 (m, 3H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.85 – 1.73 (m, 4H), 1.51 (q, *J* = 6.8, 6.3 Hz, 4H), 1.43 (dt, *J* = 14.5, 7.4 Hz, 4H). ^{19}F NMR (471 MHz, Acetone) δ –63.02, –66.41.

Fig. S31. ^{1}H NMR spectrum of S11 in $(CD_3)_2CO$.

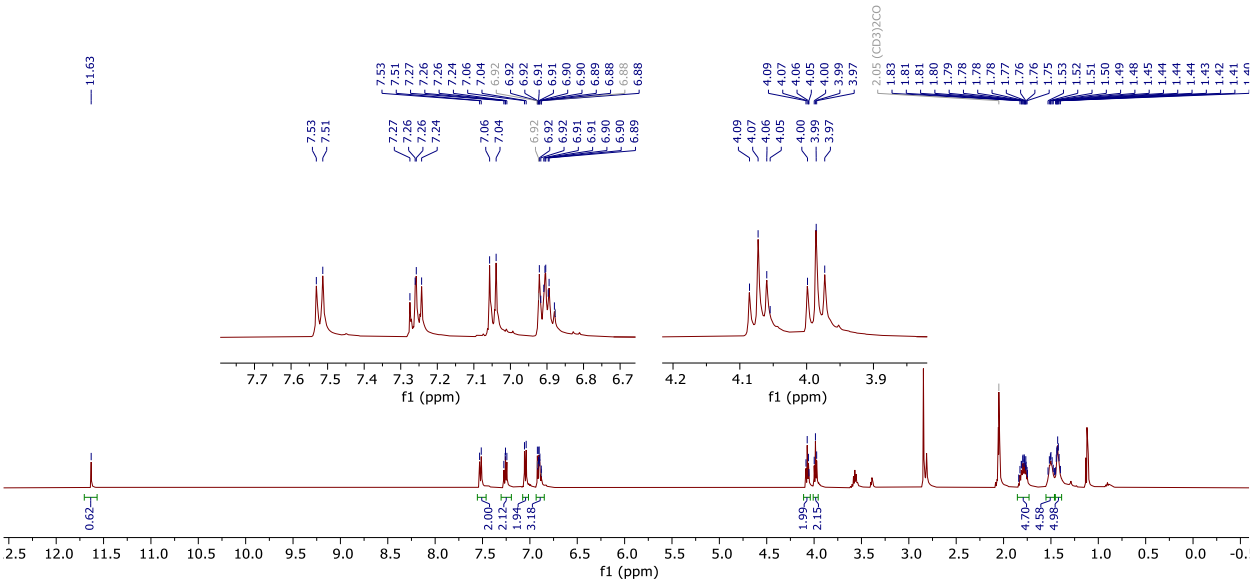
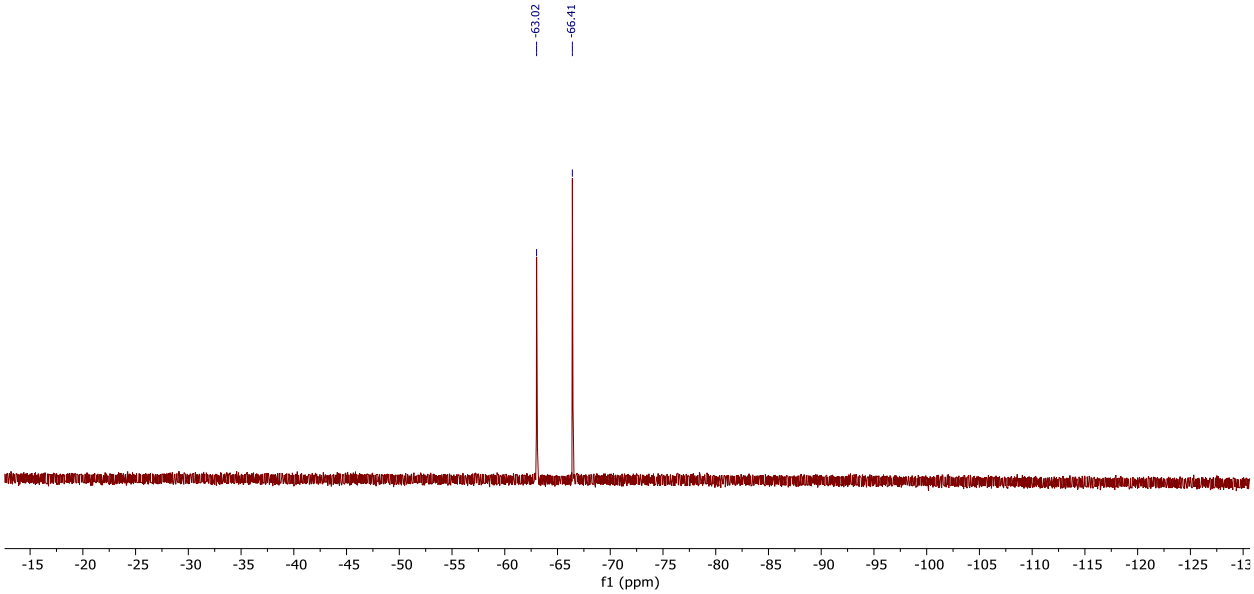
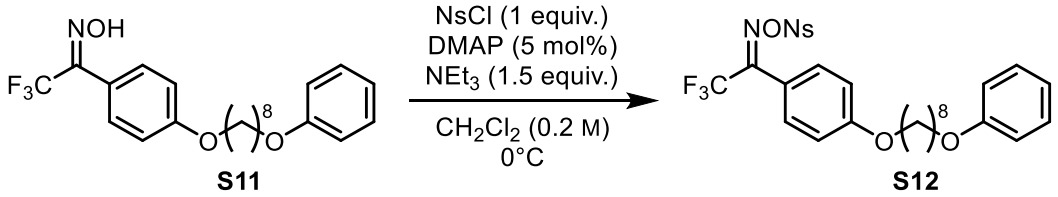


Fig. S32. ^{19}F NMR spectrum of S11 in $(CD_3)_2CO$.



Synthesis of 2,2,2-trifluoro-1-(4-((8-phenoxyoctyl)oxy)phenyl)ethan-1-one O-((2-nitrophenyl)sulfonyl) oxime (S12)



Compound **S11** (261 mg, 0.638 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (4 mL), and triethylamine (0.133 mL, 0.957 mmol, 1.5 equiv.), DMAP (4 mg, 0.032 mmol, 5 mol%) and nosyl chloride (141.4 mg, 0.638 mmol, 1 equiv.) were successively added at 0 °C. The ice bath was removed after 5 min, and the reaction mixture was stirred at room temperature for 30 min. The mixture was then treated with sat. aq. NH_4Cl and extracted with CH_2Cl_2. The combined organic extracts were dried with magnesium sulfate, filtered, and concentrated to afford the desired crude nosyloxime **S12** (380 mg), which was submitted to the next step without further purification. ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 7.93 – 7.78 (m, 3H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.92 – 6.86 (m, 3H), 4.00 – 3.91 (m, 4H), 1.87 – 1.73 (m, 8H), 1.65 – 1.57 (m, 2H), 1.52 – 1.45 (m, 8H).^{19}F NMR (471 MHz, $CDCl_3$) δ –61.16, 65.60 (major isomer).

Fig. S33. ^{1}H NMR spectrum of S12 in $CDCl_3$.

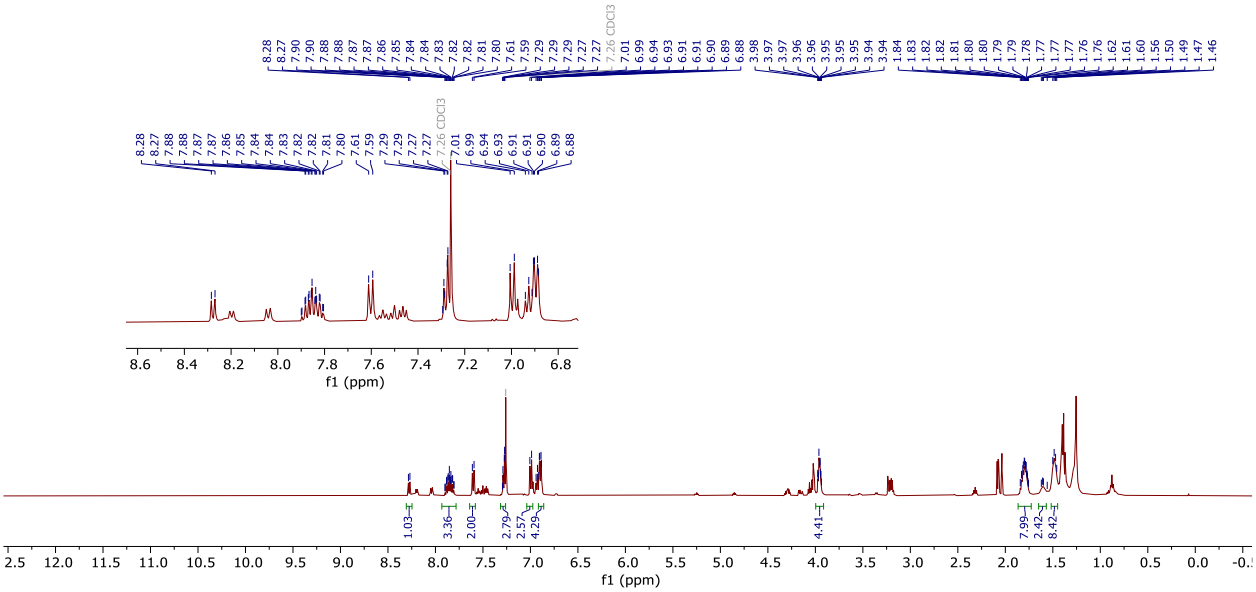
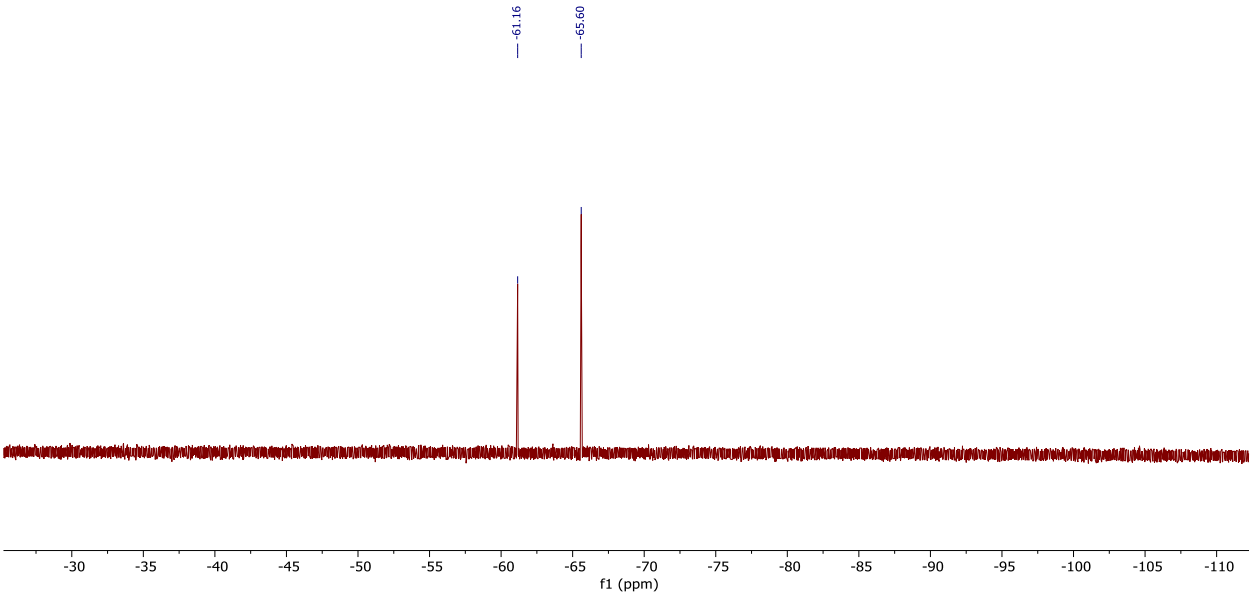
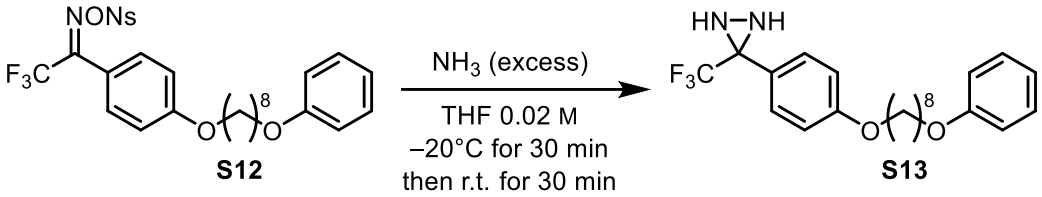


Fig. S34. ^{19}F NMR spectrum of S12 in $CDCl_3$.



Synthesis of 3-(4-((8-phenoxyoctyl)oxy)phenyl)-3-(trifluoromethyl)diaziridine (S13)



Nosyloxime **S12** (380 mg, 0.63 mmol, 1 equiv.) in anhydrous THF (20 mL) was transferred to a flame-dried 3-neck flask under argon and cooled to –20 °C. Anhydrous gaseous ammonia was bubbled into the stirred solution for 30 min. Then, the reaction was left stirring for 30 min, during which time it was allowed to warm from –20 °C to room temperature. The mixture was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 times). The combined organic layers were washed with brine and then dried with magnesium sulfate, filtered, and concentrated to afford the desired crude diaziridine **S13** (256 mg) as yellow solid, which was submitted to the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.25 (m, 2H), 6.98 – 6.84 (m, 5H), 3.96 (q, *J* = 6.3 Hz, 4H), 2.74 (d, *J* = 8.8 Hz, 1H), 2.16 (d, *J* = 8.9 Hz, 1H), 1.79 (p, *J* = 6.7 Hz, 4H), 1.54 – 1.44 (m, 4H), 1.43 – 1.36 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.56, 159.24, 129.58, 129.55, 123.61, 122.51 (d, *J* = 41.7 Hz), 120.62, 114.76, 114.63, 68.21, 67.94, 29.85, 29.46, 29.44, 29.41, 29.26, 26.15, 26.08. ^{19}F NMR (471 MHz, $CDCl_3$) δ –75.87. IR (diamond-ATR) v: 3258, 2928, 2856, 1727, 1613, 1518, 1471, 1245, 1152, 1033, 754, 692.

Fig. S35. ^{1}H NMR spectrum of S13 in $CDCl_3$.

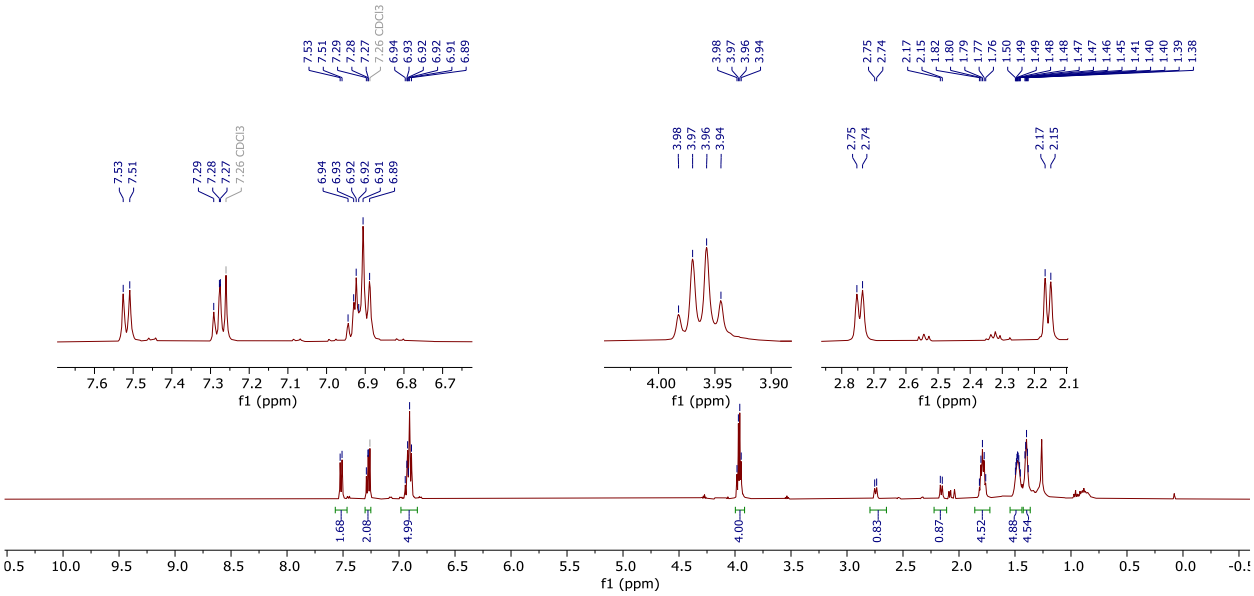


Fig. S36. ^{13}C NMR spectrum of S13 in $CDCl_3$.

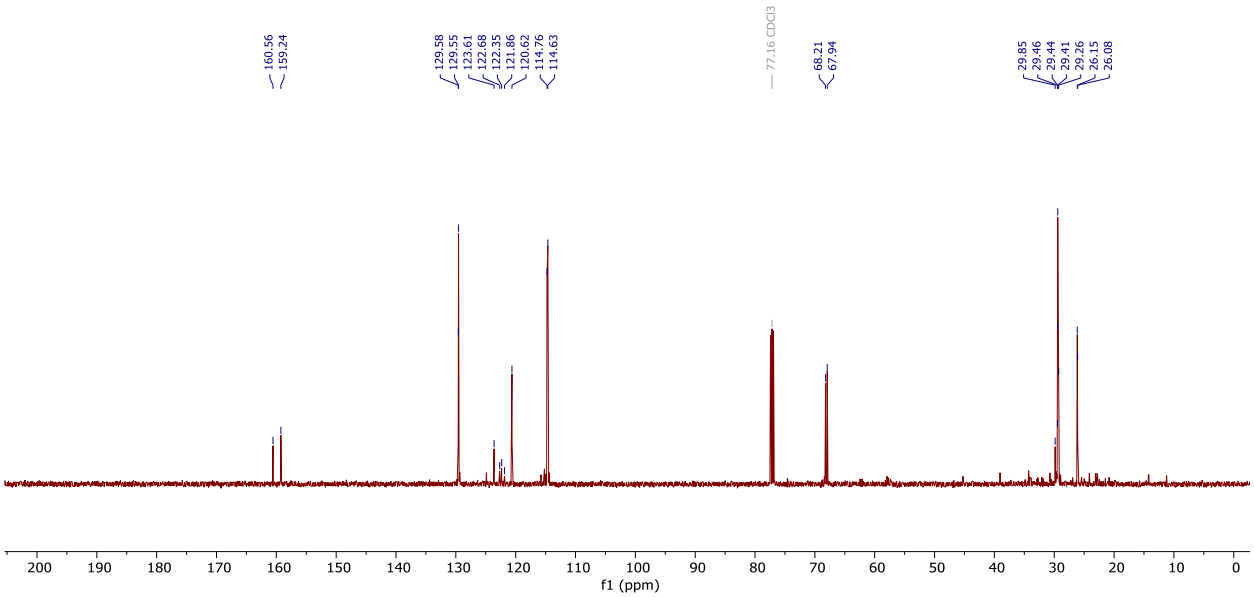
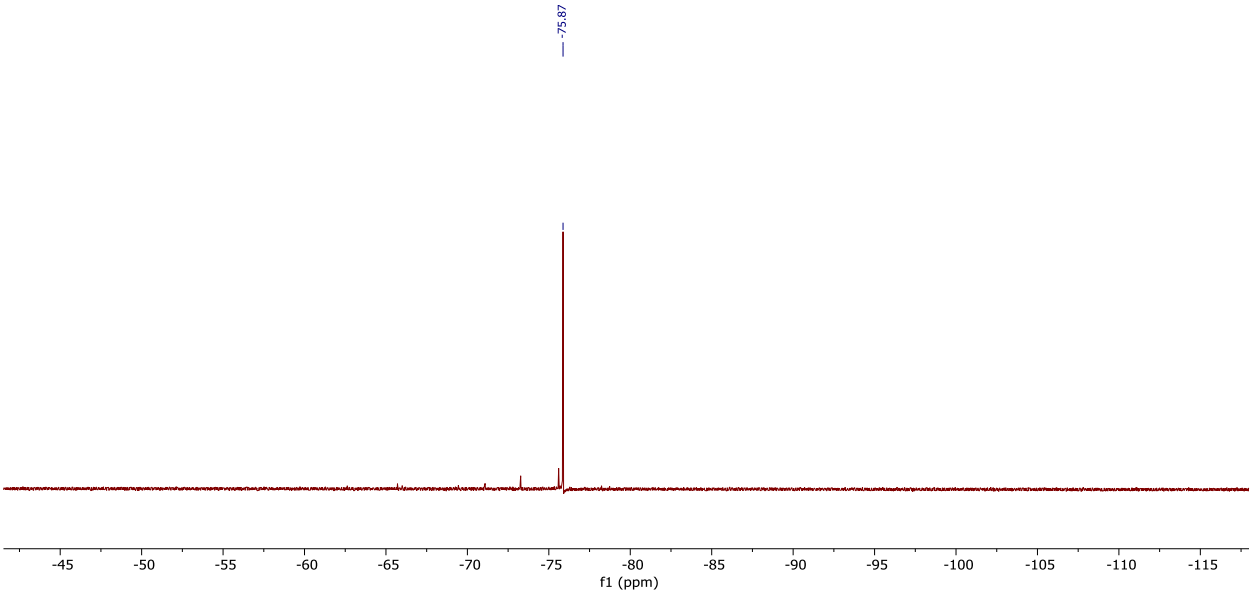
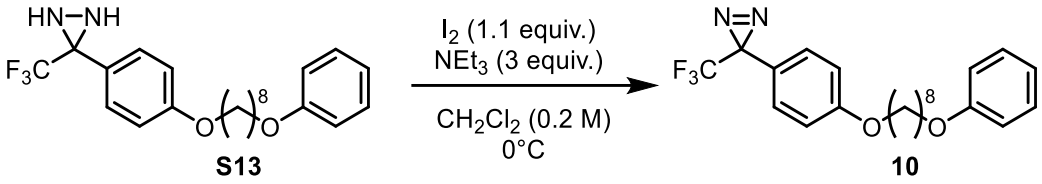


Fig. S37. ^{19}F NMR spectrum of S13 in $CDCl_3$.



Synthesis of 3-(4-((8-phenoxyoctyl)oxy)phenyl)-3-(trifluoromethyl)-3H-diazirine (10)



To a solution of the crude diaziridine **S13** (256 mg) in CH_2Cl_2 (4 mL) at 0 °C were added successively triethylamine (0.27 mL, 1.91 mmol, 3 equiv.) and iodine (178 mg, 0.702 mmol, 1.1 equiv.). The coloured mixture was stirred at 0 °C for 1 h. The mixture was diluted with CH_2Cl_2 and washed with sat. aq. sodium thiosulfate. The aqueous layer was re-extracted with CH_2Cl_2 (3 times). Then the combined organic extracts were washed with brine and dried with magnesium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography using pentane: Et_2O (8:2, R_f =0.71) as eluent to afford the desired diazirine **10** (250 mg, 0.62 mmol, 98%) as a yellow solid. Melting point = 41–42 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.26 (dd, *J* = 8.7, 7.2 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.98 – 6.89 (m, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 3.95 (q, *J* = 6.5 Hz, 4H), 1.81 – 1.73 (m, 4H), 1.52 – 1.43 (m, 4H), 1.40 (dt, *J* = 6.7, 4.6 Hz, 4H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.81, 159.63, 129.77, 128.50, 123.86, 120.78, 120.76, 120.74, 115.28, 114.80, 68.63, 68.25, 29.70, 29.68, 29.48, 26.38, 26.29. ^{19}F NMR (471 MHz, $CDCl_3$) δ –65.67. IR (diamond-ATR) v: 2929, 2857, 1723, 1601, 1518, 1497, 1244, 1180, 1154, 1054, 939, 754, 692. HRMS (FD+) m/z $[M^{\bullet}]^+$ calculated for $C_{22}H_{25}F_3N_2O_2$: 406.1863, found: 406.1877.

Fig. S38. ^{1}H NMR spectrum of 10 in CD_2Cl_2.

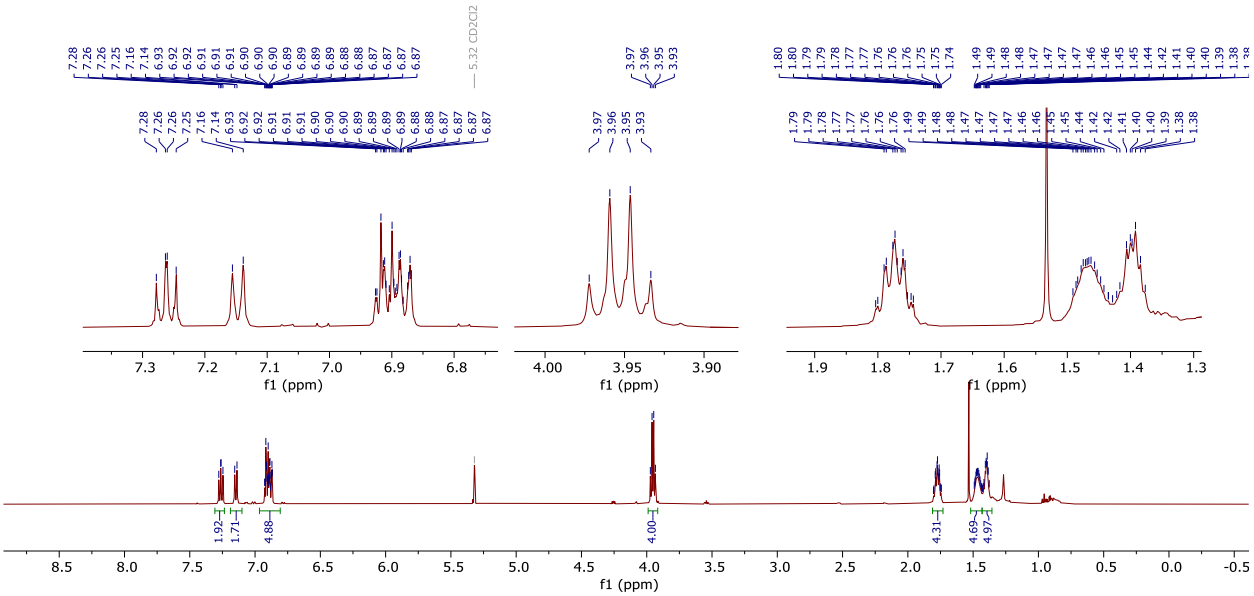


Fig. S39. ^{13}C NMR spectrum of 10 in CD_2Cl_2.

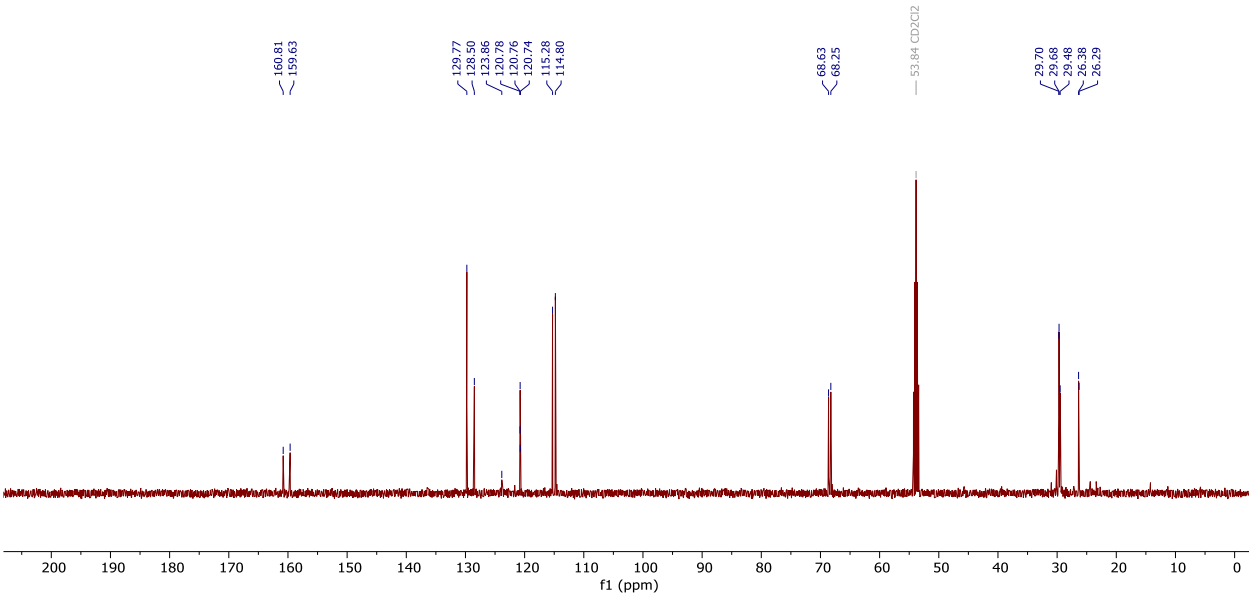
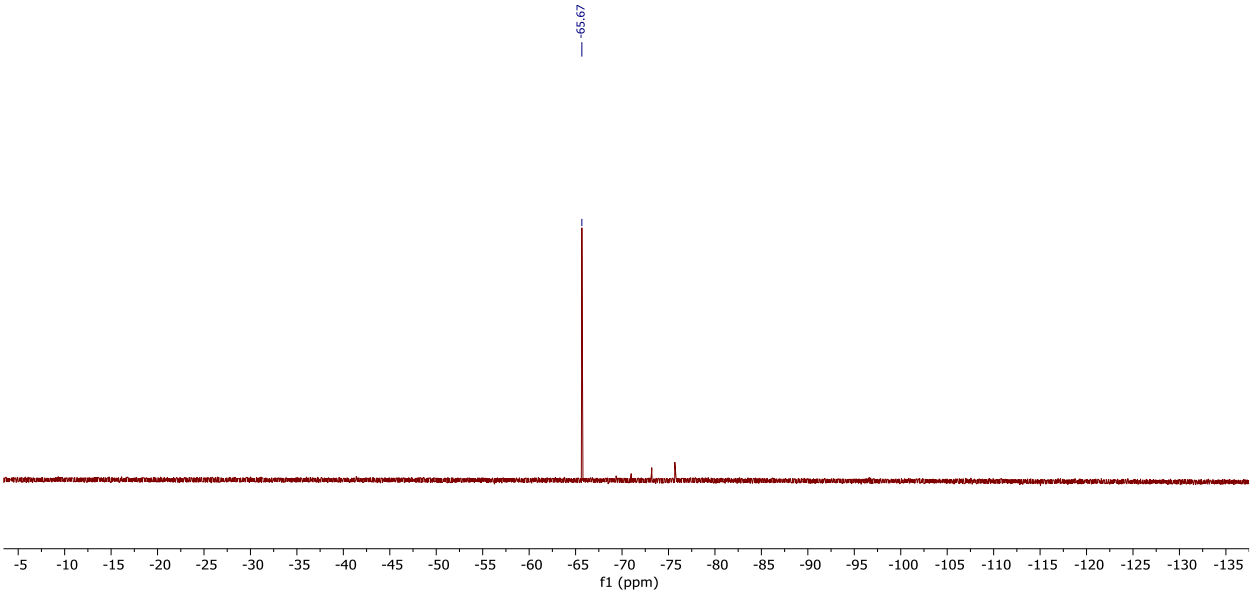
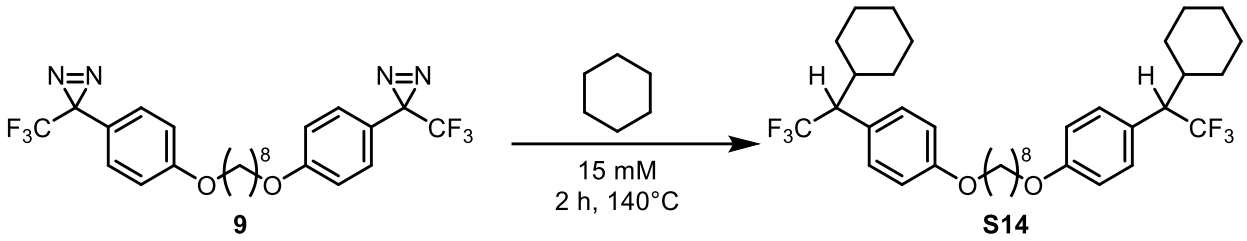


Fig. S40. ^{19}F NMR spectrum of 10 in $CDCl_3$.



Evaluation of crosslinker efficacy by crosslinking of cyclohexane

Cyclohexane crosslinking with bis-diazirine 9



In a flame-dried sealed tube, *bis*-diazirine **9** (11.3 mg, 0.022 mmol, 1 equiv.) in cyclohexane (15 mM), flushed gently with argon and capped, was heated at 140 °C for 2 h. After cooling the mixture to room temperature, the reaction mixture was transferred into a round bottom flask and concentrated in vacuo to provide crude product (14 mg). Flash-column chromatography over silica gel using 100% petroleum ether afforded 1,8-*bis*(4-(1-cyclohexyl-2,2,2-trifluoroethyl)phenoxy)octane **S14** (12 mg, 0.02 mmol) in 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 3.94 (t, *J* = 6.5 Hz, 4H), 2.97 (qd, *J* = 10.3, 7.9 Hz, 2H), 2.04 – 1.86 (m, 4H), 1.84 – 1.65 (m, 8H), 1.68 – 1.57 (m, 4H), 1.45 – 1.35 (m, 8H), 1.34 – 1.28 (m, 2H), 1.20 – 1.02 (m, 6H), 0.84 – 0.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.78, 132.34, 130.34, 128.94 (q, *J* = 118.0 Hz), 114.45, 68.01, 55.31 (q, *J* = 25.8 Hz), 38.68, 31.67, 30.81, 29.85, 29.46, 29.43, 26.34, 26.26, 26.17. ^{19}F NMR (283 MHz, $CDCl_3$) δ –63.73. HRMS (FD+) m/z $[M^{\bullet}]^{+}$ calculated for $C_{36}H_{48}F_6O_2$: 626.3553, found: 626.3565.

Fig. S41. ^{1}H NMR spectrum of S14 in $CDCl_3$.

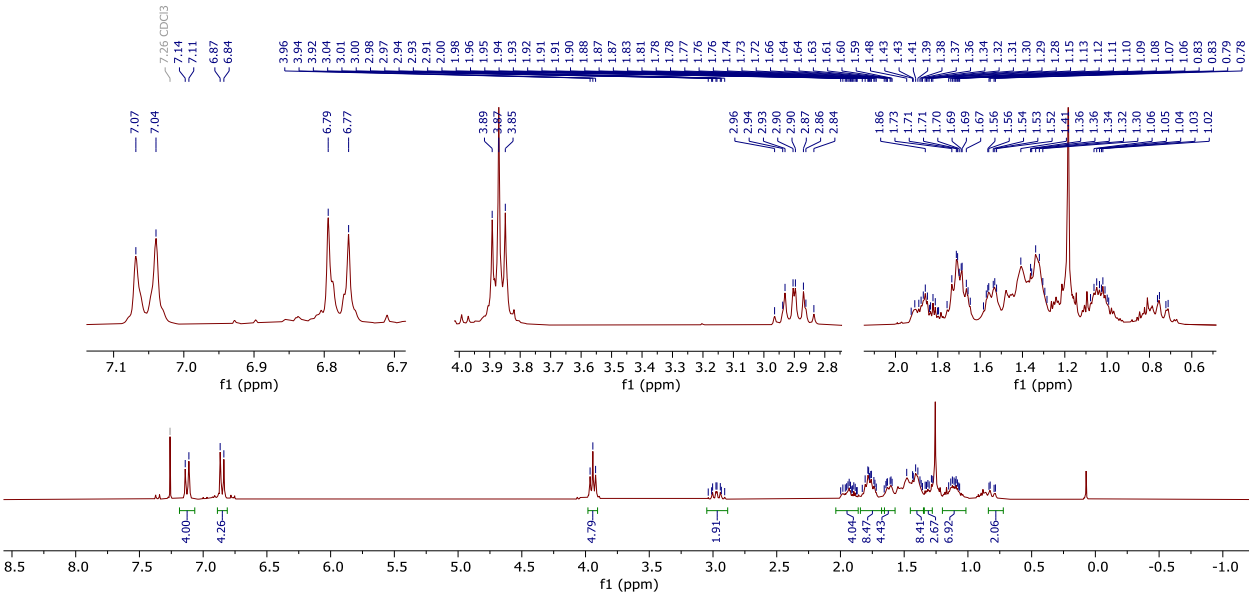


Fig. S42. ^{13}C NMR spectrum of S14 in $CDCl_3$.

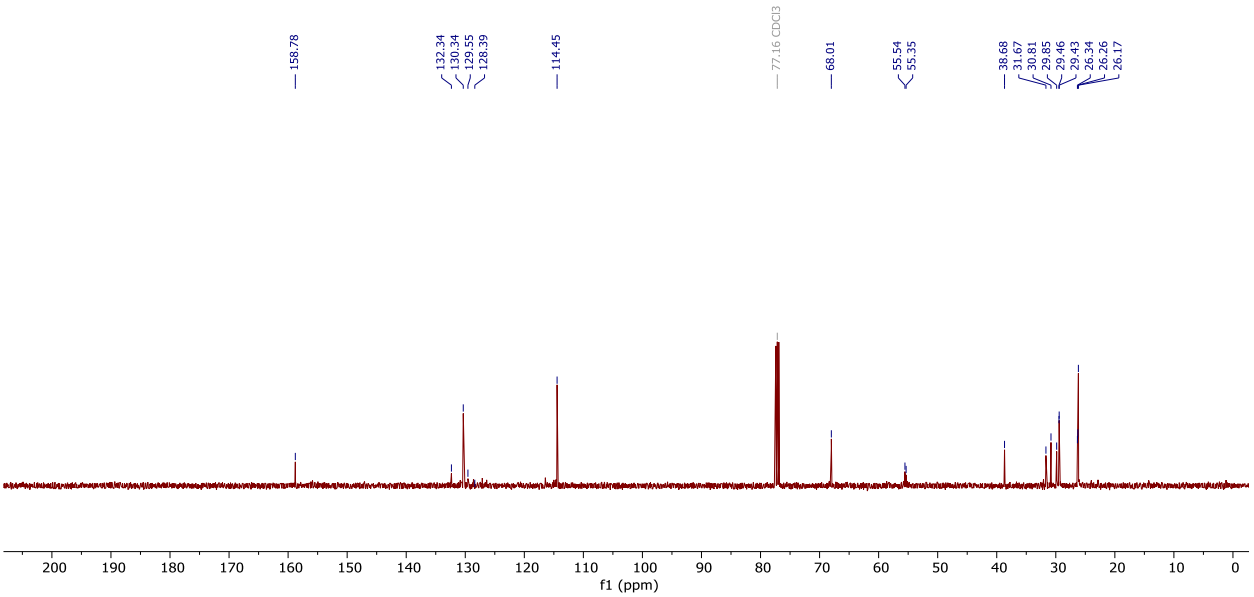
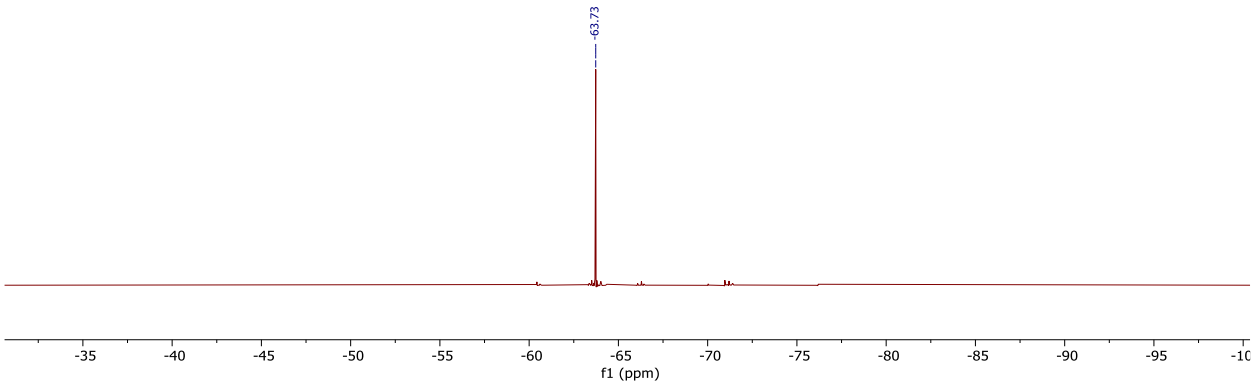
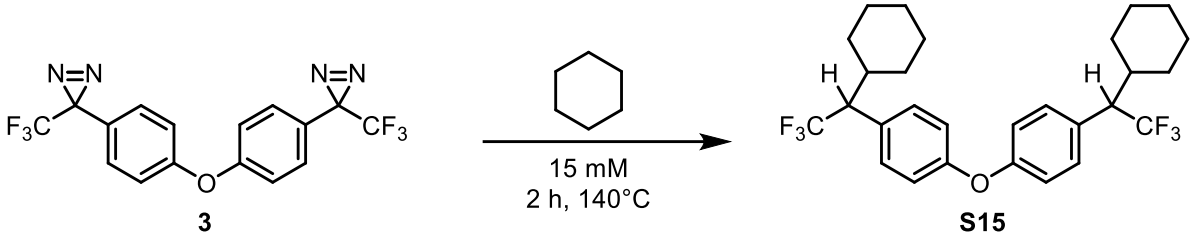


Fig. S43. ^{19}F NMR spectrum of S14 in $CDCl_3$.



Cyclohexane crosslinking with bis-diazirine 3



In a flame-dried sealed tube, *bis*-diazirine **3** (24.9 mg, 0.064 mmol, 1 equiv.) in cyclohexane (15 mM), flushed gently with argon and capped, was heated at 140 °C for 2 h. After cooling the mixture to room temperature, the reaction mixture was transferred into a round bottom flask and concentrated in vacuo to provide crude product (34.6 mg). Flash-column chromatography overs silica gel 100% petroleum ether afforded 4,4'-oxy-*bis*((1-cyclohexyl-2,2,2-trifluoroethyl)benzene) **S15** (17.6 mg, 0.034 mmol) in 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.7 Hz, 4H), 6.98 (d, *J* = 8.7 Hz, 4H), 3.03 (qd, *J* = 10.4, 9.9 Hz, 2H), 2.03 – 1.84 (m, 5H), 1.84 – 1.71 (m, 2H), 1.68 – 1.59 (m, 5H), 1.22 – 1.01 (m, 8H), 0.85 – 0.72 (m, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 156.68, 130.69, 118.92, 55.61 (q, *J* = 25.2 Hz), 38.69, 31.63, 30.85, 29.85, 26.30, 26.24, 26.15. ^{19}F NMR (283 MHz, $CDCl_3$) δ –63.60. HRMS (FD+) m/z $[M^{\bullet}]^{+}$ calculated for $C_{28}H_{32}F_6O$: 498.2352, found: 498.2340.

Fig. S44. ^{1}H NMR spectrum of S15 in $CDCl_3$.

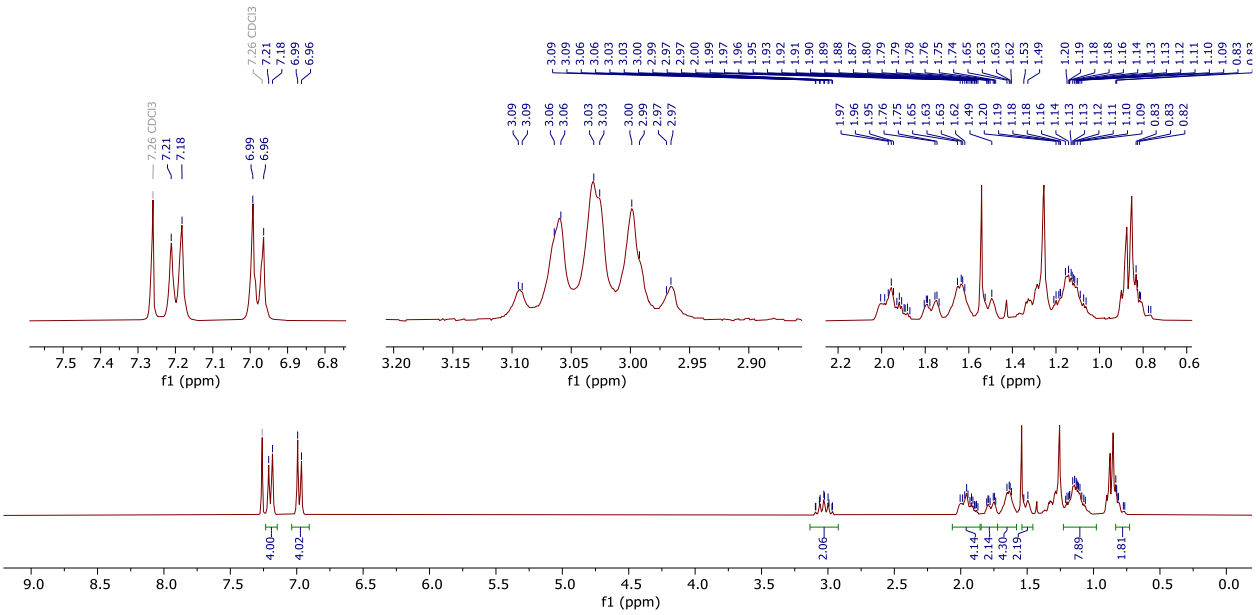


Fig. S45. ^{13}C NMR spectrum of S15 in $CDCl_3$.

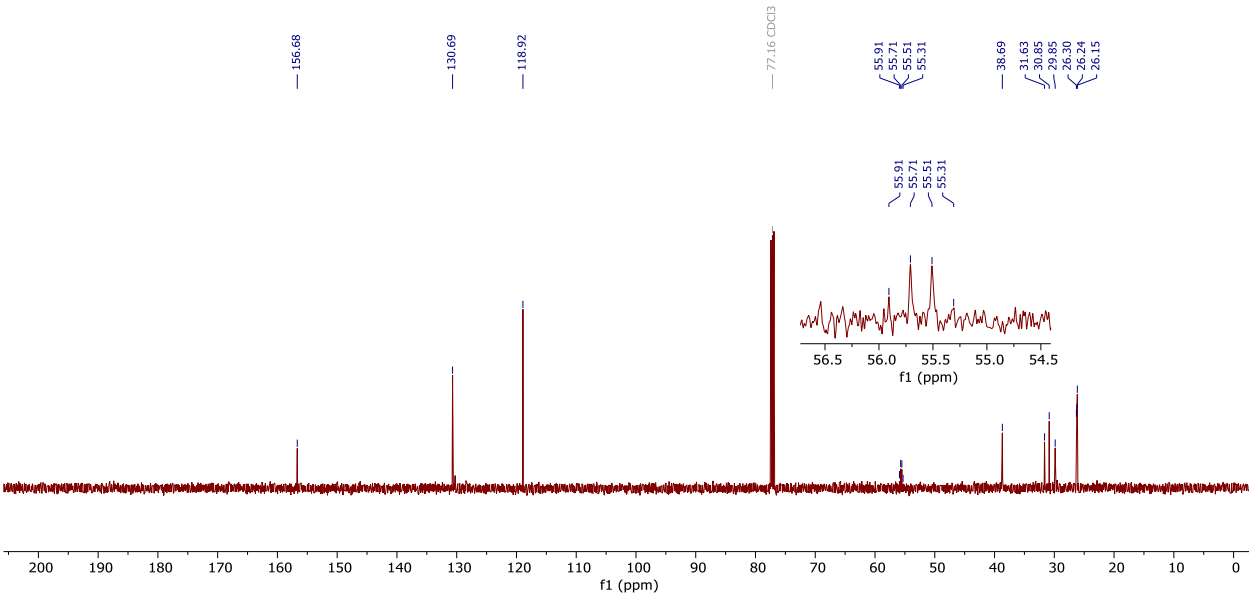
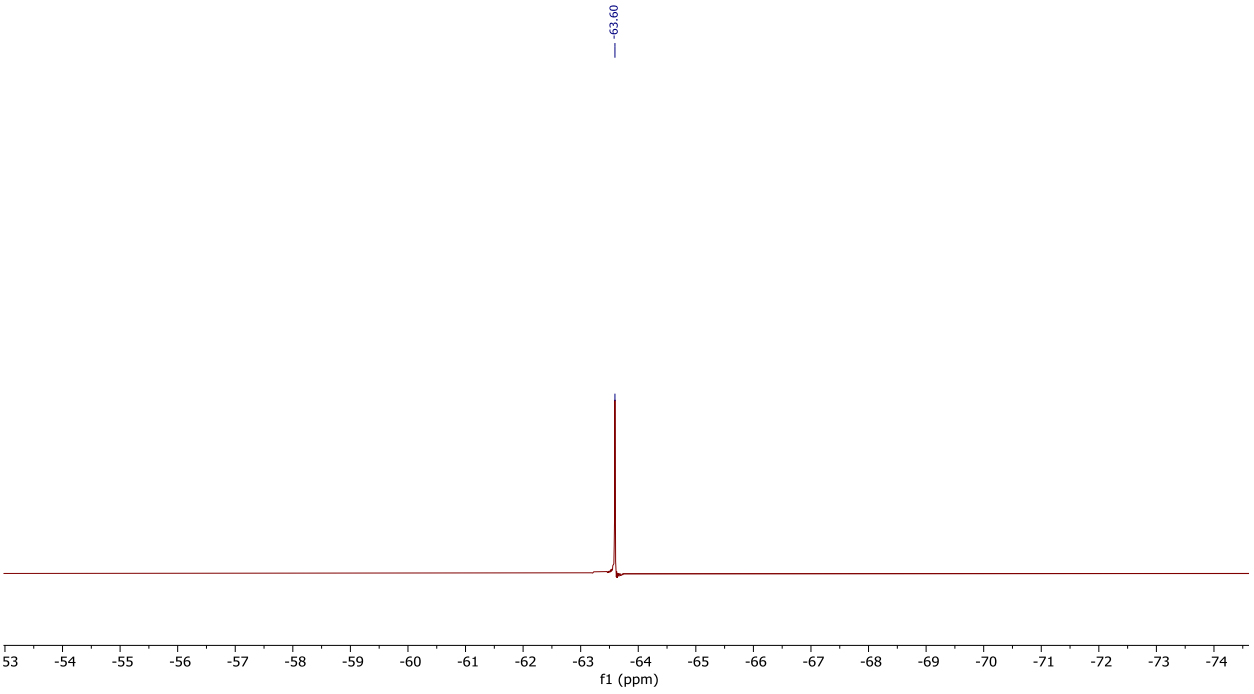


Fig. S46. ^{19}F NMR spectrum of S15 in $CDCl_3$.



Crosslinking of cyclohexane under mild conditions

General protocols for insertion reactions

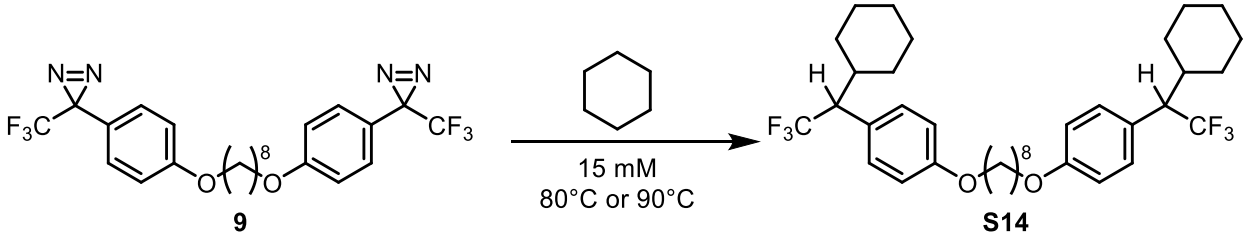
A) Thermal insertion reaction: a 15 mM solution of the desired crosslinker in cyclohexane was prepared in a vial. The reaction was immersed in an oil bath at the desired temperature and stirred at that temperature for the desired time. After cooling the mixture to room temperature, the reaction was concentrated in vacuo to provide the crude product.

B) Photochemical insertion reaction (365 nm): a 15 mM solution of the desired crosslinker in cyclohexane was prepared in a vial. The reaction was irradiated with a 365 nm UV spotlight (ThorLabs, 3685 lux, 38 W/m^2) for the desired time. The reaction was concentrated in vacuo to provide the crude product.

C) Photochemical insertion reaction (395 nm): a 15 mM solution of the desired crosslinker in cyclohexane was prepared in a vial. The reaction was irradiated with 395 nm LED Strip Lights (Waveform Lighting, 5129 lux, 53 W/m^2) for the desired time. The reaction was concentrated in vacuo to provide the crude product.

All reactions were conducted under an air atmosphere. Crude ^{19}F NMR ($CDCl_3$) spectra were collected and compared.

Cyclohexane crosslinking of bis-diazirine 9 at low temperatures



Following the above general protocol (**A**), three reactions (***a***, ***b***, ***c***) were performed at 80 °C, and two reactions were performed at 90 °C using compound **9** (12.4 mg, 0.024 mmol) dissolved in cyclohexane (1.6 mL). The reactions were heated for 1 h (***a*** and ***d***); 2 h (***b*** and ***e***); 3 h (***c***). Silica plug filtration using petroleum ether as eluent afforded *bis*-adduct product **S14;** yields are reported in the following table. Spectroscopic data are consistent with those reported above for compound **S14**.

Table S1. Thermal insertion reactions at low temperatures.

	temperature (°C)	time (h)	*bis*-adduct (%)
a	80	1	46
b	80	2	73
c	80	3	75
d	90	1	52
e	90	2	82

Fig. S47. Crude ^{19}F NMR spectra of compound 9 under thermal C–H insertion condition at 80 °C.

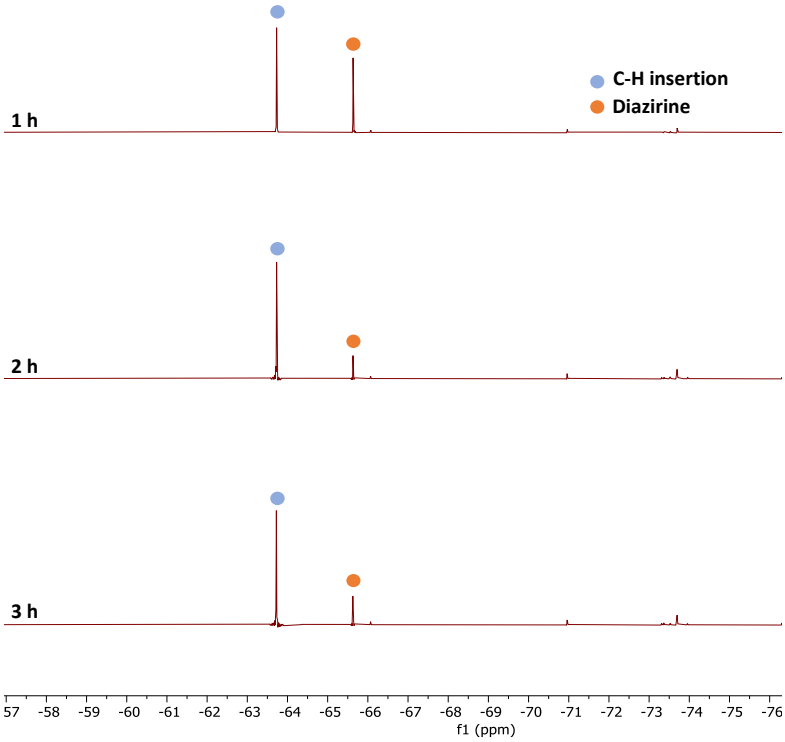
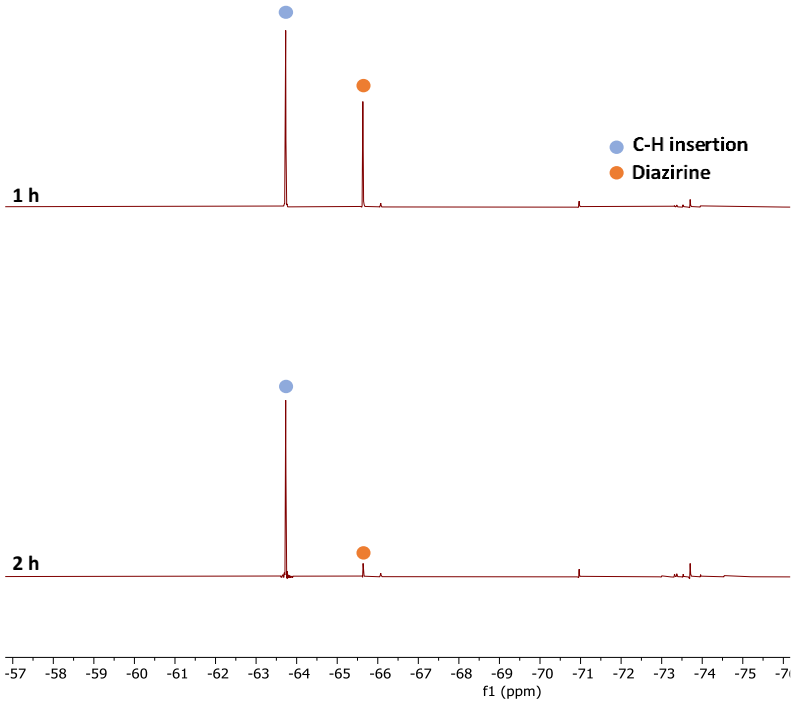
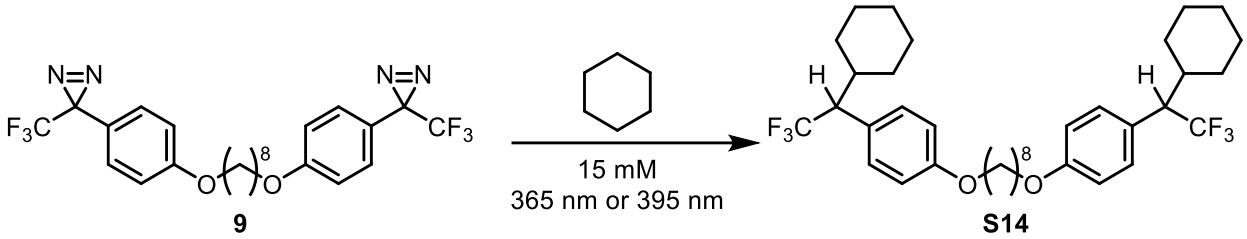


Fig. S48. Crude ^{19}F NMR spectra of compound 9 under thermal C–H insertion condition at 90 °C.



Cyclohexane crosslinking of bis-diazirines 9 and 1 at 365 and 395 nm.



Following the above general protocol (**B**), three reactions (***a***, ***b***, ***c***) were performed under 365 nm light using compound **9** (12.6 mg, 0.024 mmol) dissolved in cyclohexane (1.6 mL). The reactions were irradiated for 1 min (***a***); 5 min (***b***); 10 min (***c***).

Following the above general protocol (**C**), three reactions (***d***, ***e***, ***f***) were performed under 395 nm light using compound **9** (12.4 mg, 0.024 mmol) dissolved in cyclohexane (1.6 mL). The reactions were irradiated for 1 min (***d***); 5 min (***e***); 10 min (***f***); 60 min (***g***).

Following the above general protocol (**C**), two reactions (***h***, ***i***) were performed under 395 nm light using compound **1** (12.5 mg, 0.024 mmol) dissolved in cyclohexane (1.6 mL). The reactions were irradiated for 1 min (***h***); 10 min (***i***). *Bis*-adduct product was not observed.

Conversions of *bis*-adduct product **S14** are reported in the following table. Product **S14** in reaction (***g***) was isolated after filtration through a silica plug, using petroleum ether as eluent. Spectroscopic data are consistent with the ones reported above for compound **S14**.

Table S2. Photochemical insertion reactions.

	compound	λ (nm)	time (min)	*bis*-adduct (%)
a	**9**	365	1	40
b	**9**	365	5	75
c	**9**	365	10	76
d	**9**	395	1	67
e	**9**	395	5	75
f	**9**	395	10	81
g	**9**	395	60	93 (92)[a]
h	**1**	395	1	-
i	**1**	395	10	-

[a] Numbers in parentheses indicate isolated yield.

Fig. S49. Crude ^{19}F NMR spectra of compound 9 under photochemical C–H insertion condition, 365 nm.

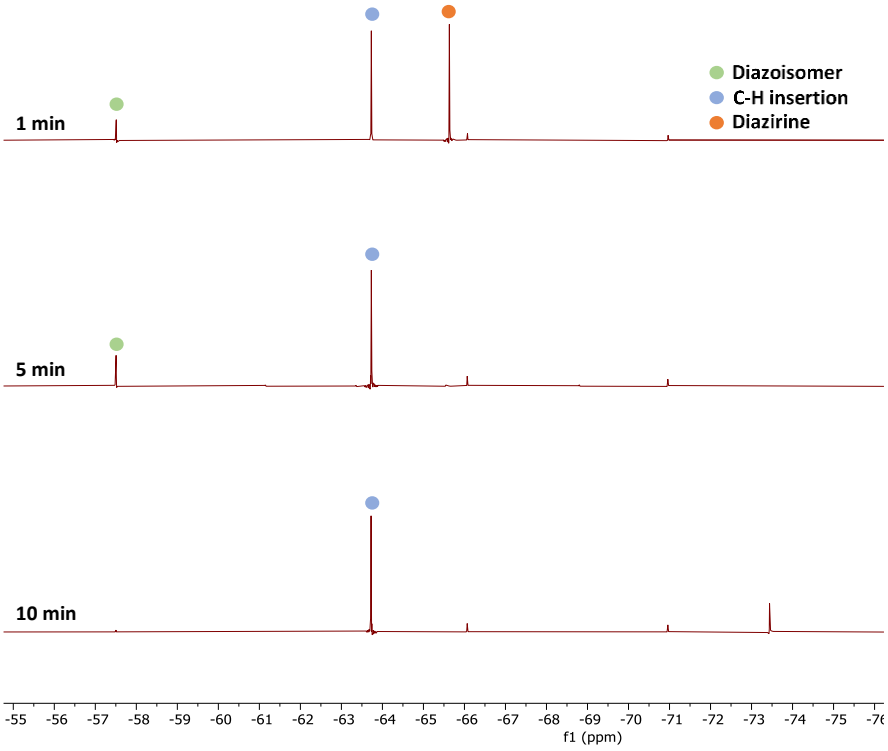


Fig. S50. Crude ^{19}F NMR spectra of compound 9 under photochemical C–H insertion condition, 395 nm.

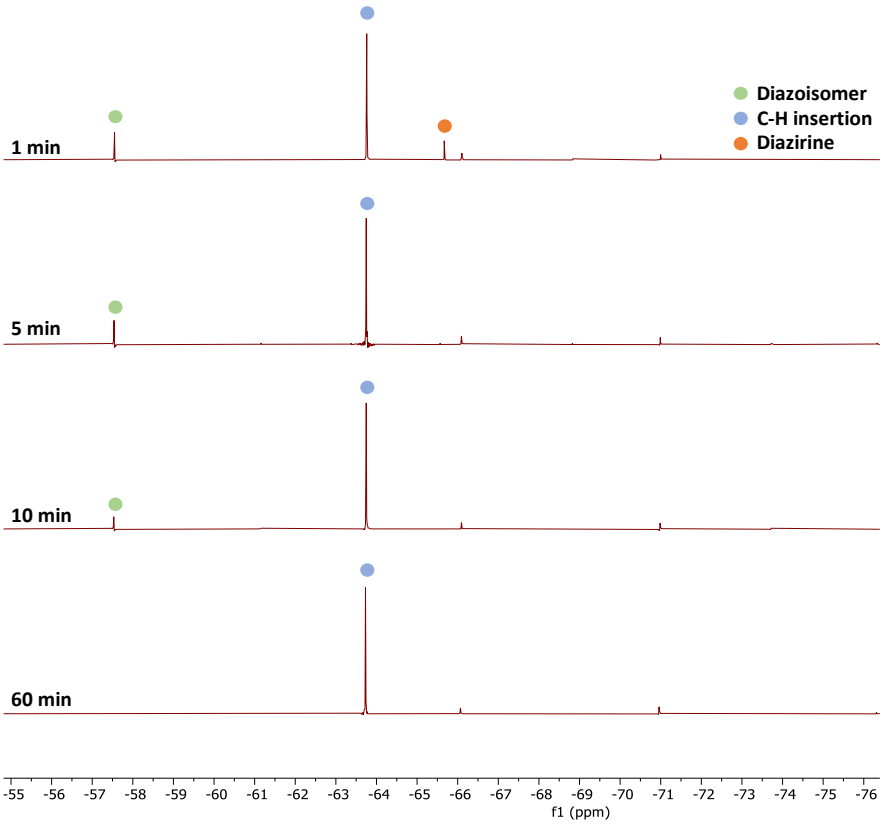
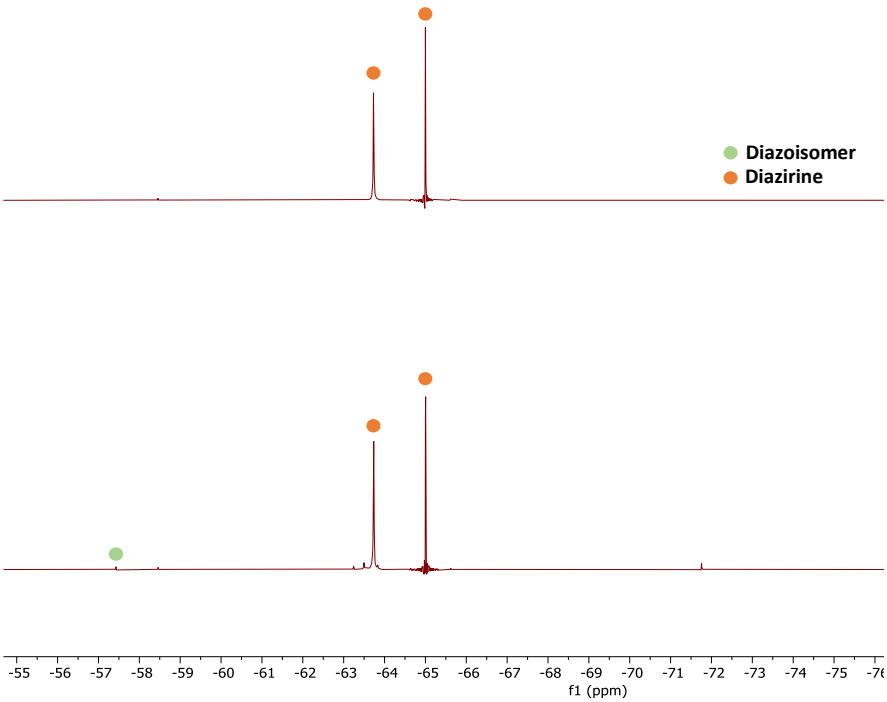


Fig. S51. Crude ^{19}F NMR spectra of compound 1 under photochemical C–H insertion condition, 395 nm.

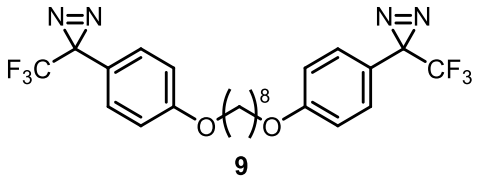


Assessment of thermal parameters for representative aryl ether crosslinkers

General Protocol for DSC analysis

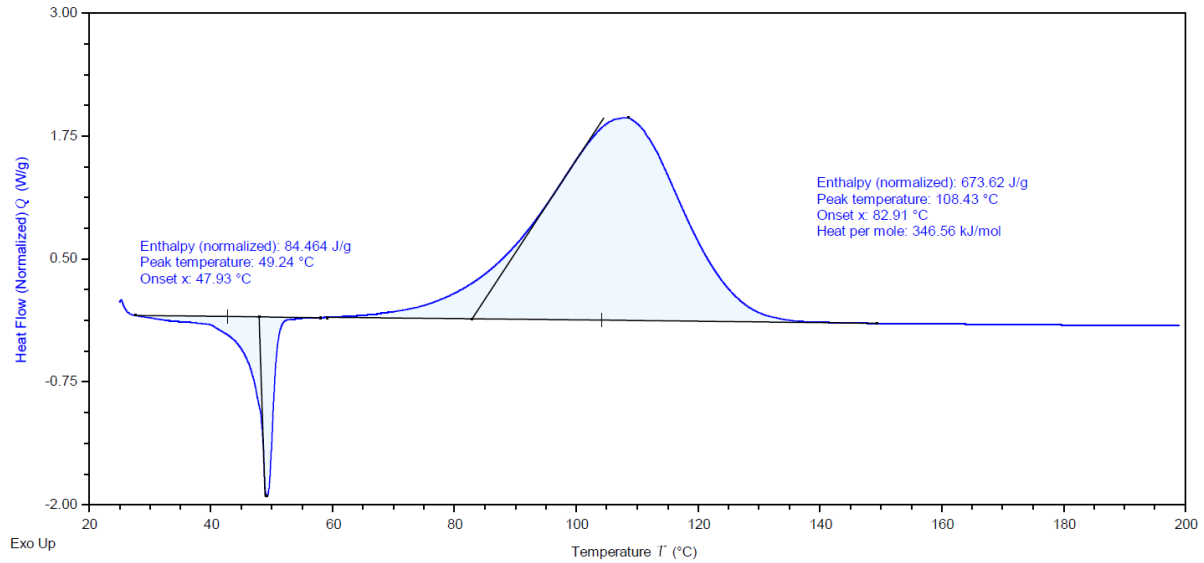
A sample of the substance to be analyzed (typically 3-5 mg) was placed in a Tzero aluminum hermetic pan and sealed by a matching lid. The pan was pierced with a small pinhole to allow evolution of nitrogen gas. The pan was placed in the oven of a DSC25 device (TA instruments) and heated from 40 °C to 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, allowing the assignment of T_{onset} and T_{max}. DSC analysis for each substrate was conducted 8 times for compound **9** and 7 times for compound **3**. Representative DSC traces for crosslinkers **9** and **3** are provided below.

DSC plot of 9

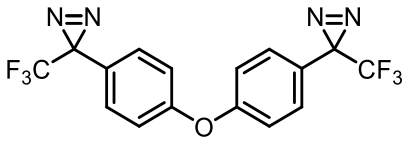


9

Fig. S52. Representative DSC trace for crosslinker 9.



DSC plot of 3



3

Fig. S53. Representative DSC trace for crosslinker 3.

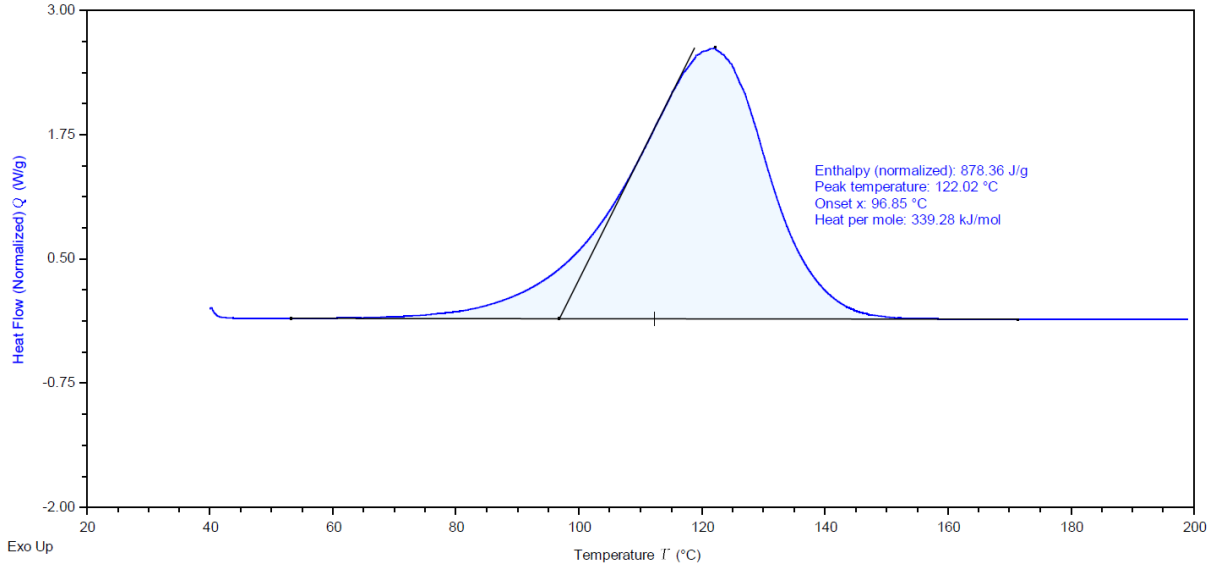
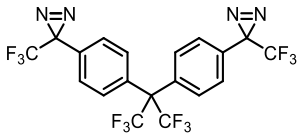
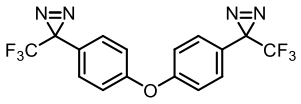
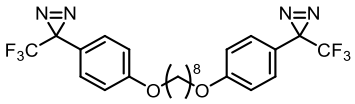


Table S3. Collected thermal data for representative bis-diazirine crosslinkers.[a]

			
	1	**3**	**9**
MP[b]	34 °C	n.d.	48.9 ± 0.2 °C
T_{onset}[c]	112.8 ± 0.2 °C	96.8 ± 0.2 °C	81.2 ± 1.3 °C
T_{peak}[d]	138.5 ± 0.2 °C	121.9 ± 0.1 °C	105.8 ± 1.5 °C
ΔH (by mass)[e]	683 ± 9 J/g	920 ± 35 J/g	680 ± 25 J/g
ΔH (by mole)[e]	355 ± 5 kJ/mol	355 ± 13 kJ/mol	350 ± 13 kJ/mol
SS[f]	–0.17 ± 0.01	+0.03 ± 0.02	–0.03 ± 0.02
EP[g]	–0.20 ± 0.01	–0.03 ± 0.02	–0.12 ± 0.02

[a] Error bars indicate standard error across multiple DSC runs. n=15 for compound 1; n=7 for compound **3**; n=8 for compound **9**.

[b] The melting point (MP) for compound **1** was taken from reference [2]. No melting point was determined for compound **3**, which was an oil at room temperature and did not freeze upon long term storage at –18 °C. The melting point for compound **9** was taken as the peak of the endothermic melting transition visible in the DSC trace.

[c] The onset temperature (T_{onset}) was determined by extrapolation of the tangent of the upward slope in the DSC experiment, to the fitted baseline of the plot.

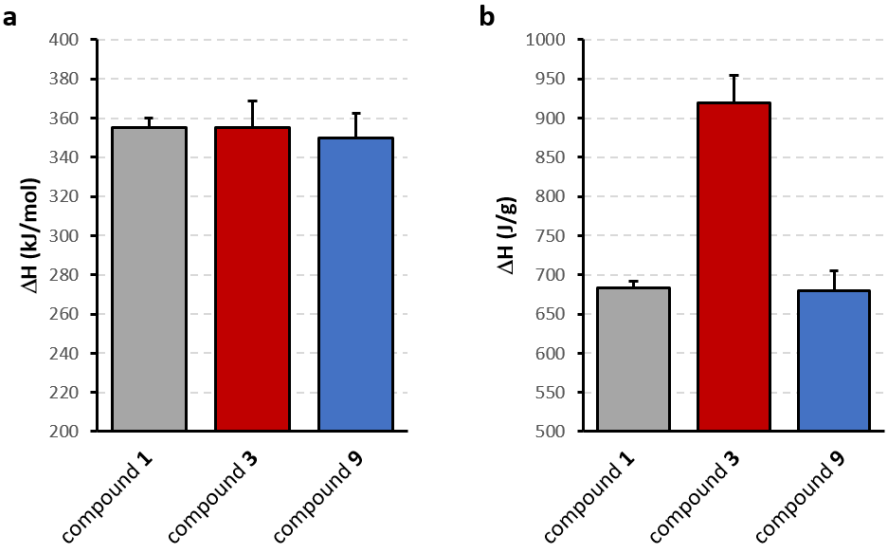
[d] The peak temperature (T_{peak}) was determined as the temperature at which the maximum heat flow was observed in the DSC experiment.

[e] ΔH refers to the total integrated peak area (per unit mass or per mole), for the exotherm associated with diazirine activation.

[f] The shock sensitivity metric (SS) was determined according to the method of Yoshida and co-workers.[3] SS = log (Q_{DSC}) – 0.72 x log (T_{onset} – 25) – 0.98; where Q_{DSC} is the enthalpy of nitrogen release (in cal/g), and T_{onset} is measured as described above. A value of >0 indicates a risk of shock sensitivity for the compound.

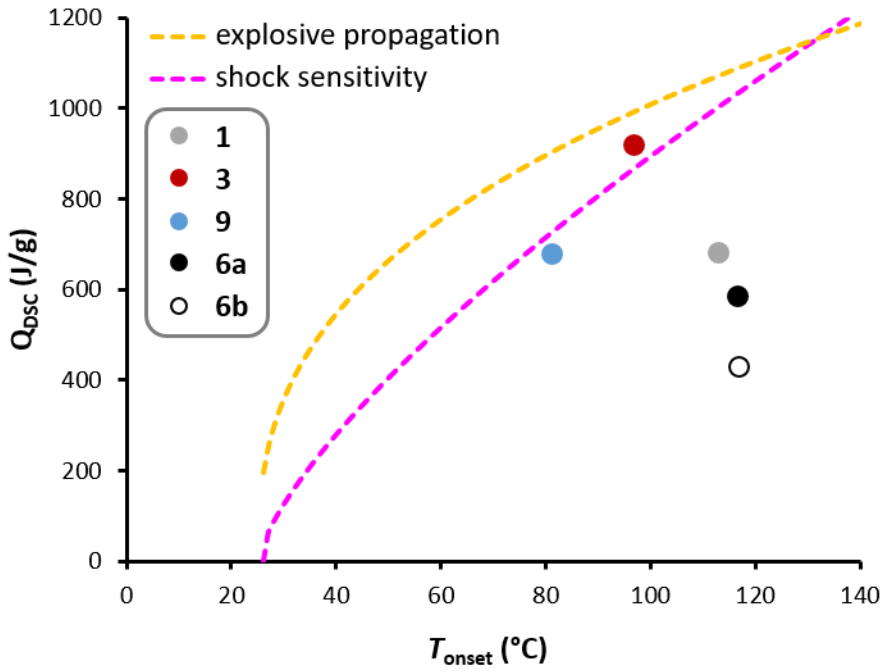
[g] The explosive propagation metric (EP) was likewise determined according to Yoshida's methods. EP = log (Q_{DSC}) – 0.38 x log (T_{onset} – 25) – 1.67; where Q_{DSC} is the enthalpy of nitrogen release (in cal/g), and T_{onset} is measured as described above. A value of >0 indicates a risk of explosive propagation for the compound.

Fig. S54. Enthalpy output associated with thermal diazirine activation for three representative bis-diazirines.



a. Enthalpy per molar unit. b. Enthalpy per gram. The data indicate that each trifluoromethyl aryl diazirine unit produces that same amount of energy upon activation (within experimental error), regardless of the electron density associated with the aromatic ring. However, the molecular weight of the tether plays a significant role in the total energy output per unit mass. Thus, compounds 1 and 9, which have similar molecular weights (520 and 514 g/mol, respectively), produce equivalent energy per gram, while compound 3, which has a lower molecular weight (388 g/mol), produces a proportionately higher energy per gram of material. It is this larger energy output per unit mass that contributes to the potential explosion hazard associated with 3.

Fig. S55. Yoshida correlation data for compounds 1, 3, 9, 6a and 6b.



Compounds for which Q_{DSC} vs. T_{onset} falls above either of the two curves are predicted to have an inherent risk of shock sensitivity or explosive propagation. For the compounds analyzed herein, only compound 3 falls into this danger zone.

Crosslinking of monodisperse poly(ethylene glycol) (PEG-1000 Da)

A series of samples was prepared by mixing monodisperse poly(ethylene glycol) (PEG-1000 Da) (20 mg) with various amounts of **1**, **9**, or **3** in glass vials (**Table S4**). Four different stock solutions with PEG-1000, **1**, **9**, or **3** in DCM were prepared. All vials were mixed for 15 seconds on a vortex mixer, sonicated (280 W for 30 seconds), and left to dry in the fume hood overnight. The contents of the vials were further dried by placing them under high vacuum (*ca.* 10^{-2} mbar) after mixing them for 15 seconds on a vortex mixer. The removal of solvents was monitored by measuring the weights of each vial over the whole process. The samples were placed in a heat block and heated at 110 °C for 16 hours. This induced crosslinking via thermal activation. Once cooled, each sample was homogenized (vortex mixer) and 1 mg was dissolved in 1 mL THF. The solutions were then filtered through a 0.2 µm PTFE filter directly into vials for GPC analysis. A vehicle control was prepared in the same way without the addition of any crosslinker and an untreated sample was prepared by dissolving 1 mg of PEG-1000 into 1 mL of THF and filtering the resulting solution through a 0.2 µm PTFE filter. All filtered samples were clear solutions.

Gel Permeation Chromatography (GPC)

GPC was carried out using Malvern Viscotek TDAmax system. Measurements were carried out at 1.0 mL/min with HPLC-grade tetrahydrofuran (Fisher) containing tetrabutylammonium bromide (0.1% w/w) as the eluent at 35 °C. Results were calibrated against polystyrene standards. All samples were dissolved in the eluent (1 mg/mL) and filtered with a polytetrafluoroethylene membrane of 0.2 µm pore size before analysis.

Fig. S56. GPC data showing increasing polydispersity (Mw/Mn) as a result of crosslinking.

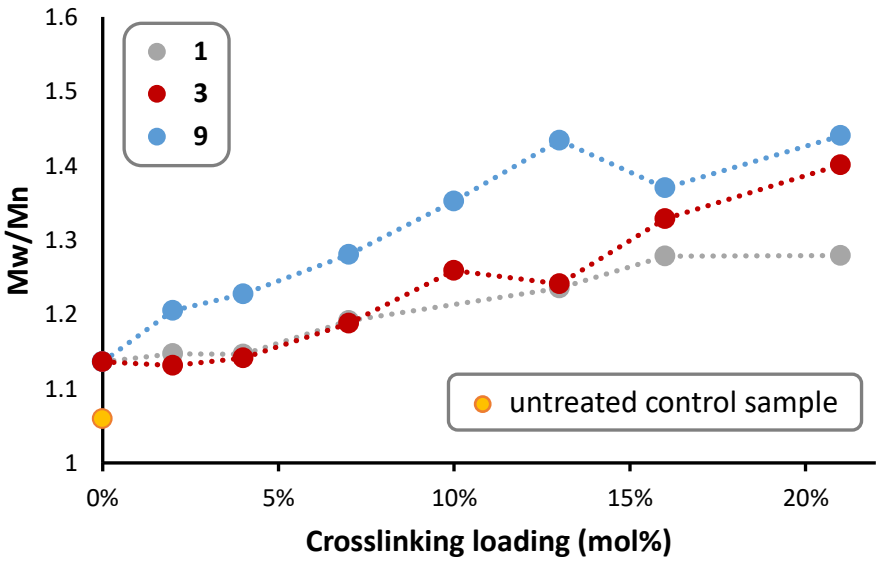


Table S4. Composition of samples prepared for crosslinking PEG-1000.

vial	crosslinker	MW (g/mol)	loading (µmol/g)	PEG (mg)	crosslinker (µmol)	crosslinker (mg)	loading (wt%)	loading (mol%)
A1	**1**	520.28	20	20	0.4	0.21	1.0%	2.1%
A2	**1**	520.28	40	20	0.8	0.42	2.1%	4.1%
A3	**1**	520.28	70	20	1.4	0.73	3.6%	7.2%
A4	**1**	520.28	100	20	2	1.04	5.2%	10.3%
A5	**1**	520.28	130	20	2.6	1.35	6.8%	13.4%
A6	**1**	520.28	160	20	3.2	1.66	8.3%	16.5%
A7	**1**	520.28	200	20	4	2.08	10.4%	20.6%
B1	**9**	514.47	20	20	0.4	0.21	1.0%	2.1%
B2	**9**	514.47	40	20	0.8	0.41	2.1%	4.1%
B3	**9**	514.47	70	20	1.4	0.72	3.6%	7.2%
B4	**9**	514.47	100	20	2	1.03	5.1%	10.3%
B5	**9**	514.47	130	20	2.6	1.34	6.7%	13.4%
B6	**9**	514.47	160	20	3.2	1.65	8.2%	16.5%
B7	**9**	514.47	200	20	4	2.06	10.3%	20.6%
C1	**3**	386.26	20	20	0.4	0.15	0.8%	2.1%
C2	**3**	386.26	40	20	0.8	0.31	1.5%	4.1%
C3	**3**	386.26	70	20	1.4	0.54	2.7%	7.2%
C4	**3**	386.26	100	20	2	0.77	3.9%	10.3%
C5	**3**	386.26	130	20	2.6	1.00	5.0%	13.4%
C6	**3**	386.26	160	20	3.2	1.24	6.2%	16.5%
C7	**3**	386.26	200	20	4	1.55	7.7%	20.6%
D1	vehicle ctrl	N/A	0	20	0	0	0%	
D2	untreated							

Adhesion testing

Preparation of HDPE–HDPE samples

Pairs of 4"x1"x¼" bars of HDPE (Quadrant Engineering Plastics) were treated with 1 or 5 mg of crosslinkers **1**, **9**, or **3**, or 1 mg of molecular control **10**. After cutting the HDPE sheet into bars of the appropriate size, the edges were scraped to smoothness using a utility knife and the bars were wiped with Kimwipes and a solution of 70% isopropanol to remove grease/dust/plastic particles. Stock solution of crosslinkers and molecular control in diethyl ether were prepared and 60 µL was deposited onto the 1"x 0.5" overlap zone using a micropipette. The solvent was allowed to evaporate at room temperature, and then each pair of bars was held together with binder clamps and placed into an oven pre-heated to 110 °C. After 4 h, the samples were removed from the oven, cooled to room temperature, and challenged on a lap-shear experiment. Negative (vehicle) controls were prepared in an identical manner, except that 60 µL of pure diethyl ether was added to the bars in place of the crosslinker solution described above. Vehicle control samples were incubated at the same temperature (110 °C) as the other samples, for an identical length of time.

Lap-shear test

The lap-shear test was implemented according to ASTM D5868. The two trailing ends of the adhered HDPE samples prepared as described above were clamped in a universal testing system (Instron, Series 5969) and pulled apart at a rate of 5 mm/min until breakage of the bond.

Fig. S57. Adhesion strength of HDPE–crosslinker–HDPE lap-shear composites; numerical values indicate the number of samples that were sufficiently well adhered to be measured.

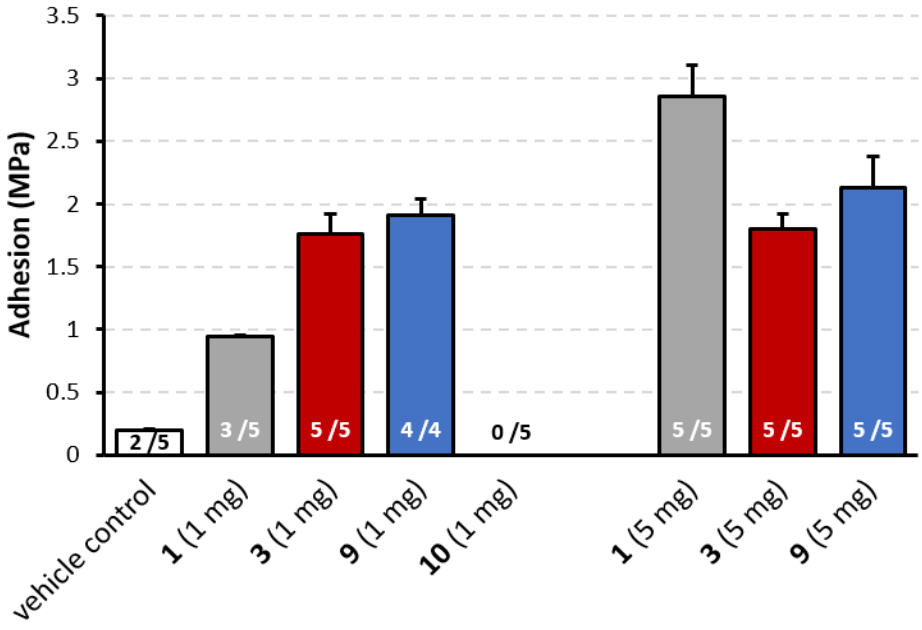


Table S5. Adhesion data for HDPE–crosslinker–HDPE lap-shear composites.

sample	fraction bonded[a]	adhesion (MPa)
vehicle control	2 / 5	0.20 ± 0.01
1 (1 mg)	3 / 5	0.94 ± 0.03
9 (1 mg)	4 / 4	1.91 ± 0.25
3 (1 mg)	5 / 5	1.76 ± 0.37
10 (1 mg)	0 / 5	0.00 ± n/a
1 (5 mg)	5 / 5	2.86 ± 0.56
9 (5 mg)	5 / 5	2.13 ± 0.56
3 (5 mg)	5 / 5	1.80 ± 0.27

[a] The number of samples that were sufficiently well bonded to permit analysis.

Loading of crosslinker into UHMWPE fabric

Irreversible crosslinking of ultra-high molecular weight polyethylene (UHMWPE)

Commercial 75 g/m^2 UHMWPE fabric was impregnated with either **1** or **9**, by placing 1" x 1" pieces of fabric into close-fitting aluminum pans filled with solutions of the desired *bis*-diazirine in pentane. The concentration of the solution was calculated to correspond to 1.25 wt%, 6.25 wt%, or 12.5 wt% of crosslinker, relative to the mass of fabric being employed in the experiment. The bath was covered with aluminum foil and incubated at room temperature for 30 min. The cover was then removed to allow the pentane to evaporate in a fume hood for 20 min. After pentane evaporation, the impregnated sheets were wrapped in aluminum foil and placed into an oven at 110 °C for 4 h.

Control samples were prepared following an identical procedure, but without adding crosslinker to the pentane bath.

Following thermal curing, the samples were weighed to determine the total mass of reacted crosslinker that was associated with each square of fabric. Each sample was then extracted for 5 min at room temperature using 20 mL of methanol, to remove any reaction products that were not irreversibly attached to the fabric. After drying the treated fabrics in an oven (5 min at 100 °C), each sample was weighed again to determine the mass of reaction products that were lost to the methanol extraction.

Table S6. Gravimetric analysis following methanol extraction of crosslinked UHMWPE fabric.

crosslinker	nominal loading (wt%)	percent retention after loading and curing	percent retention after methanol extraction
vehicle ctrl	0%	-0.27% ± 0.03%	-0.71% ± 0.08%
1	12.5%	8.75% ± 0.21%	0.14% ± 0.40%
1	6.25%	4.17% ± 0.07%	0.94% ± 0.25%
1	1.25%	0.93% ± 0.02%	0.13% ± 0.12%
9	12.5%	8.08% ± 0.49%	7.89% ± 0.53%
9	6.25%	4.35% ± 0.16%	3.79% ± 0.19%
9	1.25%	0.92% ± 0.07%	0.68% ± 0.16%

Crosslinking of apparel fabric

Loading of crosslinker into apparel fabric

Representative apparel fabric samples of low- and high-stretch modulus were crosslinked with *bis*-diazirines **1** or **9** at a nominal loading of 1wt% or 5wt%, following a similar protocol to that outlined above for UHMWPE fabric. Both types of fabrics were comprised of nylon and Lycra, but were selected on the basis of their different stretch moduli.

For each crosslinking experiment, fabric samples were cut to 5"x6" rectangles, which were matched exactly to fit inside of a 5"x6" aluminum tray. Each portion of fabric was weighed, and the appropriate amount of crosslinker was calculated. In order to account for losses to the pan, a mass of 1.25wt% crosslinker was used in order to achieve a nominal loading of 1wt% in the treated fabric. Likewise 6.25wt% of crosslinker was used to achieve a nominal loading of 5wt% in the treated fabric. The crosslinker of interest was dissolved in 75 mL of pentane. For vehicle control samples, 75 mL of pentane containing no crosslinker was used.

The crosslinker solution (in 75 mL of pentane, or else pure pentane for vehicle control samples) was then poured over the fabric sample in the close-fitting aluminum pan. The pan was covered with aluminum foil for 30 minutes to allow the crosslinker to penetrate into the fabric. The covering was then removed in a fume hood and the pentane solvent was allowed to evaporate. Following evaporation, the impregnated fabric sample was removed from the pan and weighed to confirm crosslinker adsorption (at *ca.* 1wt% or 5wt%) within the material.

Crosslinking of apparel fabrics under thermal and photochemical conditions

Thermal activation was achieved by incubating the treated samples in a 110 °C oven for 4 hours. Photochemical activation was achieved by suspending the treated samples in a Rayonet photochemical reactor (RMR-600) equipped with eight 350 nm bulbs. The light output measured at the sample location was 1640 lux (16 W/m^2). Photochemical activation was allowed to proceed for 4 hours.

Following the 4 hour curing time, the fabric samples were again weighed to confirm that no significant material losses had occurred during the activation step.

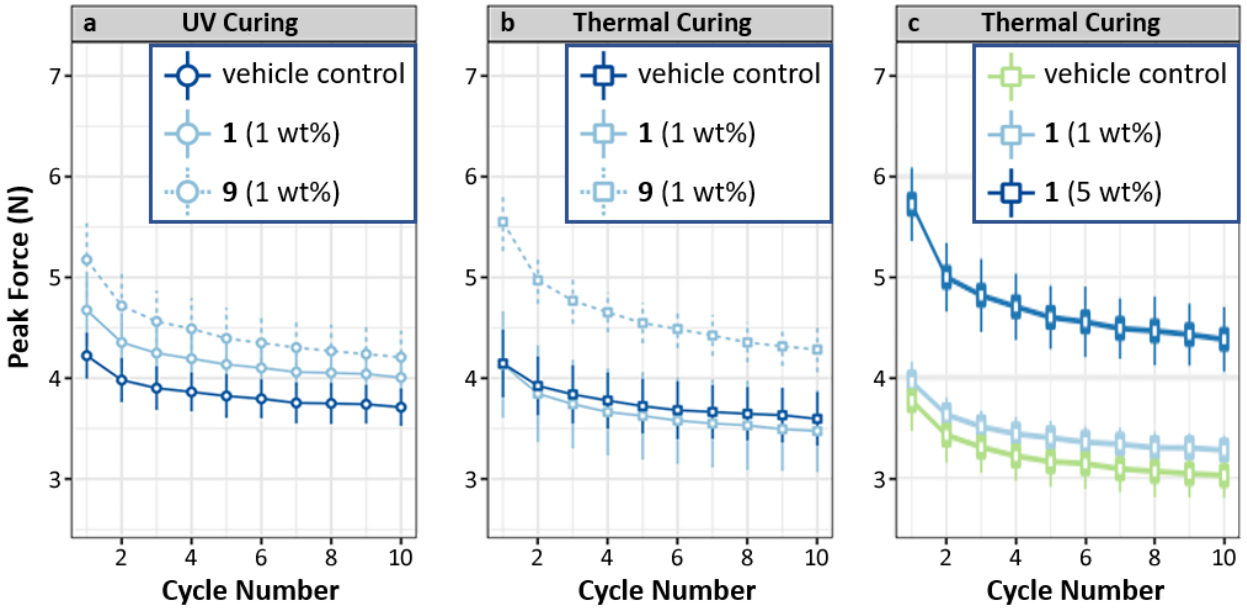
Testing of crosslinked apparel fabric samples

The treated fabric samples were cut using scissors into 150 mm x 25 mm strips, and then the mechanical performance was evaluated using a James Heal Titan fabric testing machine. Each strip of fabric was pulled to 150% of its static extension, and then allowed to relax. The extension/relaxation process was repeated for 10 cycles to assess the performance of crosslinked vs. noncrosslinked material over repeated stretches.

For apparel fabric with a low starting stretch modulus (*ca.* 0.5 N peak force), addition of 1wt% of *bis*-diazirine **1** (followed by thermal activation) was capable of doubling the stretch modulus (*ca.* 1 N peak force) while addition of 5wt% **1** resulted in another doubling of modulus (*ca.* 2 N peak force). For apparel fabric with a higher starting stretch modulus, however (*ca.* 4 N peak force), 1wt% of **1** was ineffective at improving stretch modulus relative to vehicle control samples (Fig. S58b and c). For this stronger starting fabric, 5wt% of **1** was required in order to achieve a significant increase in modulus (Fig. S58c).

By contrast, 1wt% of crosslinker **9** (following thermal activation) was found to effect roughly the same increase to stretch modulus as 5wt% of crosslinker **1** (compare Fig. S58b to Fig. S58c). These data confirm the superior crosslinking performance of **9** relative to **1**. Data from photochemically crosslinked samples (also using fabric of high starting modulus) likewise showed a greater increase in stretch modulus for fabric samples treated with **9** than for fabric samples treated with **1** (Fig. S58a). However, the maximum stretch modulus was lower for photochemically activates samples than for thermally activated samples, perhaps indicating incomplete activation under the selected UV irradiation conditions.

Fig. S58. Increasing stretch modulus through crosslinking of apparel fabric with crosslinkers 1 and 9.



Mechanical testing of crosslinked UHMWPE fabric

General fabric preparation procedure A (thermo-activation)

Commercial 75 g/m^2 UHMWPE fabric was impregnated with each test compound, by placing a piece of fabric of desired dimensions into close-fitting aluminum filled with a solution of the desired *bis*-diazirine or molecular control in pentane/diethyl ether at the appropriate concentration. The concentration was calculated to correspond to 1 wt% (plus an extra 0.25 wt% to compensate for crosslinker deposited on the sides and bottom of the aluminum pan), relative to the mass of fabric being employed in the experiment. The bath was covered with aluminum foil and incubated at room temperature for 30 min. The cover was then removed to allow the solvent to evaporate in a fume hood for 20 min. After solvent evaporation, the impregnated sheets were wrapped in aluminum foil and placed into an oven at 110 °C for 4 h.

Vehicle control samples were prepared following the same procedure, but without adding crosslinker in the solvent bath.

Molecular control samples were prepared following the same procedure but with the crosslinker replaced by the corresponding molecular control **10** bearing only one diazirine moiety.

General fabric preparation procedure B (photo-activation)

Commercial 75 g/m^2 UHMWPE fabric was impregnated with each test compound, by placing a piece of fabric of desired dimensions into close-fitting aluminum filled with a solution of the desired *bis*-diazirine or molecular control in pentane/diethyl ether at the appropriate concentration. The concentration was calculated to correspond to 1 wt% and 0.2 wt% (plus an extra 0.25 wt% to compensate for crosslinker deposited on the sides and bottom of the aluminum pan), relative to the mass of fabric being employed in the experiment. The bath was covered with aluminum foil and incubated at room temperature for 30 min. The cover was then removed to allow the solvent to evaporate in a fume hood for 20 min. After solvent evaporation, the impregnated sheets were placed into a home-built photoreactor, constructed from a 15 cm diameter pyrex crystallizing dish (7.5 cm in height), wrapped laterally with 2.5 m of 395 nm LED Strip Lights, (Waveform Lighting) and irradiated for 5 min.

Vehicle control samples were prepared following the same procedure, but without adding crosslinker in the solvent bath.

Tensile testing of crosslinked fabric using procedure A (thermo-activation)

Tensile tests were conducted on samples 75 mm × 250 mm in size, using an Instron 5969 dual column load frame. Each sample was inserted into the grips in such a way that 50 mm from each end of the fabric was clamped within each grip. Consequently, the area between the grips (i.e. the area upon which the tensile experiment was performed) had dimensions of 150 mm x 75 mm. To ensure consistent results, three samples were analyzed for each treatment condition. The loading rate was 5 mm/min. The force-displacement curves (Fig. S59) indicated that the maximum load was considerably increased in UHMWPE that had been crosslinked with *bis*-diazirines **9** and **3**, compared to both untreated and vehicle control samples.

Fig. S59. Force-displacement curves obtained during tensile testing of variously treated UHMWPE samples.

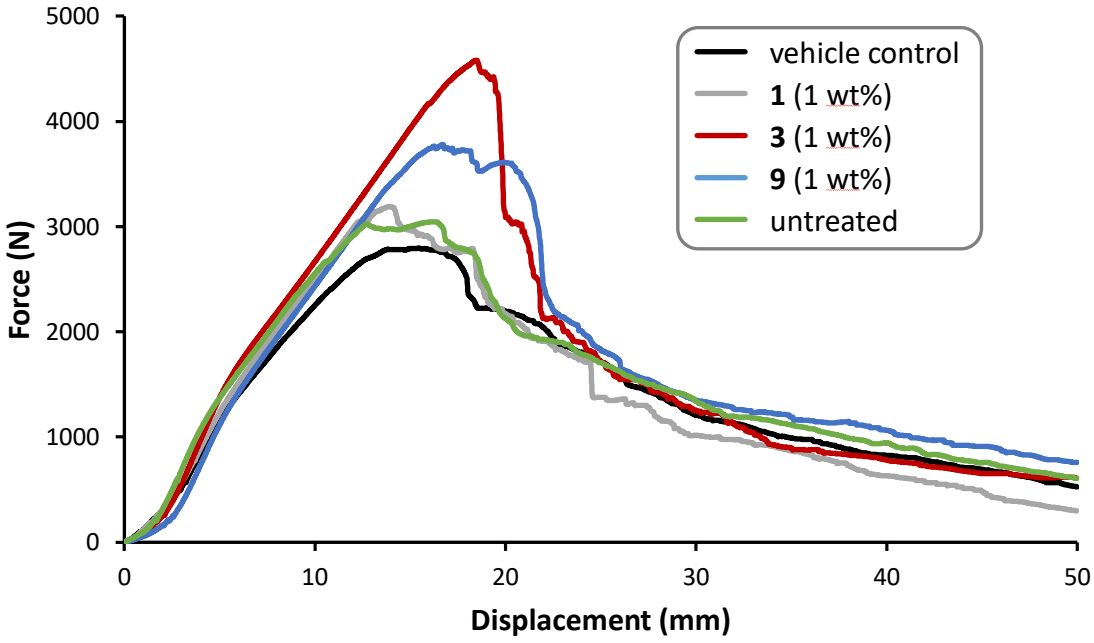


Table S7. Composition of samples prepared for tensile test.

sample	loading (wt%)	wt. of fabric (g)	wt. of crosslinker (mg)	wt. of fabric after curing (g)	wt. gain /loss (mg)	wt% gain/loss	wt. after extraction with pentane (g)	wt. gain/loss (mg)	wt% gain/loss
vehicle control	0	3.4436	---	3.4442	0.0	0.0%	3.4478	0.0	0.1%
		3.4182	---	3.4197	0.0	0.0%	3.4187	0.0	0.0%
		3.4806	---	3.4791	0.0	0.0%	3.4771	0.0	-0.1%
1	1.25	3.4034	42.5	3.4425	39.1	1.1%	3.4397	36.3	1.1%
		3.4303	42.8	3.4509	20.6	0.6%	3.4492	18.9	0.6%
		3.4214	42.7	3.4508	29.4	0.9%	3.4503	28.9	0.8%
9	1.25	3.4607	43.2	3.4948	34.1	1.0%	3.4948	34.1	1.0%
		3.4224	43.7	3.4695	47.1	1.4%	3.4628	40.4	1.2%
		3.4177	42.7	3.4476	29.9	0.9%	3.4485	30.8	0.9%
3	1.25	3.3969	42.5	3.4392	42.3	1.2%	3.427	30.1	0.9%
		3.4284	42.8	3.4711	42.7	1.2%	3.4592	30.8	0.9%
		3.4037	42.5	3.455	51.3	1.5%	3.4405	36.8	1.1%

Tear test of crosslinked fabric using procedure A (thermo-activation)

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. Five samples of each group were tested. The force–displacement results are shown in Fig. S60.

Fig. S60. Force-displacement curves obtained during tear testing of variously treated UHMWPE samples.

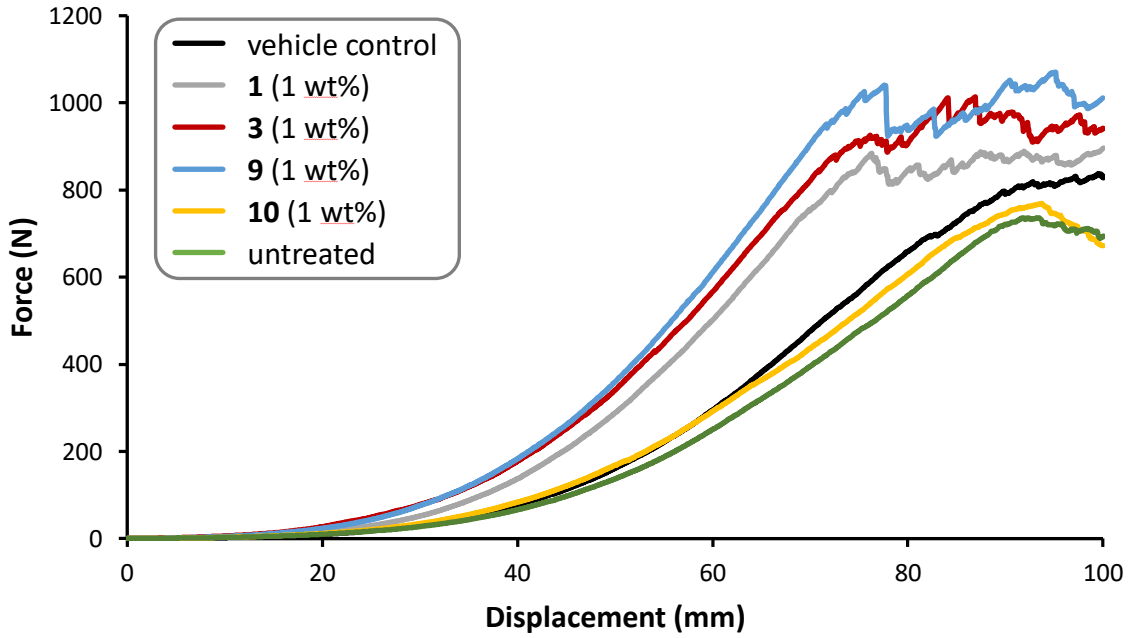


Table S8. Composition of samples prepared for tear test.

sample	loading (wt%)	wt. of fabric (mg)	wt. of crosslinker (mg)	wt. of fabric after curing (mg)	wt. gain /loss(mg)	wt% gain/loss	wt. after extraction with pentane	wt. gain/loss (mg)	wt% gain/loss
vehicle control	0	796.8	---	796.2	-0.6	-0.1%	795.2	-1.6	-0.2%
		818.6	---	805.4	-13.2	-1.6%	804.7	-13.9	-1.7%
		816.7	---	798.8	-17.9	-2.2%	799.7	-17	-2.1%
		805.2	---	809.6	4.4	0.5%	802.1	-3.1	-0.4%
		809.5	---	808.2	-1.3	-0.2%	807.5	-2	-0.2%
1	1.25	844.3	10.6	844	-0.3	0.0%	838.9	-5.4	-0.6%
		820.4	10.4	850.1	29.7	3.6%	811.6	-8.8	-1.1%
		915	11.4	942.2	27.2	3.0%	807.8	-107.2	-11.7%
		830.6	10.4	839.4	8.8	1.1%	790.8	-39.8	-4.8%
		825.8	10.3	805.6	-20.2	-2.4%	802.3	-23.5	-2.8%
9	1.25	775.1	9.7	784.9	9.8	1.3%	783.8	8.7	1.1%
		793.8	9.9	801.8	8	1.0%	801.8	8	1.0%
		797.2	10	805.6	8.4	1.1%	805.1	7.9	1.0%
		787	9.8	795.4	8.4	1.1%	795	8	1.0%
		789.8	9.9	799.3	9.5	1.2%	798.7	8.9	1.1%
3	1.25	779.8	9.7	786.8	7	0.9%	787.7	7.9	1.0%
		790.1	9.8	798.4	8.3	1.1%	799.2	9.1	1.2%
		807.6	10.1	816.1	8.5	1.1%	815.3	7.7	1.0%
		793.5	9.9	805.3	11.8	1.5%	801.7	8.2	1.0%
		802.2	10	813.1	10.9	1.4%	812.6	10.4	1.3%
10	1.25	816.3	10.4	811.1	-5.2	-0.6%	816.8	0.5	0.1%
		822.7	10.3	811.1	-11.6	-1.4%	810.2	-12.5	-1.5%
		792	9.9	795.6	3.6	0.5%	798.4	6.4	0.8%
		735.6	9.2	769.6	34	4.6%	768.4	32.8	4.5%
		790.3	9.9	790.7	0.4	0.1%	789.9	-0.4	-0.1%

Integration of tear testing curves

To better compare the results from tear testing, the force−extension curves were integrated over the first 50 mm of extension. This value was chosen because at this extension, none of the fabric samples had exhibited failure. The resulting values of tear energy, expressed in Joules (J), were then averaged for each type of cross-linked fabric.

Table S9. Integration of tear testing curves up to 50 mm extension.

treatment	average tear energy (J)		standard deviation	number of replicates
untreated	1.70	±	0.2	5
vehicle control	1.9	±	0.5	5
1 (1wt%)	3.4	±	0.7	5
9 (1wt%)	4.5	±	0.3	5
3 (1wt%)	4.2	±	0.6	5
10 (1wt%)	2.1	±	0.3	5

Tear test of crosslinked fabric using procedure B (photo-activation)

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. Five samples of each group were tested. The force–displacement results are shown in Fig. S61.

Fig. S61. Force-displacement curves obtained during tear testing of variously treated UHMWPE samples.

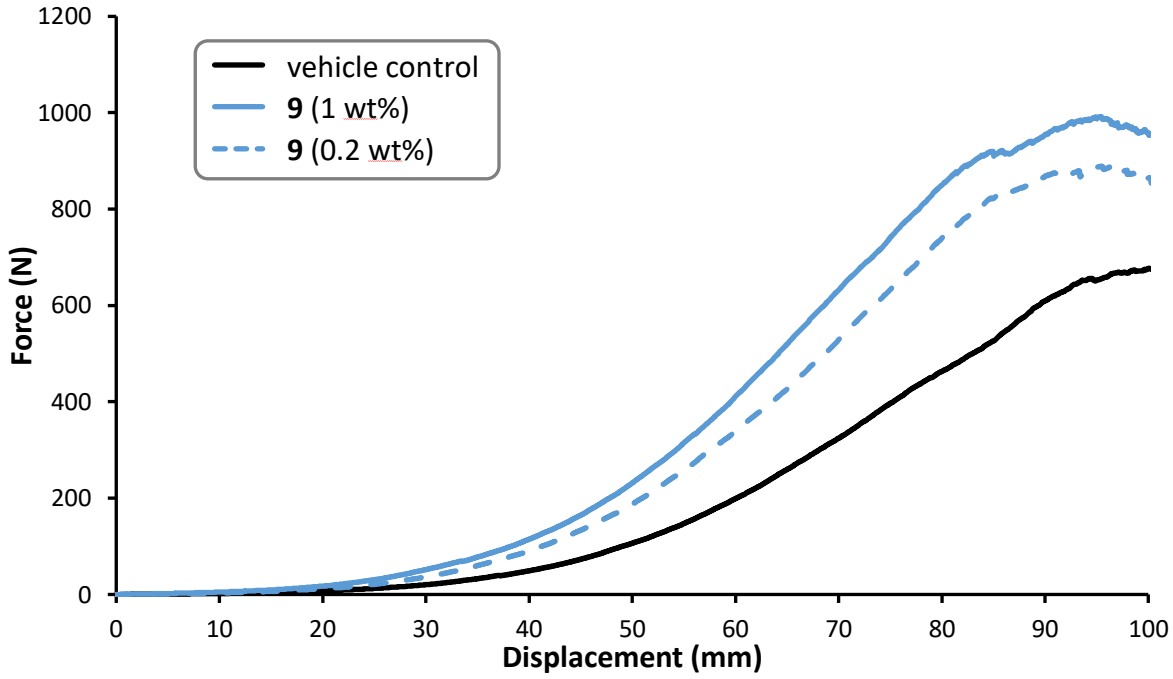


Fig. S62. Photo-crosslinking of fabrics using a home-built photoreactor operating at 395 nm for 5 min (general procedure B).

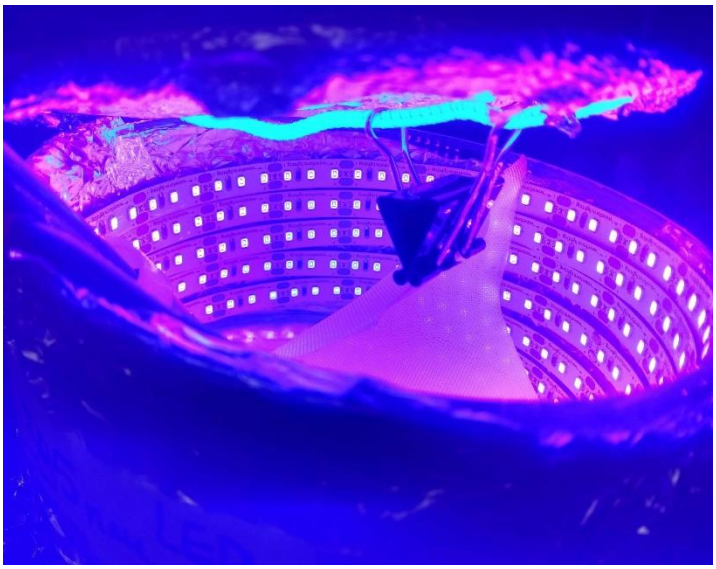
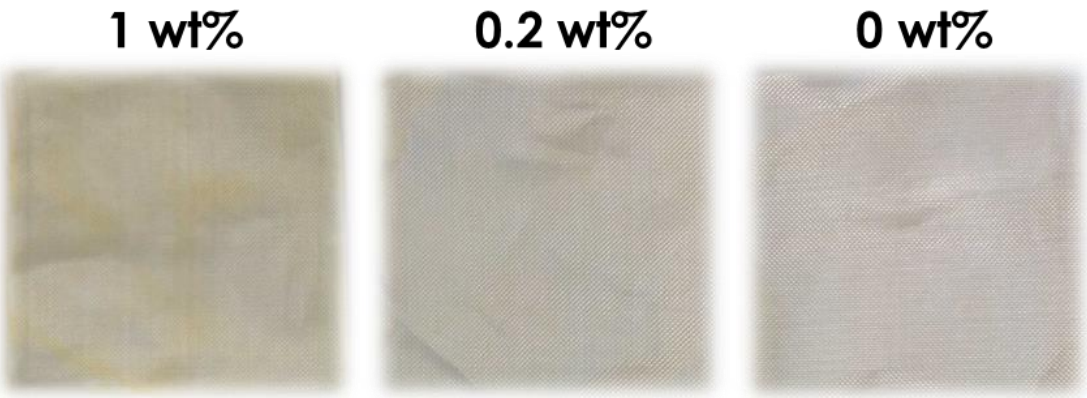


Fig. S63. Photocured fabrics with 1, 0.2, and 0 wt% of crosslinker 9.



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