
Supplementary information

Dynamic crosslinking compatibilizes immiscible mixed plastics

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Dynamic Crosslinking Compatibilises Immiscible Mixed Plastics

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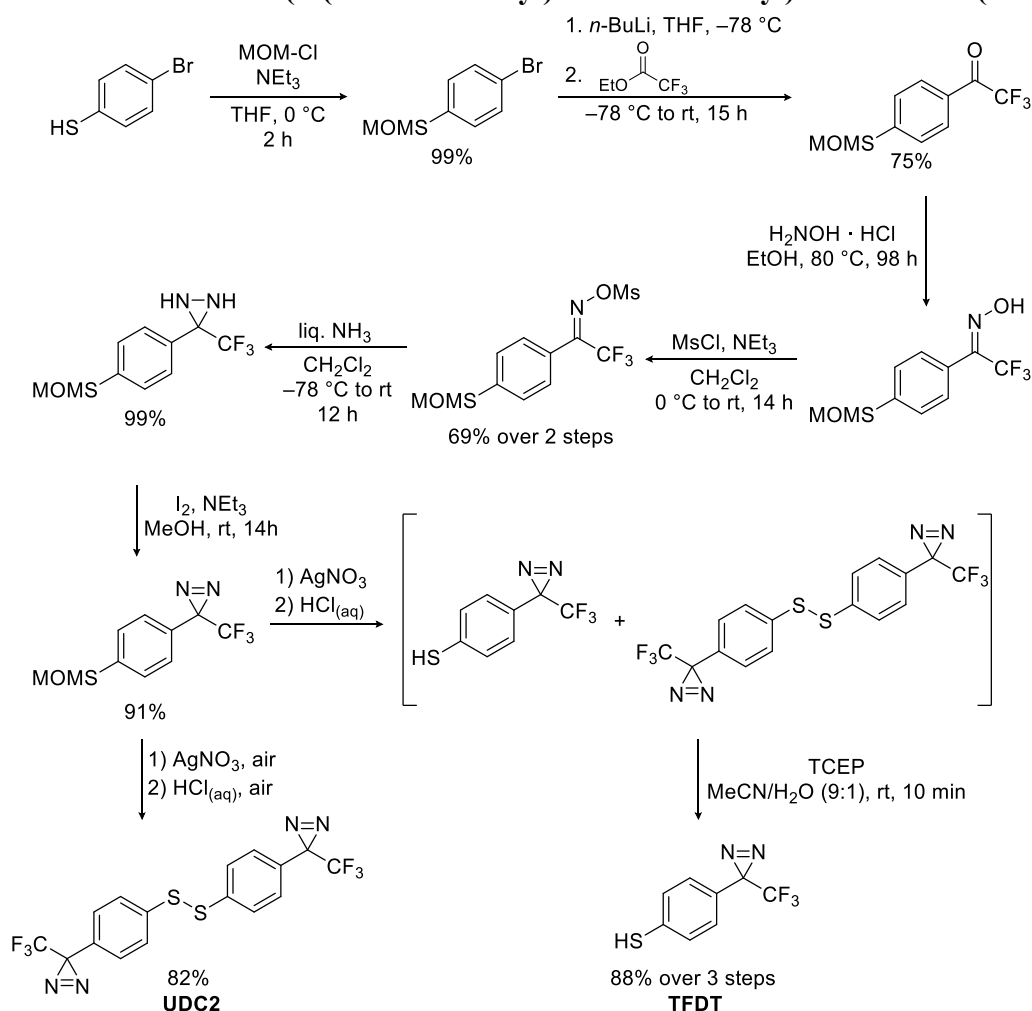
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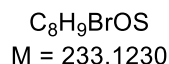
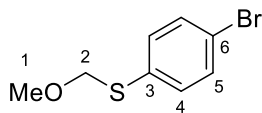
Supplementary Methods

All reactions were performed in flame-dried glassware under an atmosphere of N₂, unless stated otherwise. Reactions were stirred magnetically and monitored by analytical thin layer chromatography (TLC). TLC was performed on Merck silica gel 60 F₂₅₄ TLC glass plates and visualized with 254 nm light and aqueous potassium permanganate followed by heating. Crude products were absorbed into silica and purified by flash column chromatography on SiliaFlash, SiliCycle Silica Gel P60, 230-400 mesh, 40-63 μ m particle size and analytical grade hexane, ethyl acetate, dichloromethane, and methanol as eluents at 0.3-0.5 bar overpressure. Preparative thin-layer chromatography (PTLC) was carried out on SiliCycle 1000 μ m 20x20 cm TLC plates and visualized with a low intensity 365 nm UV-lamp. Concentration under reduced pressure (*in vacuo*) was performed by rotary evaporation at 40 °C at the appropriate pressure unless otherwise noted. The yields given refer to the purified products, unless otherwise stated. For larger scale synthesis, 4-[3-(trifluoromethyl)-3H-diazirin-3-yl]benzoic acid (TDBA) was prepared following a known literature procedure¹.

Full Synthetic Scheme for 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (TDBT)



Synthesis of (4-bromophenyl)(methoxymethyl)sulfane²:



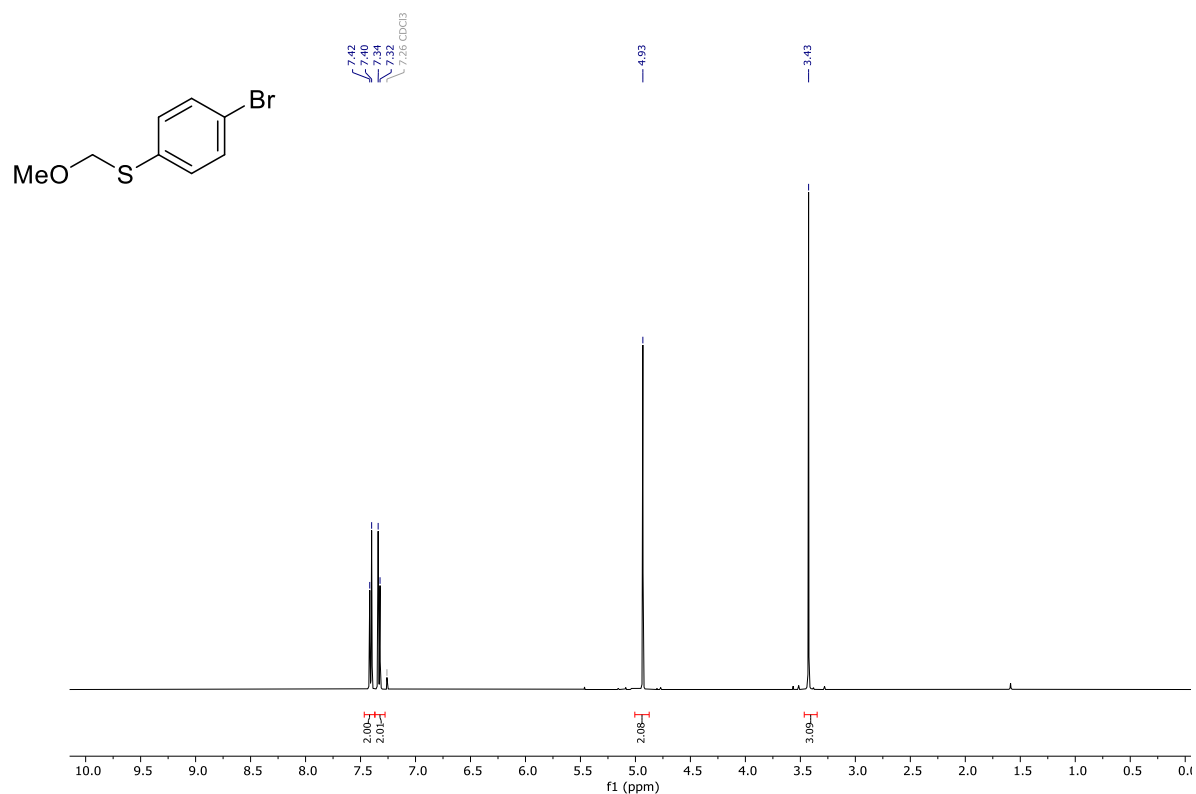
To a solution of 4-bromothiophenol (4.0 g, 21.2 mmol, 1.0 equiv.) in anhydrous THF (40 mL) was added triethylamine (5.92 mL, 42.4 mmol, 2.0 equiv.), and the resulting solution cooled to 0 °C by means of an ice bath. Chloromethyl methyl ether (2.4 mL, 31.8 mmol, 1.5 equiv.) was added dropwise under vigorous stirring at 0 °C, resulting in a sticky voluminous precipitate. The reaction mixture was stirred for 2 h at 0 °C, after which the mixture was diluted with water and the aqueous phase extracted with ethyl acetate (3x). The combined organic phases were dried (MgSO₄), filtered and concentrated in vacuo. The resulting crude mixture was purified by silica flash column chromatography (eluent: 2% ethyl acetate in hexanes), yielding the title product (4.79 g, 20.5 mmol, 97%) as colorless oil. *R_f* (20% ethyl acetate in hexanes): 0.58, ¹H NMR (500 MHz, CDCl₃) δ: 7.41 (2 H, d, *J* = 8.6 Hz, H₄), 7.33 (2 H, d, *J* = 8.6 Hz, H₅), 4.93 (2 H, s, H₂), 3.43 (3 H, s, H₁); ¹³C NMR (126 MHz, CDCl₃) δ: 135.3 (C₃), 132.1 (2 C, C₄), 131.8 (2 C, C₅), 120.9 (C₆), 77.8 (C₂), 56.2 (C₁); *m/z* HRMS ASAP+ found [M{⁷⁹Br}+H]⁺ 231.9548, found [M{⁸¹Br}+H]⁺ 233.9525, C₈H₁₀⁷⁹BrOS⁺ requires 231.9557, C₈H₁₀⁸¹BrOS⁺ requires 233.9537.

Improved synthesis of (4-bromophenyl)(methoxymethyl)sulfane:

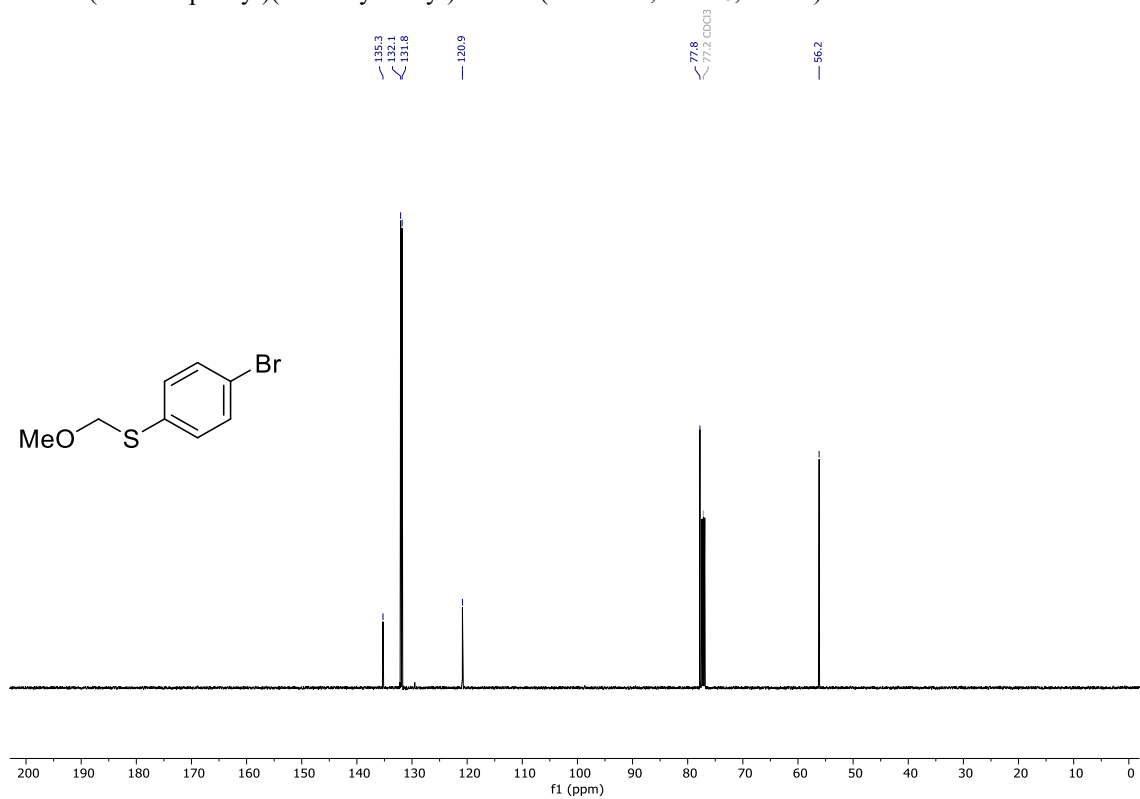
A solution of 4-bromothiophenol (0.527 g, 2.65 mmol, 1.0 equiv.) and triethylamine (0.74 mL, 5.3 mmol, 2.0 equiv.) in THF (5.0 mL) was cooled to 0 °C. Chloromethyl methyl ether (2.92 mmol, 1.1 equiv.) in THF (1.0 mL) was added resulting in the formation of a white precipitate. The suspension was stirred at 0 °C for 2 h. Additional THF (5.0 mL) was added to dilute the viscous mixture and the reaction was stirred at room temperature for 2 h. The reaction was diluted with water and extracted with EtOAc (3 times). The organic phases were combined, dried over MgSO₄, filtered, and concentrated. The crude mixture was analyzed by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. The yield of (4-bromophenyl)(methoxymethyl) sulfane was determined to be 94% (2.49 mmol).

Note: technical-grade chloromethyl methyl ether was used for this experiment. The purity of the reagent was determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard prior to use.

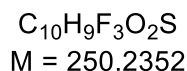
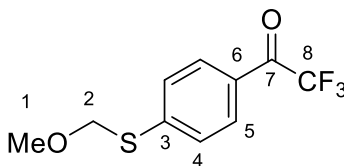
^1H NMR of (4-bromophenyl)(methoxymethyl)sulfane (500 MHz, CDCl_3 , 300 K)



^{13}C NMR of (4-bromophenyl)(methoxymethyl)sulfane (126 MHz, CDCl_3 , 300 K)

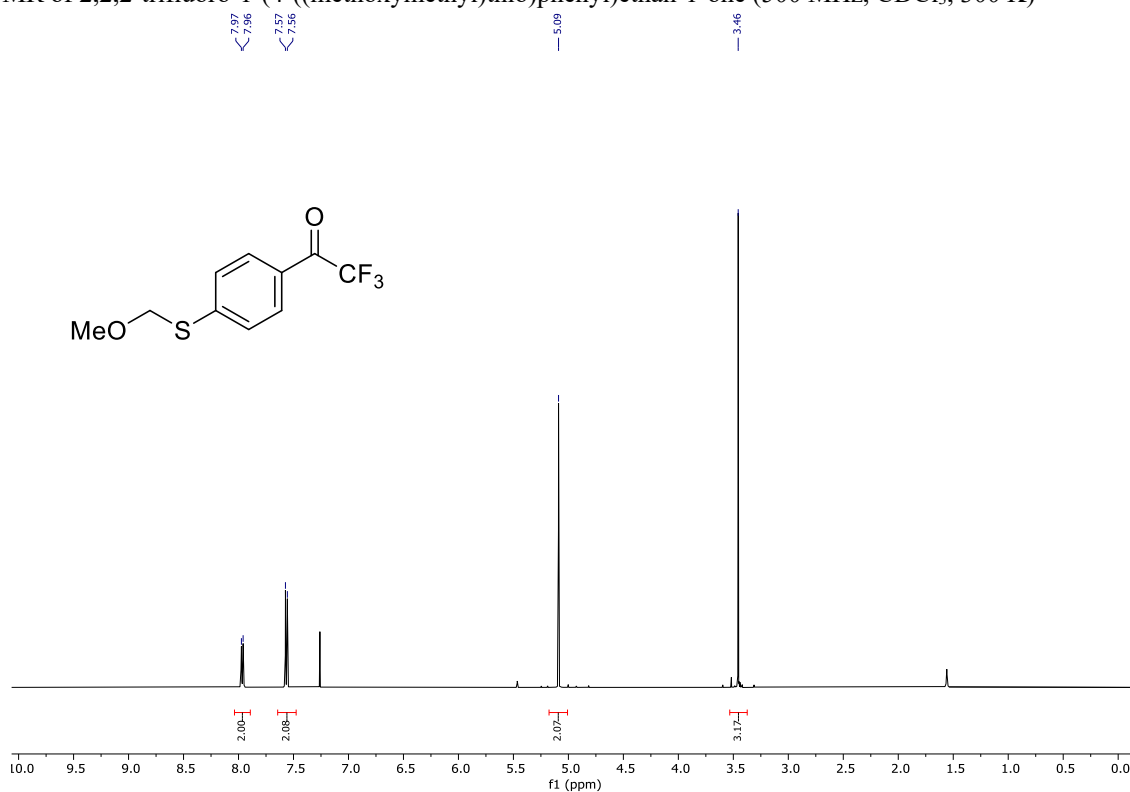


Synthesis of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one:

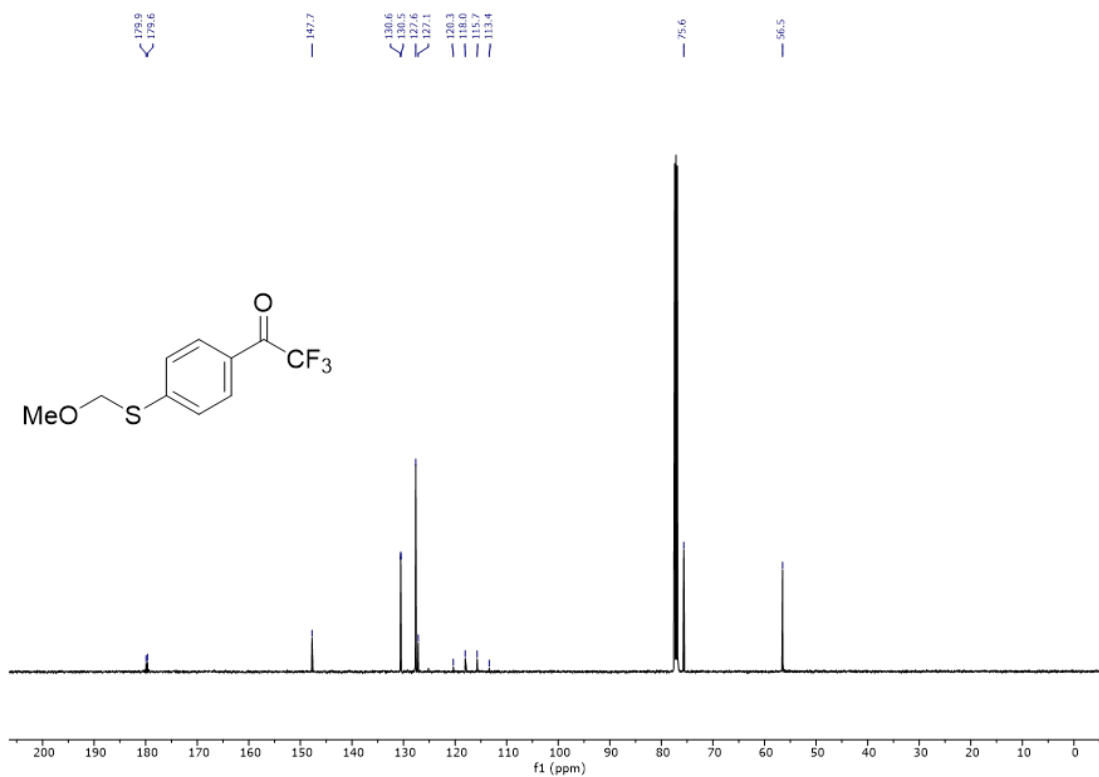


A solution of (4-bromophenyl)(methoxymethyl)sulfane (4.79 g, 20.5 mmol, 1.0 equiv) in anhydrous THF (100 mL) was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of *n*-BuLi (2.5 M in hexanes, 9.48 mL, 24.6 mmol, 1.2 equiv) was added dropwise with stirring and the resulting solution was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$. Ethyl trifluoroacetate (2.93 mL, 24.6 mmol, 1.2 equiv) was then added dropwise at $-78\text{ }^{\circ}\text{C}$. After complete addition, the cooling was removed, and the reaction mixture stirred for 14 h at room temperature. The mixture was quenched by addition of saturated ammonium chloride solution and the resulting biphasic mixture was extracted with ethyl acetate (3x). The combined organic phases were dried (MgSO_4), filtered and concentrated in vacuo. The resulting crude oil was purified by silica flash column chromatography (eluent: 3% ethyl acetate in hexanes), yielding the title product (3.40 g, 13.6 mmol, 66%) as a colorless oil. R_f (15% ethyl acetate in hexanes): 0.46 (diffuse); ^1H NMR (500 MHz, CDCl_3) δ : 7.96 (2 H, d, $J = 8.8$ Hz, H_4), 7.56 (2 H, d, $J = 8.8$ Hz, H_5), 5.09 (2 H, s, H_2), 3.46 (3 H, s, H_1); ^{13}C NMR (126 MHz, CDCl_3) δ : 179.8 (q, $^2J = 34.8$ Hz, C_7), 147.7 (C_3), 130.5 (2 C, C_4), 127.6 (2 C, C_5), 127.2 (C_6), 116.9 (q, $^1J = 291.3$ Hz, C_8), 76.7 (C_2), 56.5 (C_1); ^{19}F NMR (471 MHz, CDCl_3) δ : -70.4 ; m/z HRMS ASAP+ found $[\text{M}+\text{H}]^+$ 251.0359, $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_2\text{S}^+$ requires 251.0354.

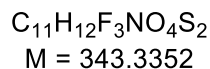
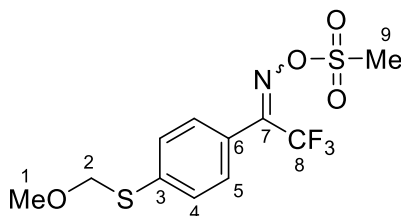
^1H NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one (500 MHz, CDCl_3 , 300 K)



^{13}C NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one (126 MHz, CDCl_3 , 300 K)



Synthesis of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime:



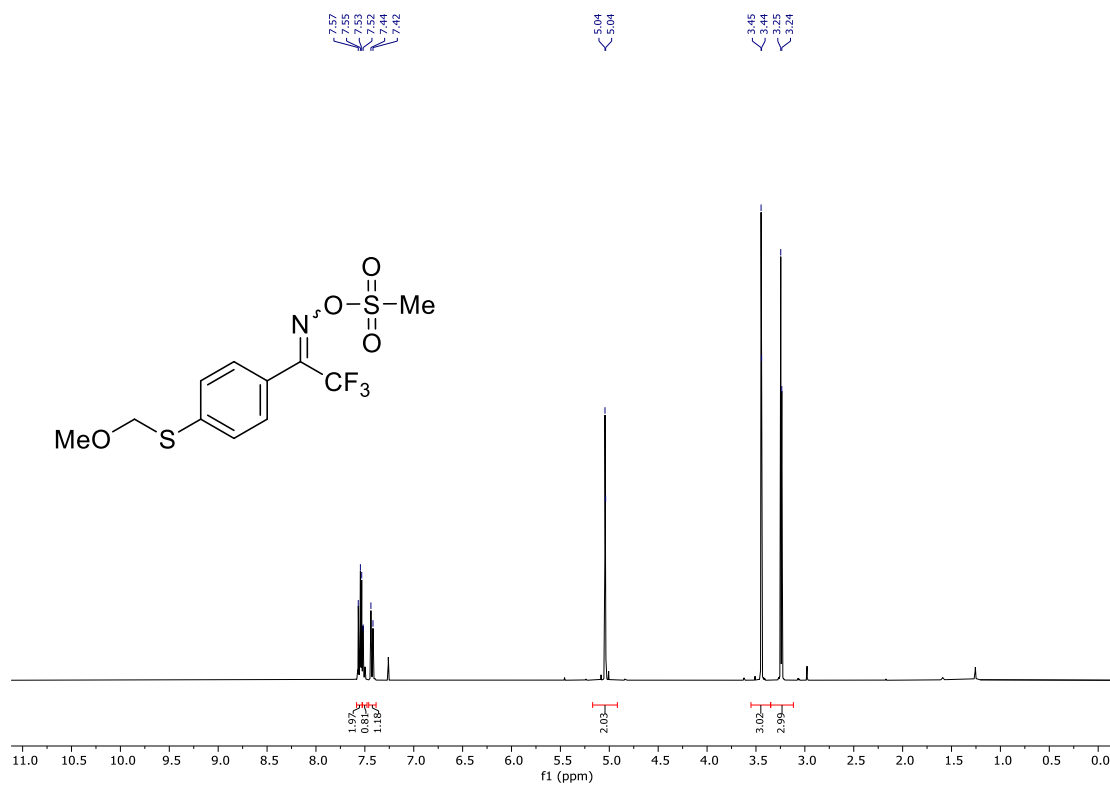
Step 1: Oxime formation

2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one (3.40 g, 13.6 mmol, 1.0 equiv), hydroxylamine hydrochloride (4.25 g, 61.2 mmol, 4.5 equiv) and sodium hydroxide (2.44 g, 61.2 mmol, 4.5 equiv) were dissolved in anhydrous ethanol (50 mL). The vessel was sealed under nitrogen and the mixture stirred vigorously at 80 °C for 18 h. The suspension was allowed to cool to room temperature and subsequently diluted with ethyl acetate, washed with dilute aqueous hydrochloric acid (0.1 M, 3x) and brine. The organic phase was then dried (MgSO₄), filtered, and concentrated in vacuo. The crude oxime was obtained as a clear oil and used directly in the next step.

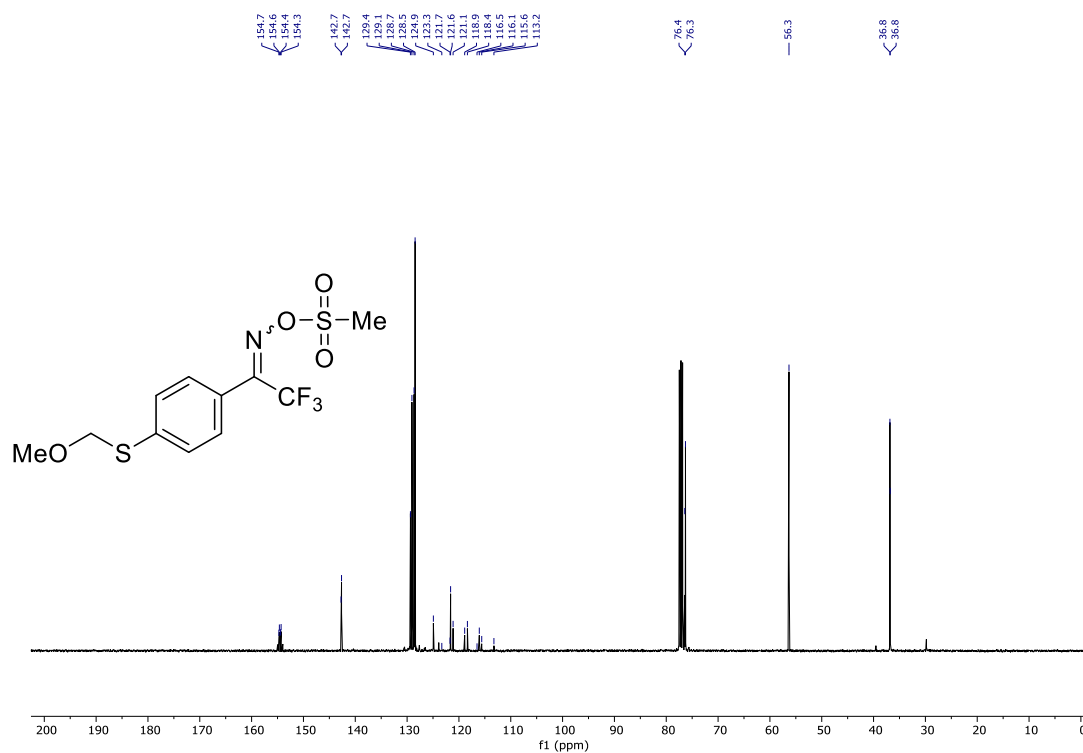
Step 2: Mesylation

The crude oxime obtained from step 1 was dissolved in anhydrous dichloromethane (40 mL) and the resulting solution cooled to 0 °C by means of an ice-bath. Triethylamine (3.03 mL, 21.8 mmol, 1.6 equiv) was added dropwise to the stirred solution at 0 °C, followed by dropwise addition of methanesulfonyl chloride (1.05 mL, 13.6 mmol, 1.0 equiv). The cooling was then removed, and the reaction mixture stirred at room temperature for 14 hours. Equal parts of water and saturated aqueous ammonium chloride solution were then added, and the resulting biphasic mixture extracted with diethyl ether (3x). The combined organic phases were dried (MgSO₄), filtered, and concentrated in vacuo. The residue was purified by silica flash column chromatography (eluent: 100% dichloromethane), yielding the title product (3.97 g, 11.6 mmol, 85%, d.r. = 1.5 : 1) as a pale yellow oil that solidifies on standing. *R_f* (100% dichloromethane): 0.64; ¹H NMR (400 MHz, CDCl₃) δ: 7.58–7.48 (3 H, m, H_{4,5}), 7.45–7.37 (1 H, m, H_{4,5}), 5.044 (2 H, s, H₂, *major*) [5.037 (2 H, s, H₂, *minor*)], 3.45 (3 H, s, H₁, *major*) [3.44 (3 H, s, H₁, *minor*)], 3.25 (3 H, s, H₉, *major*) [3.24 (3 H, s, H₉, *minor*)]; ¹³C NMR (101 MHz, CDCl₃) δ: 154.5 (q, ³J_F = 33.7 Hz, C₇, *major*) [154.6 (q, ²J_F = 32.6 Hz, C₇, *minor*)], 142.65 (C₃, *major*) [142.74 (C₃, *minor*)], 129.1 (C_{4/5}, *major*) [129.4 (C_{4/5}, *minor*)], 128.4 (C_{4/5}, *major*) [128.7 (C_{4/5}, *minor*)], 121.6 (C₆, *major*) [124.9 (*minor*)], 119.7 (q, ¹J_F = 278.2 Hz, C₈, *major*), [117.4 (q, ¹J_F = 283.6 Hz, C₈, *minor*)], 76.3 (C₂, *major*) [76.4 (C₂, *minor*)], 56.3 (C₁), 36.8 (C₉, *major*) [36.9 (C₉, *minor*)]; ¹⁹F NMR (376 MHz, CDCl₃) δ: –66.21 (*major*) [–61.4 (*minor*)]. *m/z* HRMS ESI⁺ found [M+H]⁺ 344.0242, C₁₁H₁₃F₃NO₄S₂⁺ requires 344.0238.

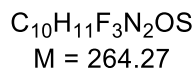
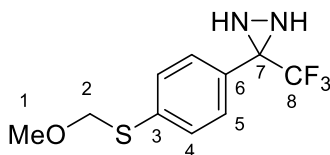
^1H NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime (400 MHz, CDCl_3 , 300 K)



^{13}C NMR of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime (101 MHz, CDCl_3 , 300 K)

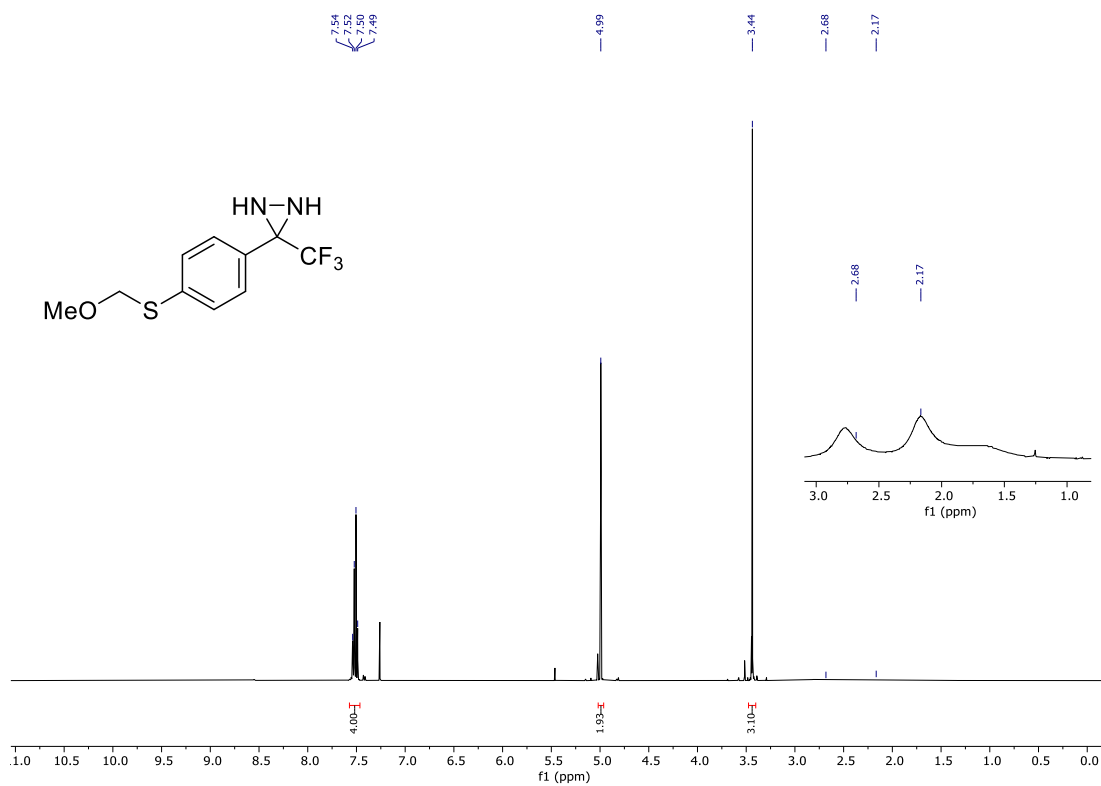


Synthesis of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine:

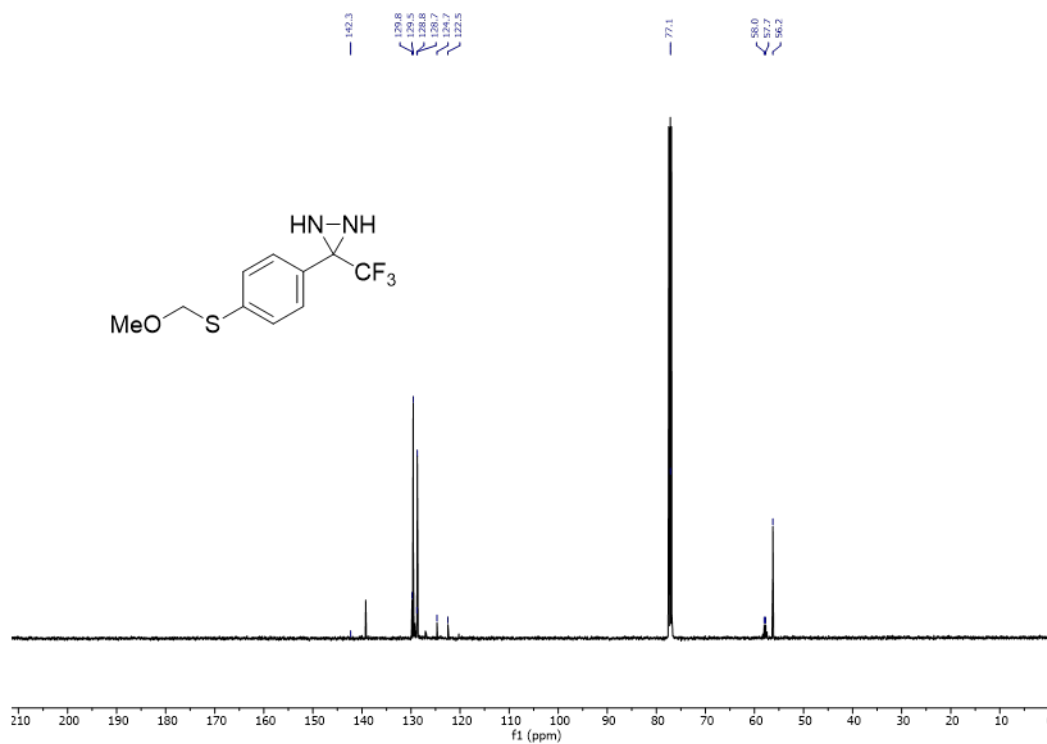


Anhydrous ammonia was condensed (approx. 15 mL) into a pre-cooled flask at $-78\text{ }^{\circ}\text{C}$ using a dry-ice acetone cold finger. To the stirred liquid ammonia, a solution of 2,2,2-trifluoro-1-(4-((methoxymethyl)thio)phenyl)ethan-1-one O-methylsulfonyl oxime (3.79 g, 11.6 mmol, 1.0 equiv) in anhydrous dichloromethane (9 mL) was added dropwise at $-78\text{ }^{\circ}\text{C}$. The solution was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$ and then gradually warmed to room temperature over the course of 12 h, while allowing excess ammonia to vent. To the residue, water (40 mL) was added, and the resulting solution was extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with brine, then dried (MgSO_4), filtered and concentrated in vacuo. The resulting crude oil was purified by silica flash column chromatography (gradient elution: 25% dichloromethane in hexanes to 100% dichloromethane), yielding the title product (2.29 g, 8.67 mmol, 75%) as a colorless oil. R_f (100% dichloromethane): 0.29; ^1H NMR (500 MHz, CDCl_3) δ : 7.55–7.47 (4 H, m, $\text{H}_{4,5}$), 4.99 (2 H, s, H_2), 3.44 (3 H, s, H_1), 2.68 (1 H, br s, NH), 2.17 (1 H, br s, NH); ^{13}C NMR (126 MHz, CDCl_3) δ : 142.3 (C_3), 129.8 (C_6), 129.5 ($\text{C}_{4/5}$), 128.7 ($\text{C}_{4/5}$), 123.5 (q, $^1J_{\text{F}} = 278.3\text{ Hz}$, C_8), 77.1 (C_2), 57.9 (q, $^2J_{\text{F}} = 36.3\text{ Hz}$, C_7), 56.2 (C_1). ^{19}F NMR (471 MHz, CDCl_3) δ : -74.59 ; m/z HRMS ESI+ found $[\text{M}+\text{H}]^+$ 265.0635, $\text{C}_{10}\text{H}_{12}\text{F}_3\text{N}_2\text{OS}^+$ requires 265.0623.

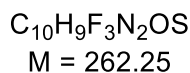
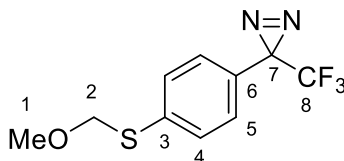
^1H NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine (500 MHz, CDCl_3 , 300 K)



^{13}C NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine (126 MHz, CDCl_3 , 300 K)

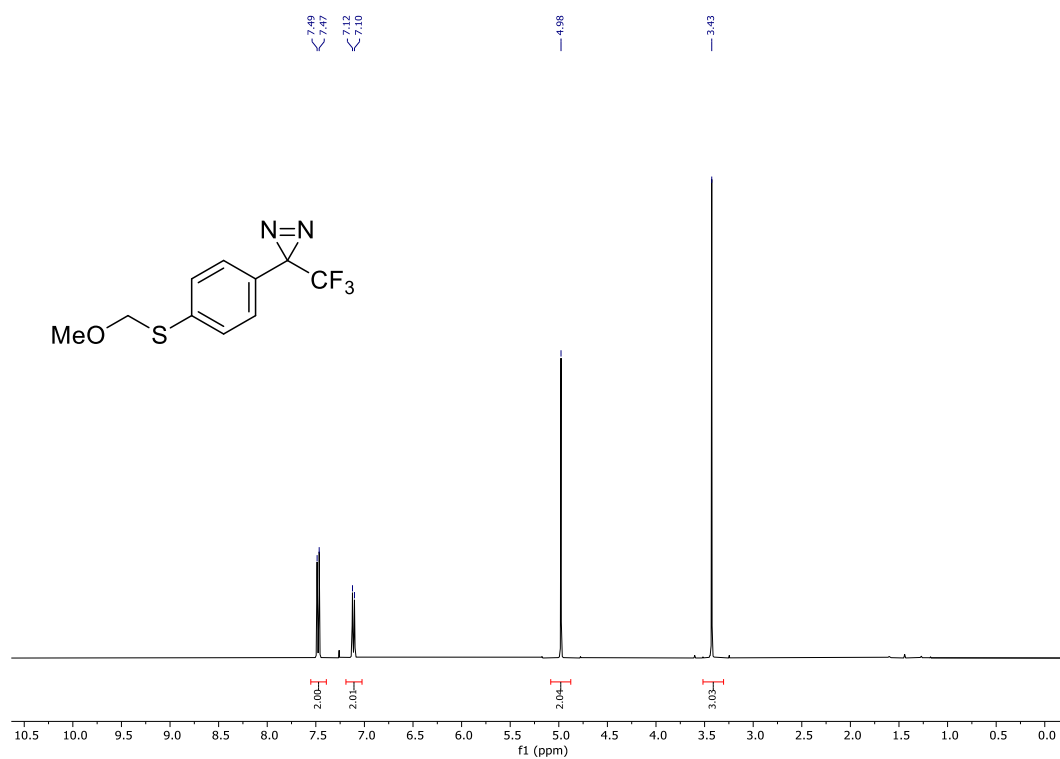


Synthesis of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine:

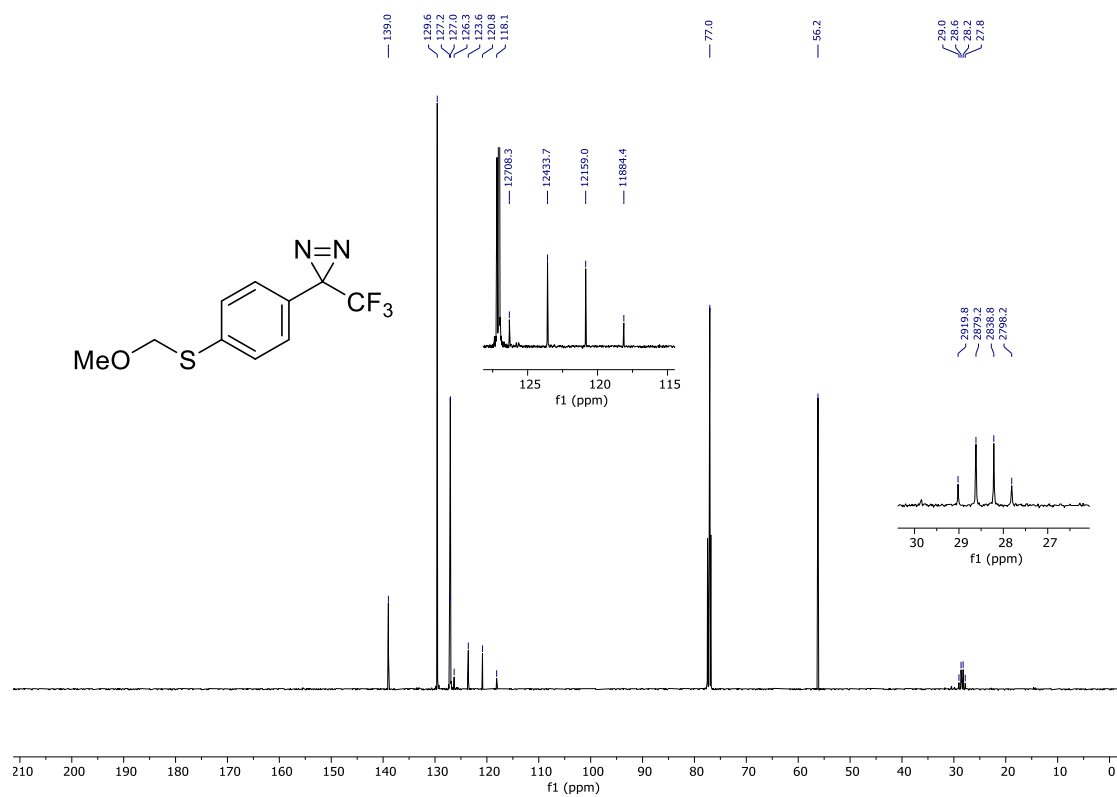


To a solution of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)diaziridine (2.29 g, 8.67 mmol, 1.0 equiv) in methanol (60 mL) was added triethylamine (3.62 mL, 26.0 mmol, 3.0 equiv) followed by portion-wise addition of iodine (6.60 g, 26.0 mmol, 3.0 equiv) with vigorous stirring at room temperature. The resulting dark solution was stirred for 14 h at room temperature under the exclusion of ambient light (tin foil) and subsequently quenched via addition of 10% aqueous sodium thiosulphate solution (60 mL). The almost colorless biphasic mixture was extracted with diethyl ether (3 x), and the combined organic phases dried (MgSO_4), filtered, and concentrated under reduced pressure. The residue was purified by silica flash column chromatography (elution: 25% dichloromethane in hexanes), yielding the title product (1.92 g, 7.32 mmol, 84%) as a pale yellow oil. R_f (50% dichloromethane in hexanes): 0.62; ^1H NMR (400 MHz, CDCl_3) δ : 7.48 (2 H, d, $J = 8.7$ Hz, $\text{H}_{4/5}$), 7.11 (2 H, d, $J = 8.7$ Hz, $\text{H}_{4/5}$), 4.98 (2 H, s, H_2), 3.43 (3 H, s, H_1); ^{13}C NMR (101 MHz, CDCl_3) δ : 139.0 (C_3), 129.6 (2 C, $\text{C}_{4/5}$), 127.2 (C_6), 127.0 (2 C, $\text{C}_{4/5}$), 122.2 (q, $^1J_{\text{F}} = 274.7$ Hz, C_8), 77.0 (C_2), 56.2 (C_1), 28.4 (q, $^2J_{\text{F}} = 28.4$ Hz, C_7); ^{19}F NMR (376 MHz, CDCl_3) δ : -65.40.

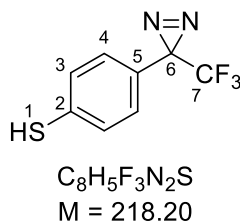
^1H NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (400 MHz, CDCl_3 , 300 K)



^{13}C NMR of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (400 MHz, CDCl_3 , 300 K)



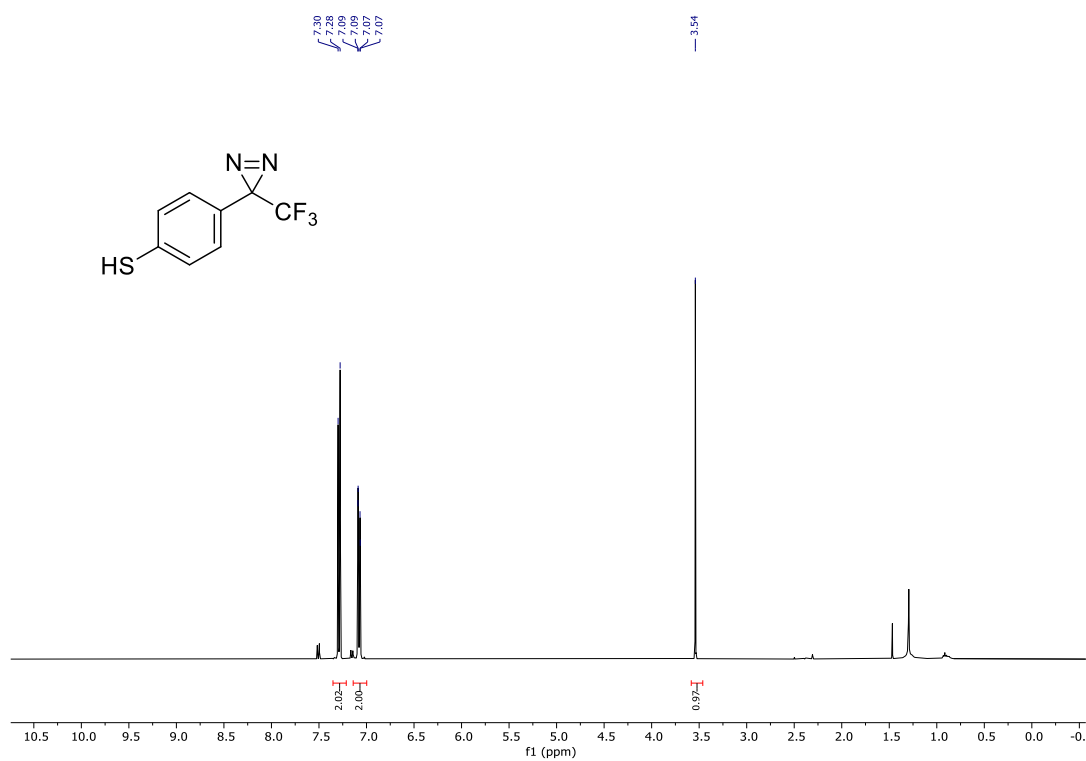
Synthesis of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol³:



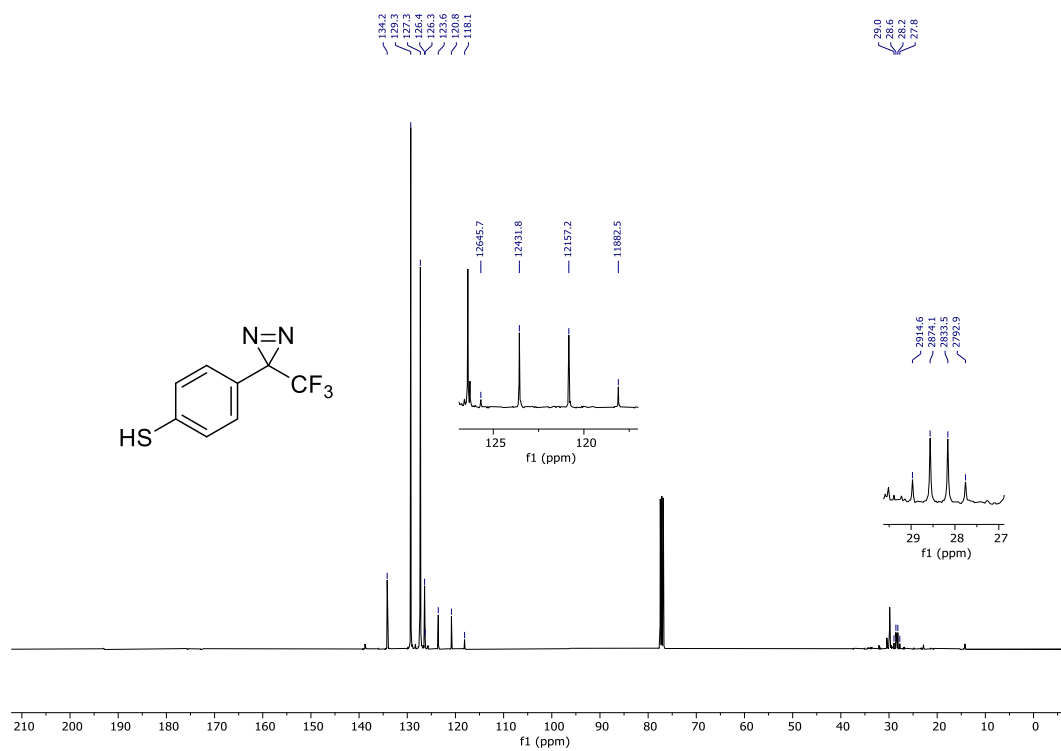
A solution of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (4.00 g, 15.3 mmol, 1.0 equiv) in anhydrous ethanol (450 mL, degassed by sparging with N_2 for 20 min) was heated to 55 °C and silver nitrate (3.11 g, 18.3 mmol, 1.2 equiv) was added in one portion with vigorous stirring. The mixture was stirred at 55 °C for 2 h, during which the reaction mixture became considerably more viscous followed by the formation of a voluminous precipitate. At this point silver nitrate (778 mg, 4.58 mmol, 0.25 equiv) was added and stirring was continued at 55 °C for 1 h. All volatiles were removed in vacuo using a rotary evaporator. The reaction flask was evacuated and backfilled with N_2 three times, and 6 M aqueous hydrochloric acid (380 mL, degassed by sparging with N_2 for 20 min) was added via cannula. The resulting suspension was stirred for 30 min before dichloromethane (160 mL, degassed by sparging with N_2 for 20 min) was added via cannula. The mixture was vigorously stirred for 1.0 h at room temperature. The reaction mixture was diluted with dichloromethane, and the organic phase washed with water and brine. The organic phase was dried (MgSO_4), filtered and concentrated in vacuo.

TLC and ^1H -NMR analysis of crude reaction mixture indicated the presence of disulfide UDC2. Hence, the crude mixture was dissolved in acetonitrile (180 mL) and water (20 mL) was added. To the resulting solution tris(2-carboxyethyl)phosphine (TCEP, 1.09 g, 3.83 mmol, 0.25 equiv) was added in one portion. The mixture was stirred at room temperature for 20 min diluted with water (200 mL) and extracted with diethyl ether (3 x 150 mL). The combined organic phases were dried over sodium sulfate, filtered and concentrated. Purification by silica flash column chromatography (elution: 0.2% diethylether in hexanes) yielded the title product (122 mg, 559 μmol , 73%) as a volatile pale-yellow oil. R_f (10 % diethylether in hexanes): 0.28; ^1H NMR (400 MHz, CDCl_3) δ : 7.29 (2 H, d, $J = 8.6$ Hz, H_3), 7.08 (2 H, d, $J = 8.6$ Hz, H_4), 3.54 (1 H, s, H_1); ^{13}C NMR (101 MHz, CDCl_3) δ : 134.2 (C_2), 129.3 (2 C, C_4), 127.3 (2 C, C_3), 126.4 (C_5), 122.2 (q, $^1J = 274.6$ Hz, C_7), 28.4 (q, $^2J = 40.5$ Hz, C_6); ^{19}F NMR (376 MHz, CDCl_3) δ : -65.4.

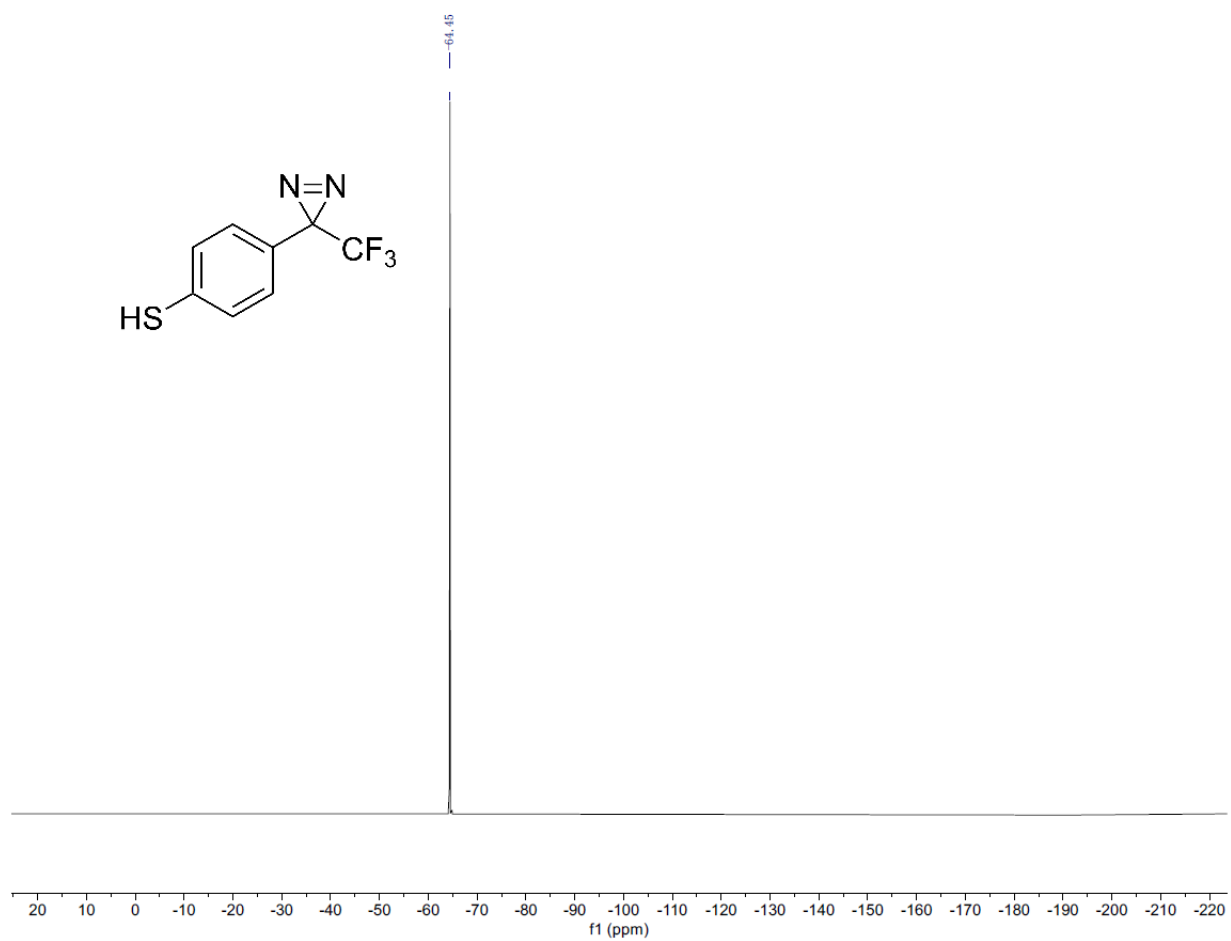
^1H NMR of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (400 MHz, CDCl_3 , 300 K)



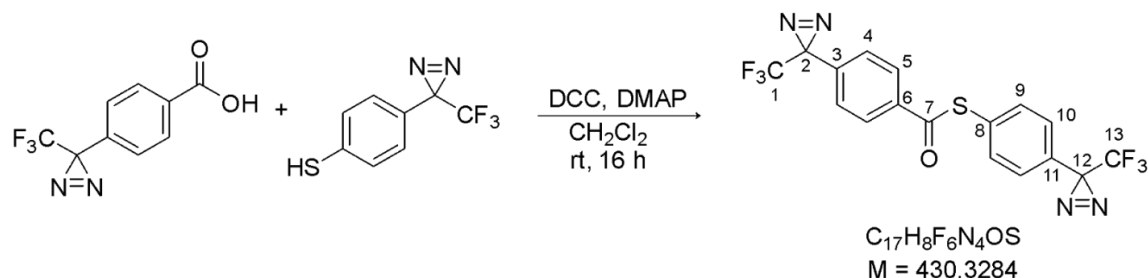
^{13}C NMR of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (101 MHz, CDCl_3 , 300 K)



^{19}F NMR of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (376 MHz, CDCl_3 , 300 K)

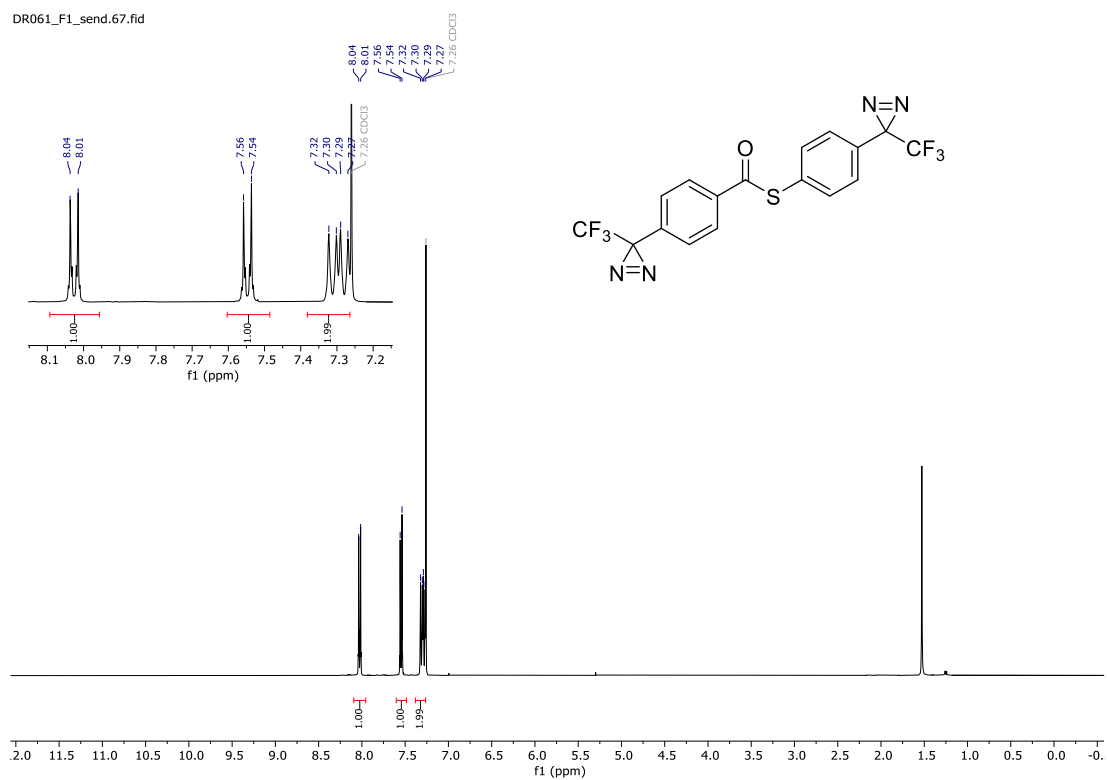


Synthesis of *S*-(4-(3-(trifluoromethyl)-3H-diazirin-3-yl)phenyl) 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzothioate (UDC1):

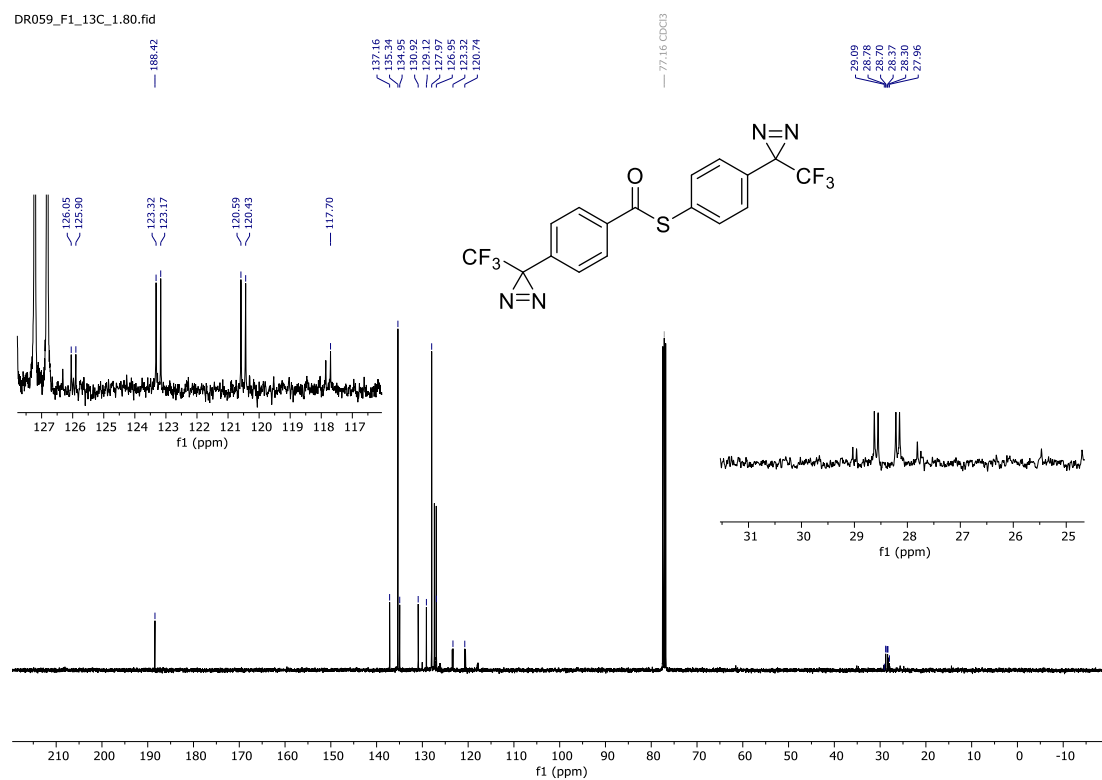


A 50 mL Schlenk flask was charged with 4-(3-trifluoromethyl)-3H-diazirin-3-yl)benzoic acid (TDBA) (2.0 g, 8.69 mmol, 1.0 equiv), DCC (2.15 g, 10.4 mmol, 1.2 equiv) and DMAP (425 mg, 3.48 mmol, 0.4 equiv), sealed and backfilled with nitrogen (3 x). A solution of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (TDBT) (1.90 g, 8.69 mmol, 1.0 equiv) in anhydrous dichloromethane (29 mL) was added via syringe, and the resulting mixture stirred at room temperature for 16 h. The reaction mixture was filtered through celite, the filter cake washed with diethyl ether, and the filtrate concentrated in vacuo. The residue was purified by silica flash column chromatography (gradient elution: hexanes then 8% dichloromethane in hexanes), yielding the title product (3.51 g, 8.16 mmol, 94%) as a colorless waxy solid. R_f (10 % diethyl ether in hexanes): 0.63; ^1H NMR (400 MHz, CDCl_3) δ : 8.02 (2 H, d, $J = 8.7$ Hz, H_5), 7.55 (2 H, d, $J = 8.7$ Hz, H_4), 7.31 (2 H, d, $J = 8.2$ Hz, $\text{H}_{9/10}$), 7.28 (2 H, d, $J = 8.2$ Hz, $\text{H}_{9/10}$); ^{13}C NMR (101 MHz, CDCl_3) δ : 188.4 (C_7), 137.2 (C_6), 135.3 (2 C, C_9), 134.9 (C_3), 130.9 ($\text{C}_{8/11}$), 129.1 ($\text{C}_{8/11}$), 128.0 (2 C, C_5), 127.4 (2 C, q, $^4J = 1.5$ Hz, C_{10}), 127.0 (2 C, q, $^4J = 1.8$ Hz, C_4), 122.1 (q, $^1J = 274.9$ Hz, $\text{C}_{1/13}$), 121.9 (q, $^1J = 274.9$ Hz, $\text{C}_{1/13}$), 28.6 (q, $^2J = 40.9$ Hz, $\text{C}_{2/12}$), 28.5 (q, $^2J = 40.9$ Hz, $\text{C}_{2/12}$); ^{19}F NMR (282 MHz, CDCl_3) δ : -64.0, -64.2 IR (film) ν_{max} : 3198, 2927, 1722, 1699, 1253, 1179, 1128, 905.

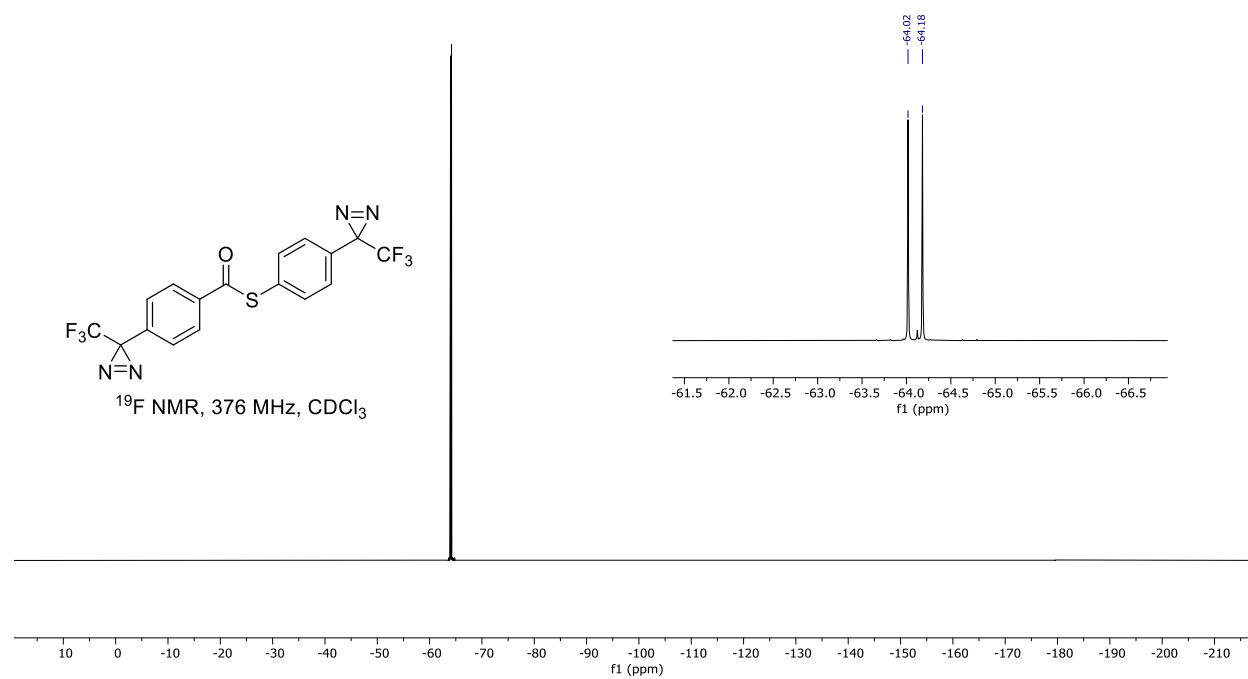
¹H NMR of UDC1 (400 MHz, CDCl₃, 300 K)



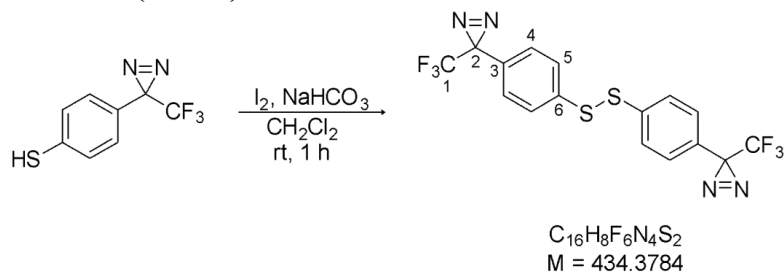
¹³C NMR of UDC1 (101 MHz, CDCl₃, 300 K)



^{19}F NMR of UDC1 (376 MHz, CDCl_3 , 300 K)

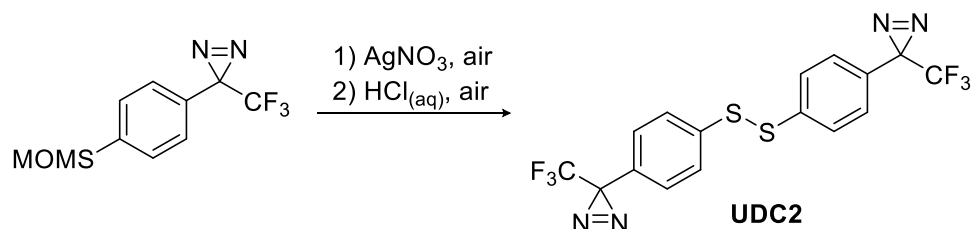


Synthesis of S-(4-(3-(trifluoromethyl)-3H-diazirin-3-yl)phenyl) 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzothioate (UDC2):



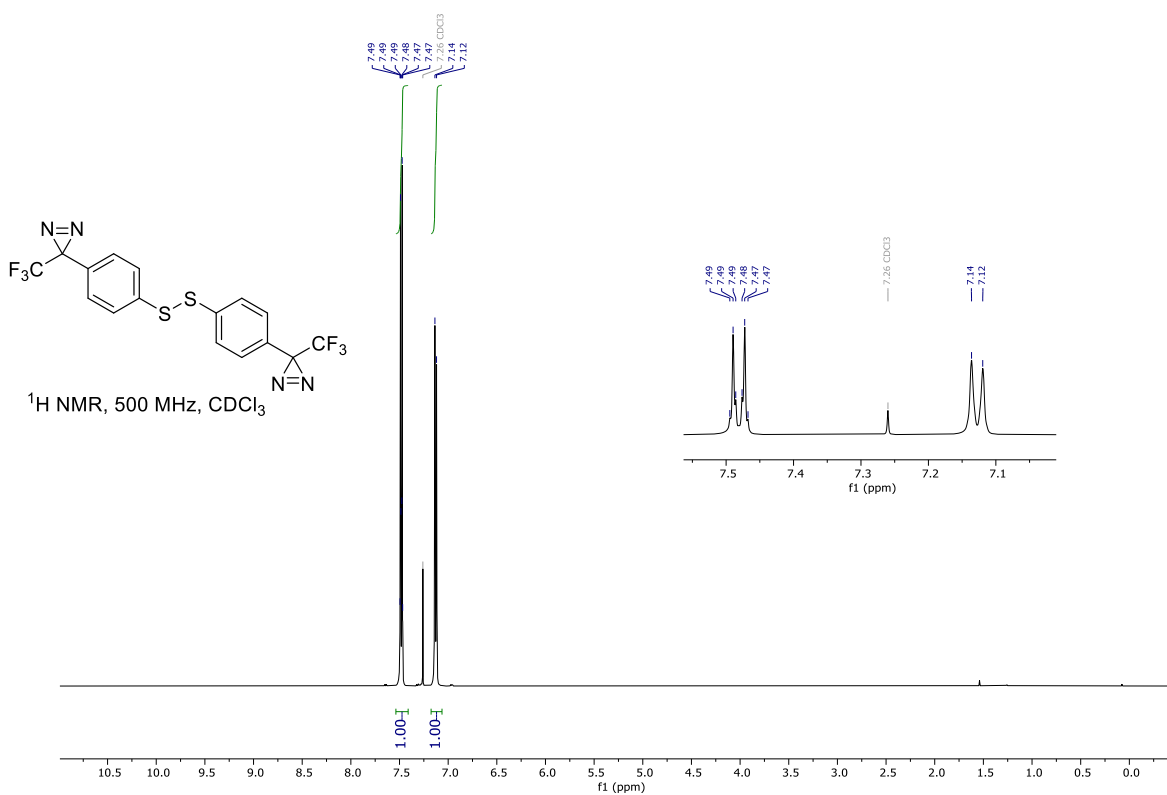
A 250 mL round-bottom flask was charged with 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (1.00 g, 4.58 mmol, 1.0 equiv) and anhydrous dichloromethane (57 mL). NaHCO_3 (481 mg, 5.73 mmol, 1.25 equiv) was added in one portion and the resulting suspension was stirred at room temperature for 15 min. Iodine (1.74 g, 6.87 mmol, 1.5 equiv) was added portion was and the resulting dark purple mixture was stirred for 40 min. Half-saturated aqueous sodium thiosulfate (50 mL) was added and the biphasic mixture was stirred vigorously until all excess iodine had been consumed as evidenced by full discoloration of the organic phase (approximately 30 min). The phases were separated, and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with brine, dried over Na_2SO_4 , filtered and concentrated. Purification by flash column chromatography (hexanes) furnished the title product (886 mg, 2.29 mmol, 89%) as a pale yellow oil (melting point $\sim 20^\circ\text{C}$). R_f (hexanes): 0.39; ^1H NMR (500 MHz, CDCl_3) δ : 7.50–7.45 (4 H, m, H_5), 7.13 (4 H, d, $J = 8.3$ Hz, H_4); ^{13}C NMR (126 MHz, CDCl_3) δ : 138.8 (2 C, C_6), 128.3 (2 C, C_3), 127.4 (4 C, C_4), 127.2 (4 C, C_5), 122.1 (2 C, q, $^1J = 274.7$ Hz, C_1), 28.4 (q, $^2J = 40.8$ Hz, C_2), ^{19}F NMR (471 MHz, CDCl_3) δ : -64.3 ; HRMS ASAP+ found $[\text{M}+\text{H}]^+ 435.0166$, $\text{C}_{16}\text{H}_8\text{F}_6\text{N}_4\text{S}_2^+$ requires 435.0173; IR (film) ν_{max} : 2990, 1715, 1341, 1181, 1148, 936, 814, 696.

Synthesis of UDC2 from 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine:

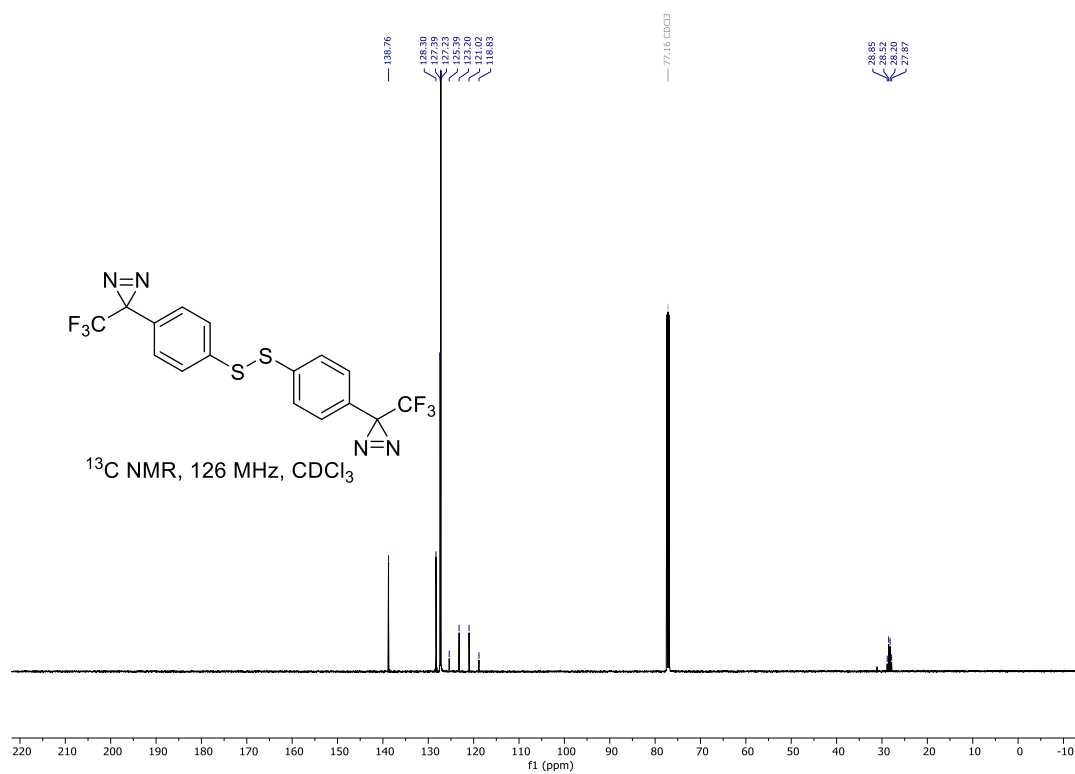


A solution of 3-(4-((methoxymethyl)thio)phenyl)-3-(trifluoromethyl)-3H-diazirine (2.00 g, 7.63 mmol, 1.0 equiv) in anhydrous ethanol (240 mL) was stirred open to air at 55 °C. Silver nitrate (1.55 g, 9.15 mmol, 1.2 equiv) was added in one portion with vigorous stirring. The mixture was stirred at 55 °C for 2 h, during which a white precipitate was formed, rendering the reaction highly viscous. All volatiles were removed in vacuo using a rotary evaporator. 6 M aqueous hydrochloric acid (218 mL) was added to the crude mixture and the reaction was stirred at ambient temperature open to air for 1.5 h. Dichloromethane (100 mL) was added and stirring was continued for 1 h. The biphasic mixture was filtered and the layers were separated. The aqueous layer was extracted with dichloromethane (2 x 100 mL). The combined organic phases were dried over Na₂SO₄ filtered and concentrated in vacuo. Purification by silica flash column chromatography (elution: hexanes) yielded the title product (1.36 g, 3.13 mmol, 82%) as a volatile pale-yellow oil that solidified at lower temperatures. Analytical data were identical to those reported above for UDC2.

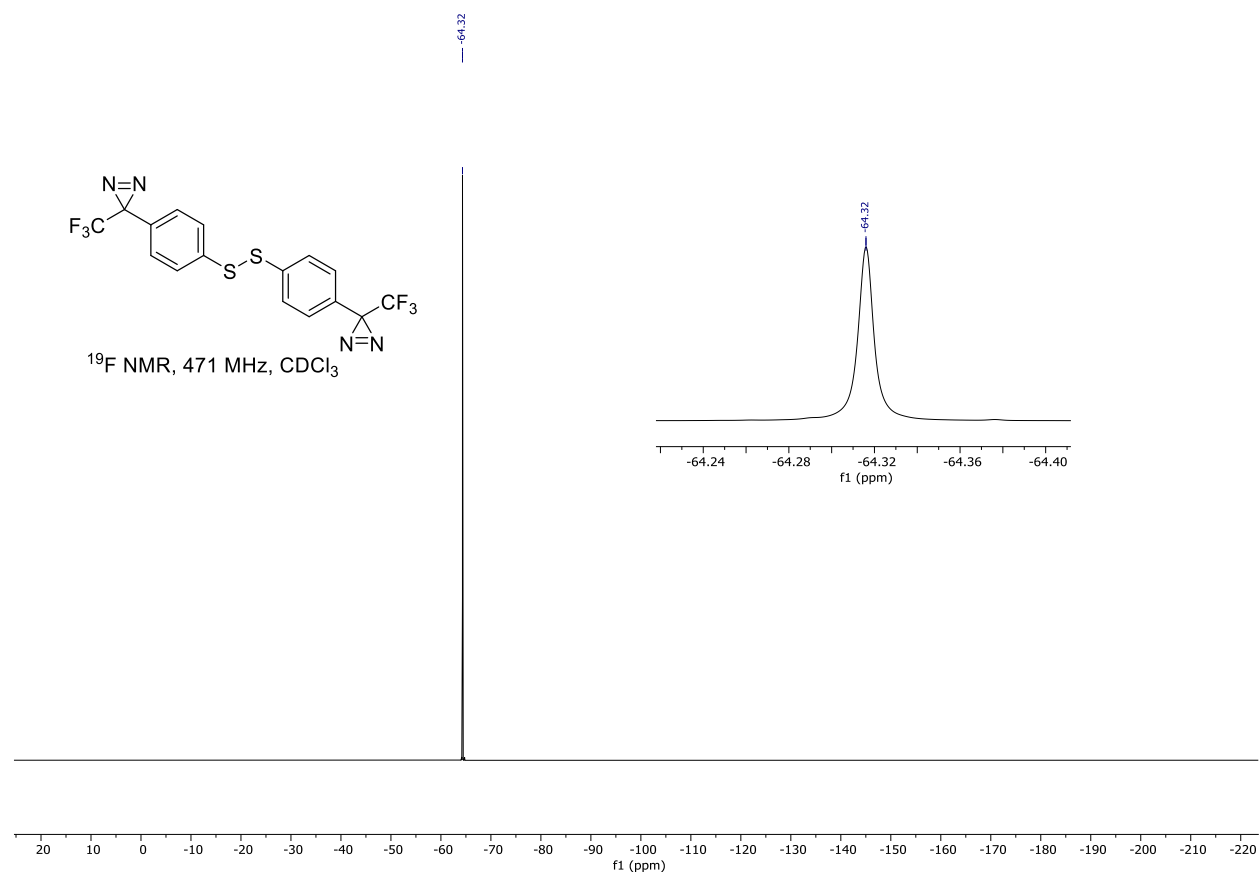
¹H NMR of UDC2 (500 MHz, CDCl₃, 300 K)



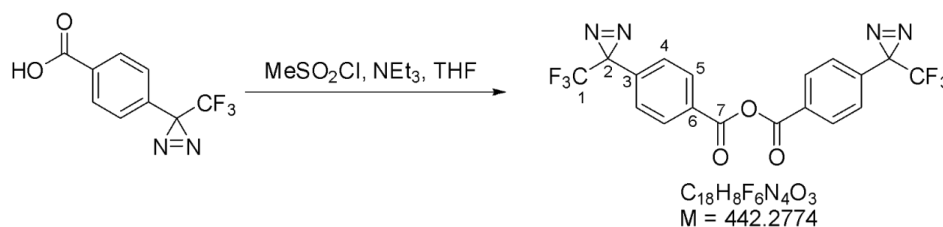
¹³C NMR of UDC2 (126 MHz, CDCl₃, 300 K)



^{19}F NMR of UDC2 (126 MHz, CDCl_3 , 300 K)

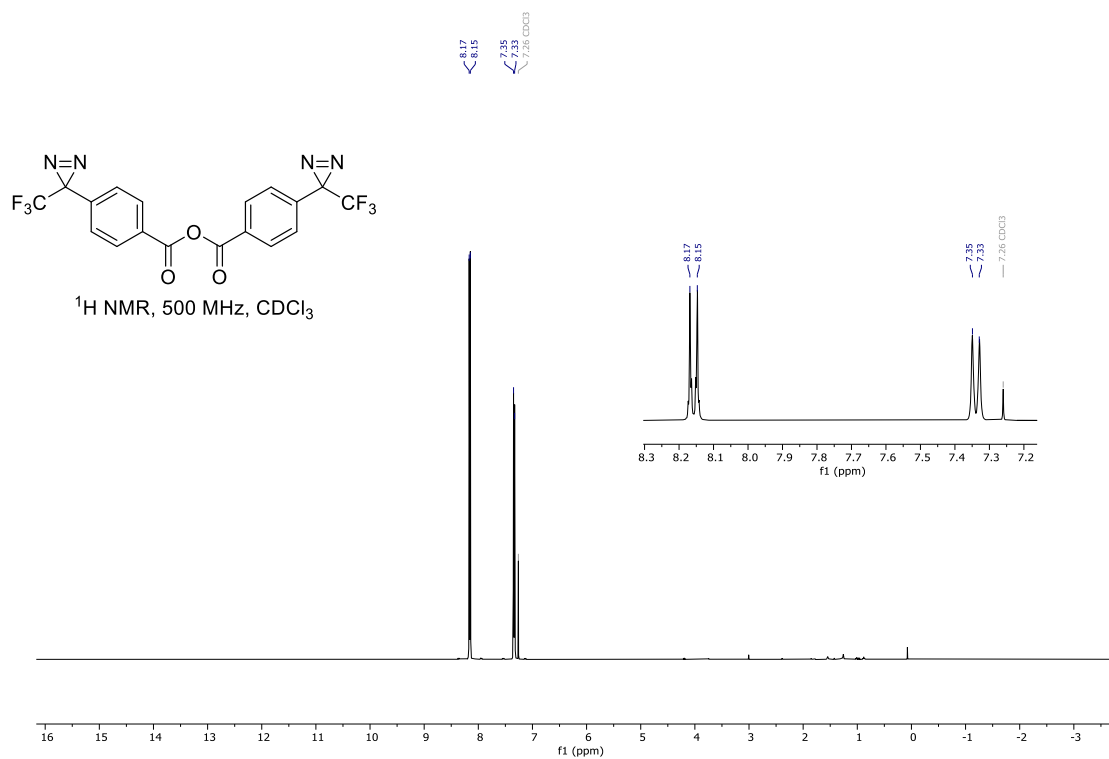
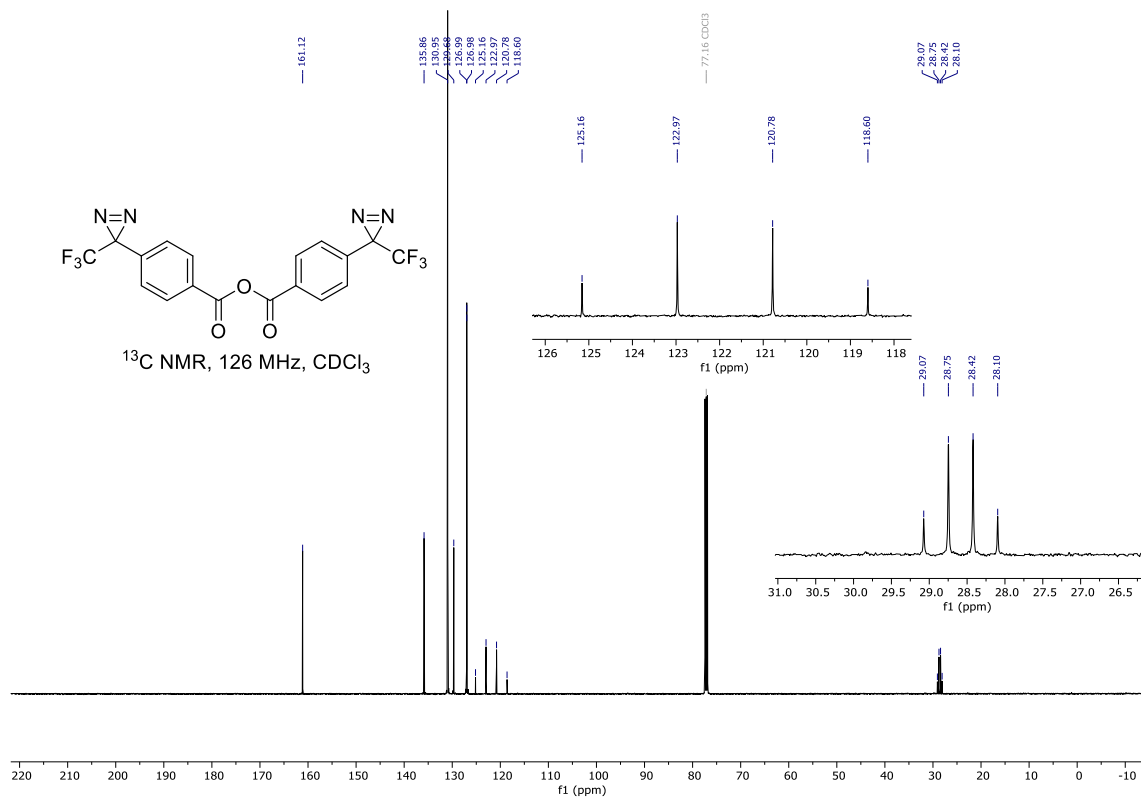


Synthesis of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzoic anhydride (UDC3):

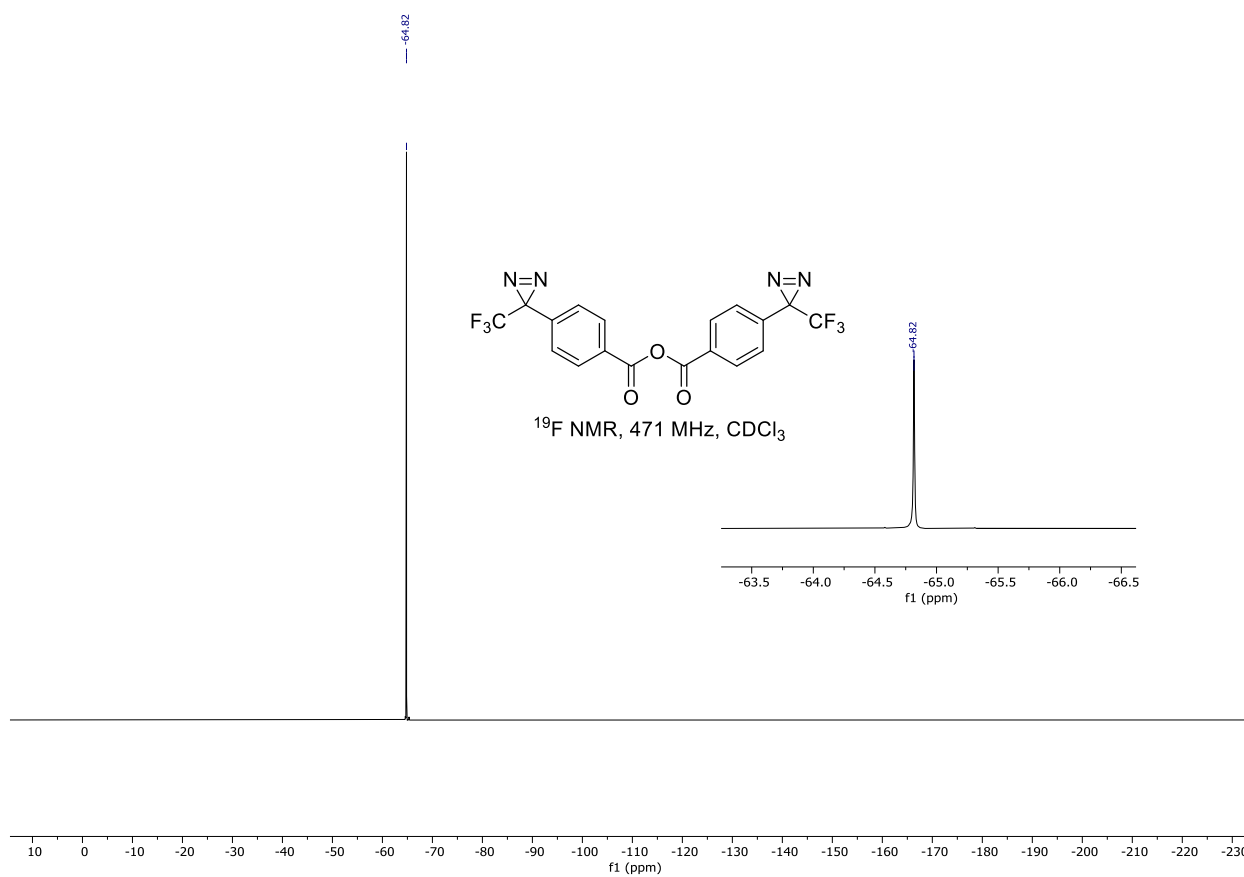


A solution of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzoic acid (1.50 g, 6.52 mmol, 1.0 equiv) in anhydrous THF (20 mL) was cooled to 0 °C, and MeSO₂Cl (277 μL, 3.58 mmol, 0.55 equiv) was added dropwise. The resulting pale-yellow solution was stirred for 5 min at 0 °C before triethylamine (1.55 mL, 11.2 mmol, 1.7 equiv) was added dropwise resulting in the formation of a white precipitate. After stirring for 1 h at 0 °C, the ice bath was removed and the reaction mixture was allowed to warm to room temperature for 10 min. The mixture was concentrated (rotary evaporation at 40 °C) and directly purified by column chromatography (10% dichloromethane in hexanes containing 1% (v/v) HCl (2 M in Et₂O), to 25% dichloromethane in hexanes containing 1% (v/v) HCl (2 M in Et₂O)) to give the title compound as a white, crystalline solid (1.38 g, 3.12 mmol, 96%). *R_f* (25% dichloromethane in hexanes + 1% (v/v) HCl (2 M in Et₂O)): 0.41; ¹H NMR (500 MHz, CDCl₃) δ: 8.16 (4 H, d, *J* = 8.6 Hz, H₅), 7.13 (4 H, d, *J* = 8.3 Hz, H₄); ¹³C NMR (126 MHz, CDCl₃) δ: 161.1 (2 C, C₇), 135.9, (2 C, C₆), 131.0 (4 C, C₅), 129.7 (2 C, C₃), 127.0 (4 C, C₄), 121.9 (2 C, q, *J* = 274.8 Hz, C₁), 28.6 (2 C, q, *J* = 41.0 Hz, C₂); ¹⁹F NMR (471 MHz, CDCl₃) δ: − 64.8; HRMS ESI+ found [M+Na]⁺ 463.0416, C₁₈H₈F₆N₄NaO₃⁺ requires 465.0398; IR (film) *v*_{max}: 2991, 2898, 2677, 1688, 1346, 1290, 1202, 1184, 1153, 942, 736.

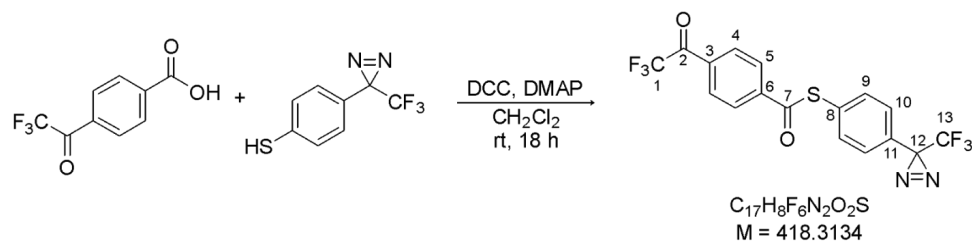
Note: UDC3 was found to be stable towards ambient moisture and even aqueous workup. However, UDC3 hydrolyzes readily on neutral or basic silica. Hence, acidification of silica prior to and during column chromatography is required in order to obtain high yields. Commercially available solutions of HCl in diethyl ether or dioxane were found to furnish the best results. Acidification using acetic or formic acid leads to undesired cross-anhydride products.

¹H NMR of UDC3 (500 MHz, CDCl₃, 300 K) ^{13}C NMR of UDC3 (126 MHz, CDCl_3 , 300 K)

^{19}F NMR of UDC3 (471 MHz, CDCl_3 , 300 K)

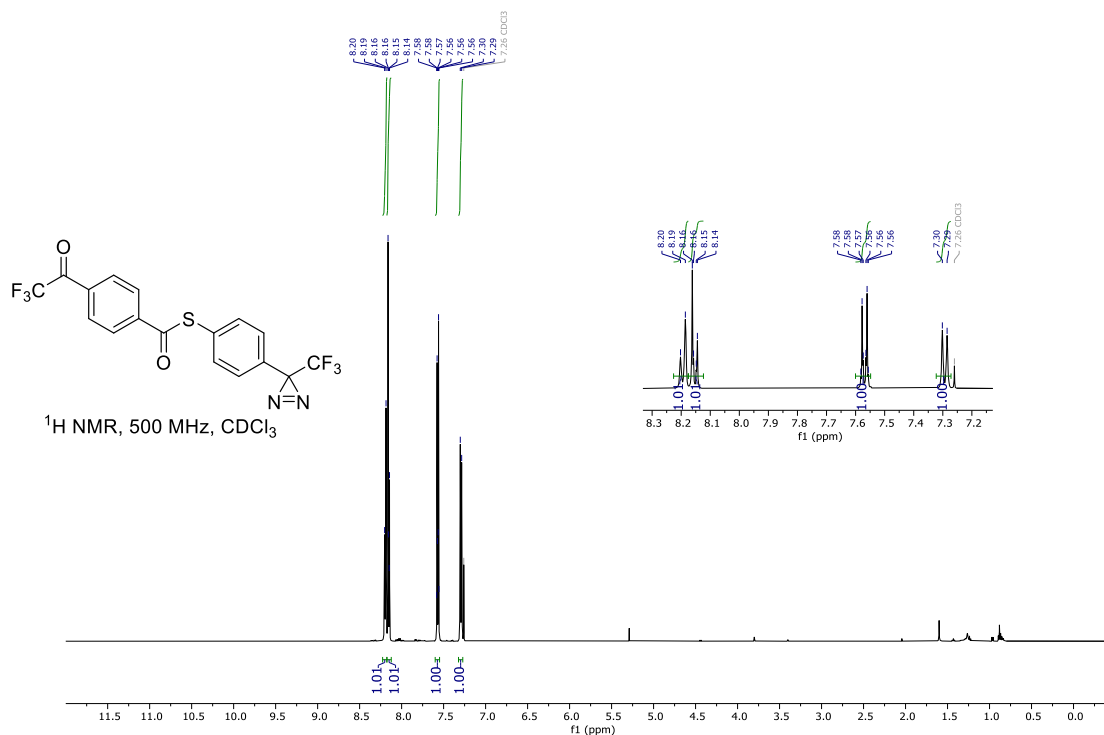


Synthesis of S-(4-(3-(trifluoromethyl)-3H-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzoate:

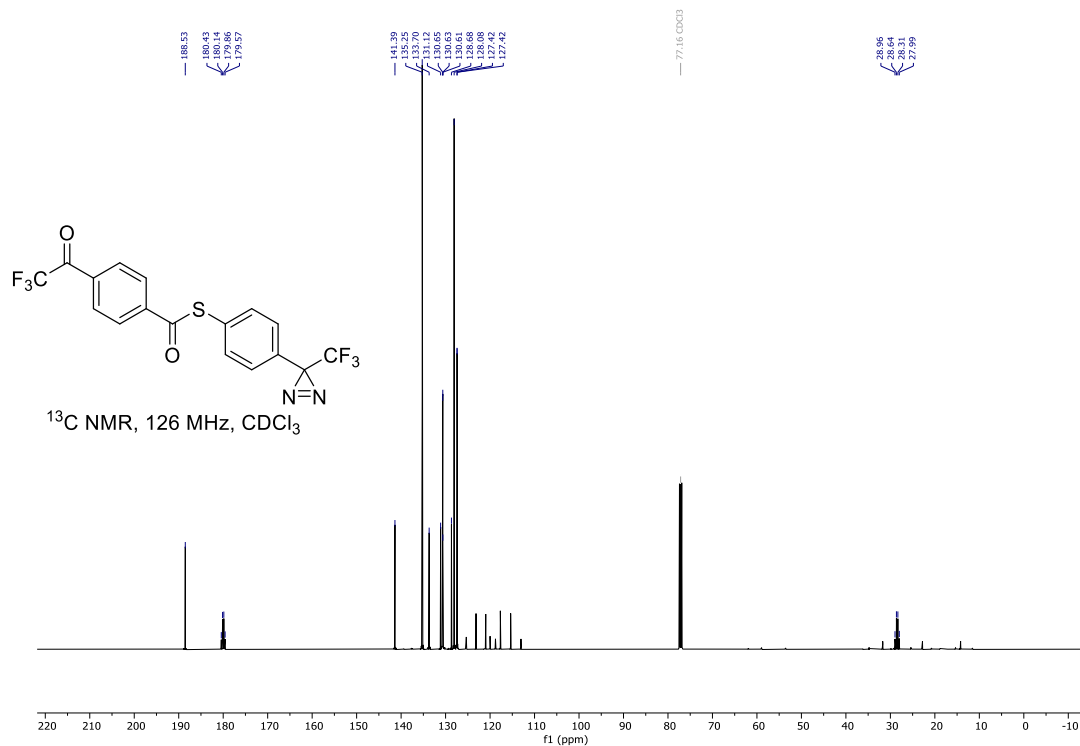


A 50 mL Schlenk flask was charged with 4-(2,2,2-trifluoroacetyl)benzoic acid (960 mg, 4.40 mmol, 1.2 equiv), DCC (1.06 g, 5.13 mmol, 1.4 equiv) and DMAP (202 mg, 1.65 mmol, 0.45 equiv), sealed and backfilled with nitrogen (3 x). A solution of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl)benzenethiol (800 mg, 3.67 mmol, 1.0 equiv) in anhydrous dichloromethane (13 mL) was added via syringe, and the resulting mixture stirred at room temperature for 18 h. The reaction mixture was filtered through celite, the filter cake washed with diethyl ether, and the filtrate concentrated in vacuo. The residue was purified by silica flash column chromatography (gradient elution: hexanes then 10% dichloromethane in hexanes), yielding the title product (1.02 g, 2.44 mmol, 67%) as a colorless oil R_f (10 % diethyl ether in hexanes): 0.53; ^1H NMR (500 MHz, CDCl_3) δ 8.19 (2 H, d, $J = 8.4$ Hz, $\text{H}_{4/5}$), 8.17 – 8.13 (2 H, m, $\text{H}_{4/5}$), 7.61 – 7.54 (2 H, m, H_{10}), 7.29 (2 H, d, $J = 8.2$ Hz, H_9); ^{13}C NMR (126 MHz, CDCl_3) δ 188.5 (C_7), 180.00 (q, $J = 36.0$ Hz, C_2), 141.4 (C_6), 135.3 (2 C, C_9), 133.7 (C_3), 131.1 ($\text{C}_{8/11}$), 130.6 (2 C, q, $J = 2.0$ Hz, C_{10}), 128.7 ($\text{C}_{8/11}$), 128.1 (2 C, C_5), 127.4 (2 C, C_4), 122.06 (q, $J = 274.7$ Hz, C_{12}), 116.5 (q, $J = 291.0$ Hz, C_1), 28.5 (q, $J = 40.7$ Hz, C_{12}); ^{19}F NMR (471 MHz, CDCl_3) δ : -64.1 (s, $\text{F}_3\text{C}-1$), -70.9 (s, $\text{F}_3\text{C}-13$);

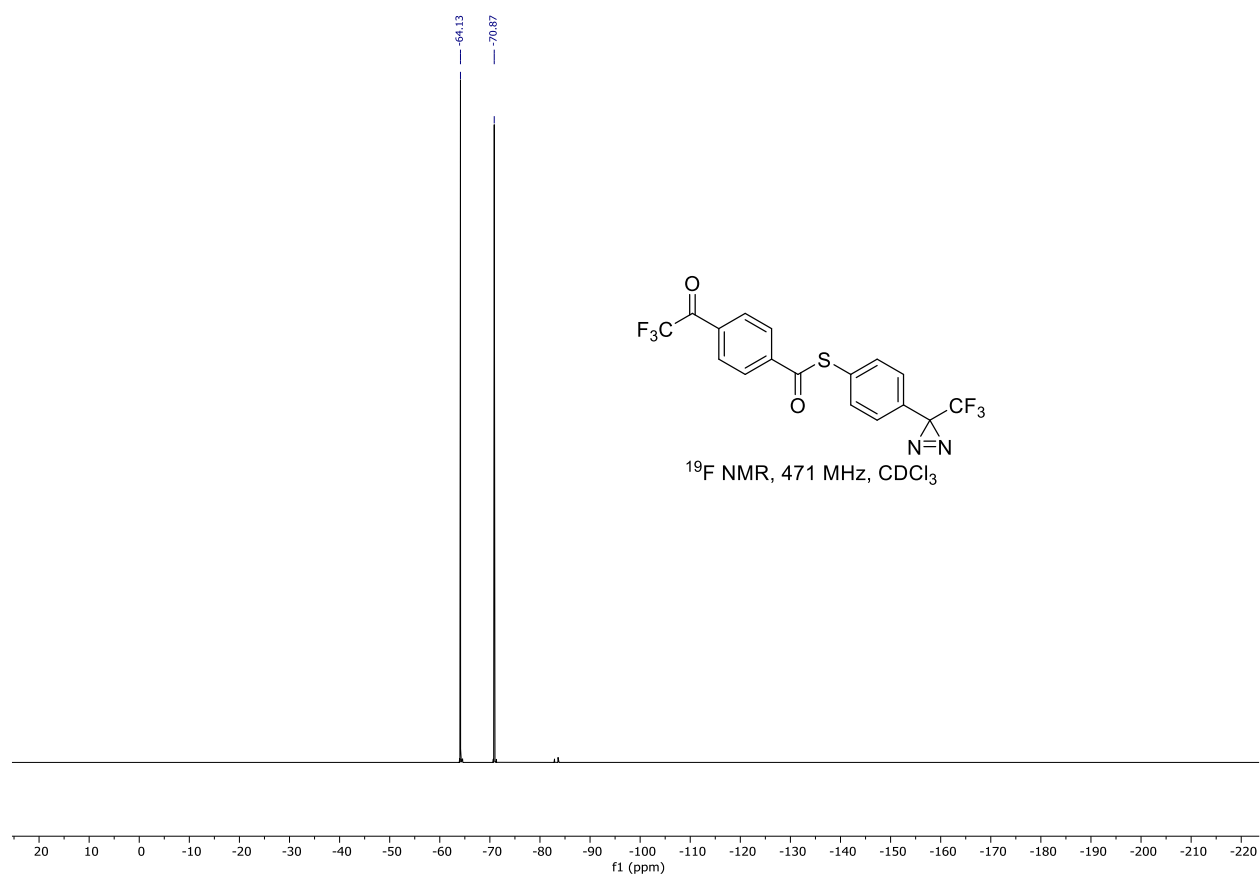
¹H NMR of *S*-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzothioate (500 MHz, CDCl₃, 300 K)



¹³C NMR of *S*-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzothioate (126 MHz, CDCl₃, 300 K)

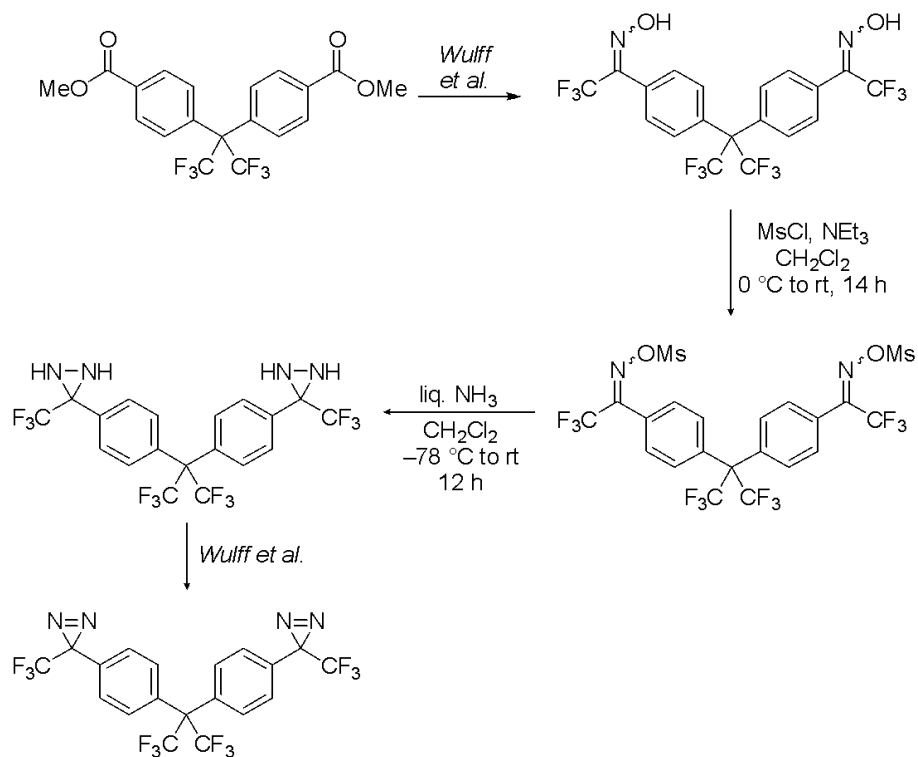


^{19}F NMR of *S*-(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl) 4-(2,2,2-trifluoroacetyl)benzothioate (471 MHz, CDCl_3 , 300 K)

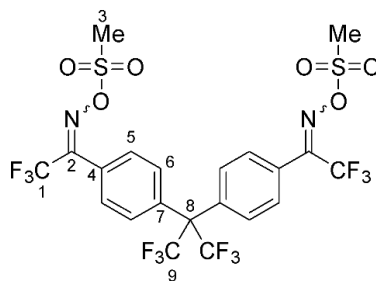


Synthesis of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)-3H-diazirine)⁴ (USC):

This compound was synthesized following the route established by Wulff *et al.*⁴ with two slight deviations: The bis-oxime synthesized by Wulff and co-workers was mesylated instead of tosylated and then treated with liquid ammonia.



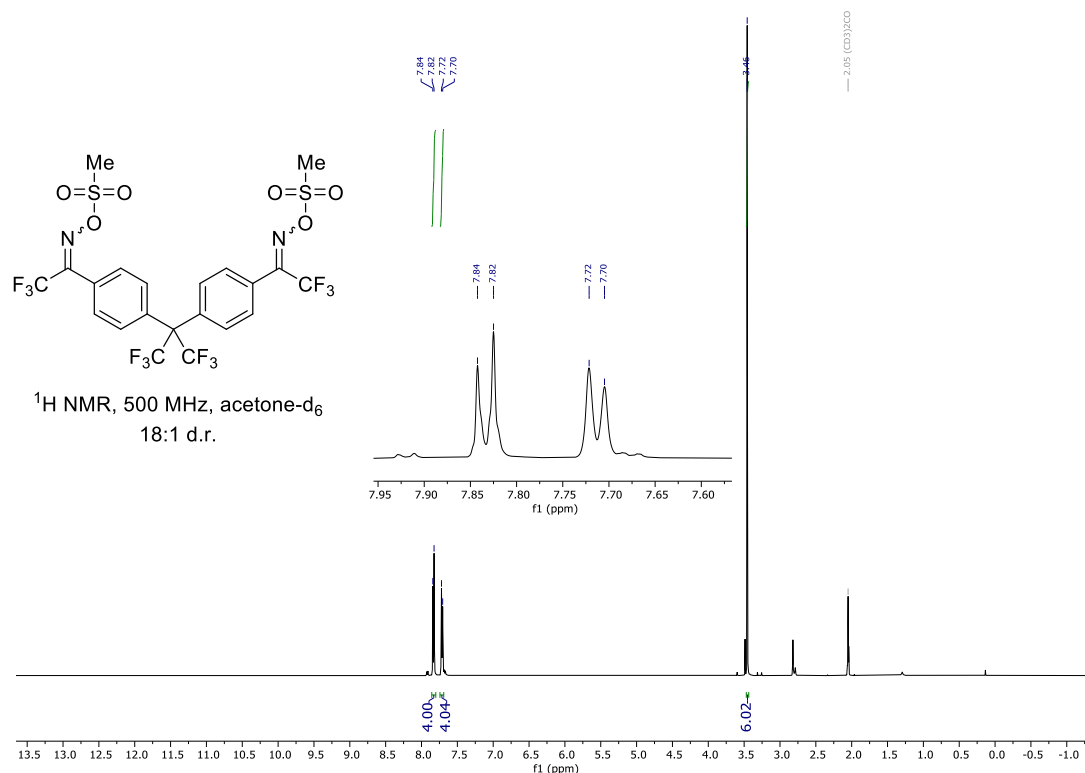
Synthesis of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethylsulfonyl dioxime:



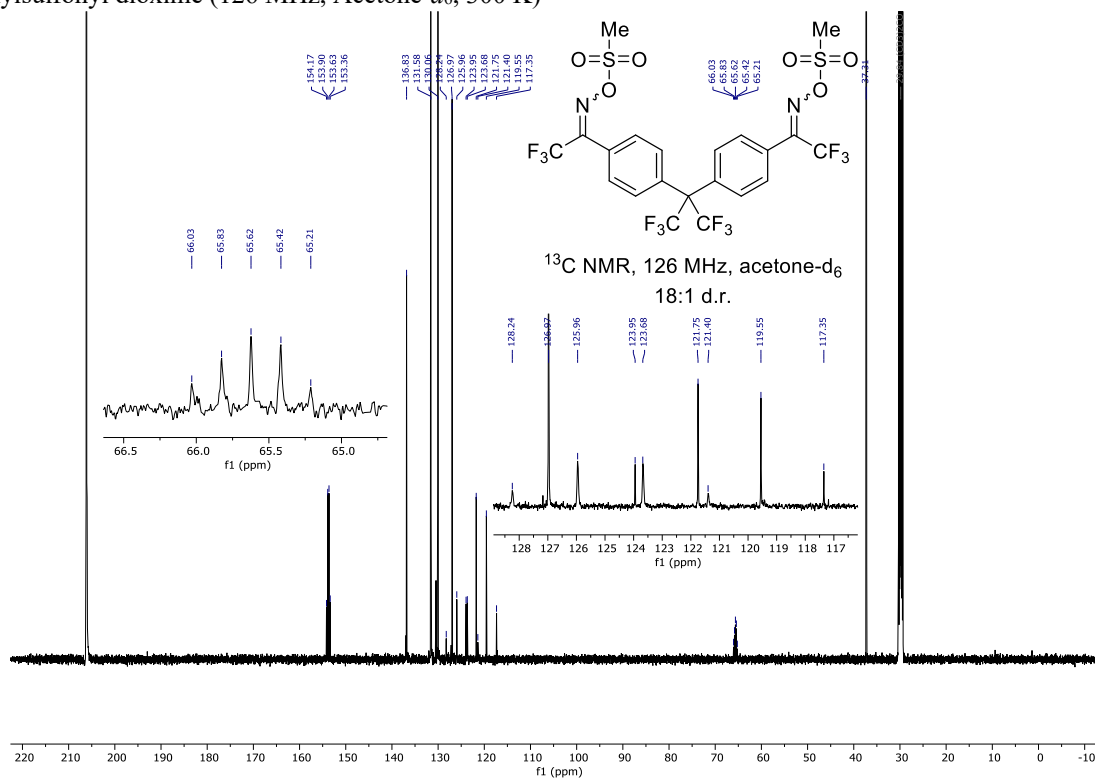
A solution of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) dioxime (4.89 g, 9.29 mmol, 1.0 equiv) in anhydrous dichloromethane (48 mL) was cooled to 0 °C, triethylamine (4.14 mL, 29.7 mmol, 3.2 equiv) was added dropwise followed by MsCl (1.58 mL, 20.4 mmol, 2.2 equiv). The reaction was allowed to warm to room temperature overnight (approximately 15 h) and then quenched by addition of sat. aq. NH_4Cl (50 mL). Water (15 mL) was added to dissolve the resulting precipitate. The mixture was extracted with diethyl ether (3 x 50 mL). The combined organic phases were dried over Na_2SO_4 , filtered, and concentrated. The resulting crude solid was purified by silica flash column chromatography (gradient elution: hexanes to 25% ethyl acetate in hexanes), yielding the title product (4.83 g, 7.08 mmol, 76%) as a colorless solid.

The title compound was isolated as a 18:1 mixture of diastereomers. Only signals corresponding to the major diastereomer are reported: R_f (25% ethyl acetate in hexanes): 0.23; ^1H NMR (500 MHz, acetone) δ 7.83 (4 H, d, J = 8.7 Hz, H_5), 7.71 (4 H, d, J = 8.3 Hz, H_6), 3.46 (6 H, s, H_2); ^{13}C NMR (126 MHz, acetone) δ : 153.8 (2 C, q, J = 33.8 Hz, C_2), 136.8 (2 C, C_4), 131.6 (4 C, C_5), 130.1 (4 C, C_6), 127.0 (2 C, C_7), 124.8 (2 C, q, J = 288.1 Hz, C_9), 120.7 (2 C, q, J = 276.5 Hz, C_1), 65.6 (app q, J = 51.8 Hz, C_8), 37.3 (2 C, C_3); ^{19}F NMR (471 MHz, acetone) δ -63.1 (s, F_3C -9), -66.7 (s, F_3C -1); HRMS ESI+ found $[\text{M}+\text{Na}]^+$ 705.0001, $\text{C}_{21}\text{H}_{14}\text{F}_{12}\text{N}_2\text{NaO}_6\text{S}_2^+$ requires 704.9994 IR (film) ν_{max} : 3030, 1702, 1381, 1249, 1187, 1142, 971, 892, 814, 756, 674, 518, 487.

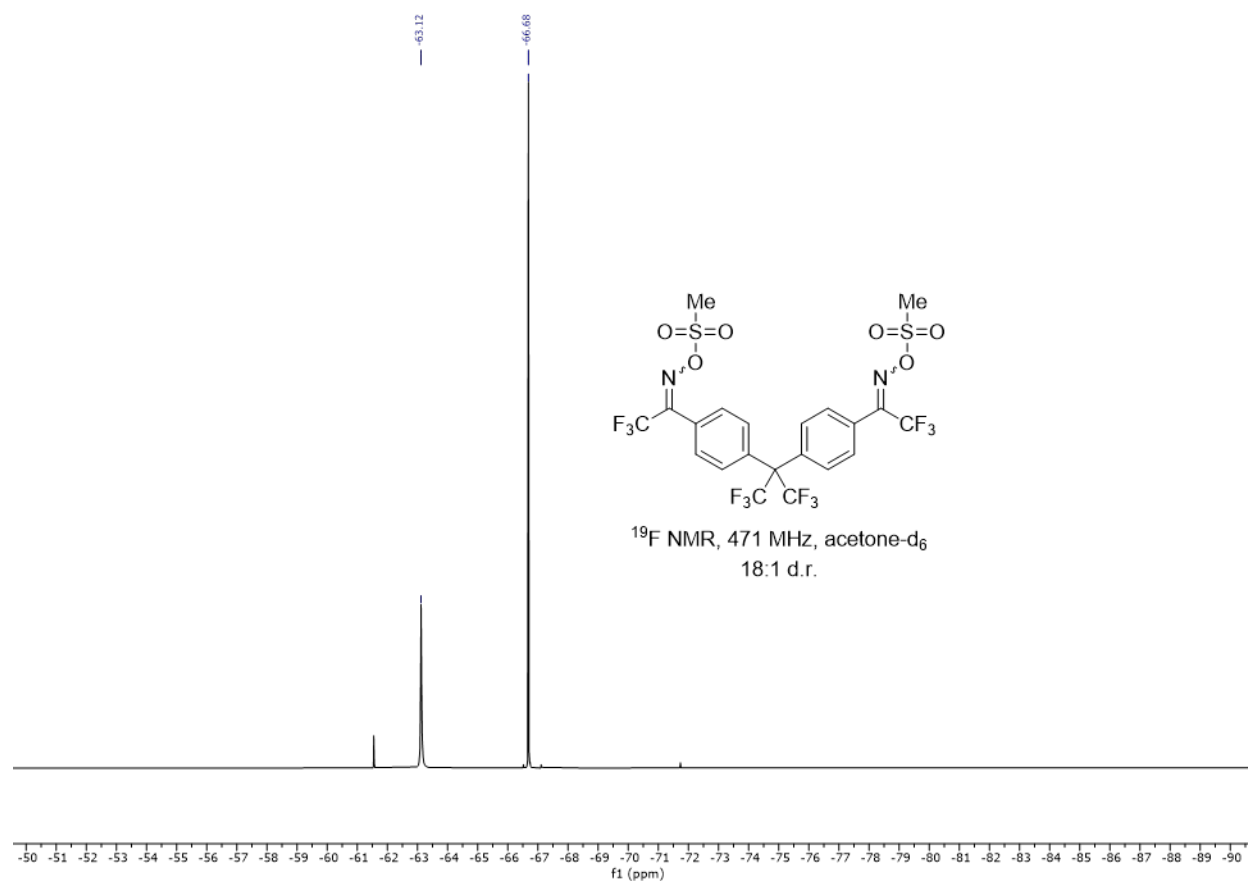
^1H NMR of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethylsulfonyl dioxime (500 MHz, Acetone- d_6 , 300 K)



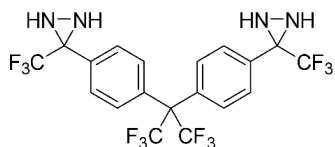
^{13}C NMR of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethylsulfonyl dioxime (126 MHz, Acetone- d_6 , 300 K)



^{19}F NMR of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethylsulfonyl dioxime (126 MHz, Acetone- d_6 , 300 K)



Synthesis of 3,3'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(3-(trifluoromethyl)diaziridine):



Anhydrous ammonia was condensed (approx. 40 mL) into a pre-cooled Schlenk flask at $-78\text{ }^{\circ}\text{C}$ using a dry-ice acetone cold finger. To the stirred liquid ammonia, a solution of 1,1'-((perfluoropropane-2,2-diyl)bis(4,1-phenylene))bis(2,2,2-trifluoroethan-1-one) O,O-dimethyl sulfonyl dioxime (4.80 g, 7.03 mmol, 1.0 equiv) in anhydrous tetrahydrofuran (40 mL) was added dropwise at $-78\text{ }^{\circ}\text{C}$. The solution was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$ and then gradually warmed to room temperature over the course of 15 h, while allowing excess ammonia to vent. Nitrogen was bubbled through the resulting suspension for 10 min to remove residual ammonia. The resulting suspension was concentrated, and dichloromethane (200 mL) was added. The resulting mixture was washed with sat. aq. NH_4Cl (150 mL). The phases were separated, and the aqueous phase was extracted with dichloromethane (2 x 100 mL). The combined organic phases were dried over Na_2SO_4 , filtered, and concentrated. The resulting crude solid was purified by silica flash column chromatography (gradient elution: 50% dichloromethane in hexanes to dichloromethane to 10% ethyl acetate in dichloromethane), yielding the title product (3.03 g, 5.78 mmol, 82%) as a colorless solid. Analytical data agreed with values reported by Wulff and co-workers.⁴

Supplementary Figures

UV-Vis Experiments

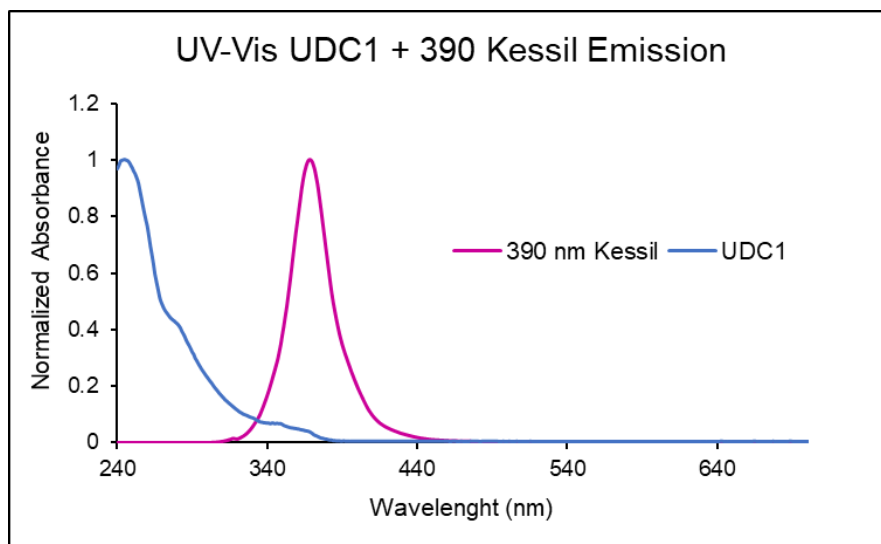


Figure S1. UV-Vis absorption profile for UDC1 (5 nM in MeCN) overlaid with 390 nm Kessil emission.

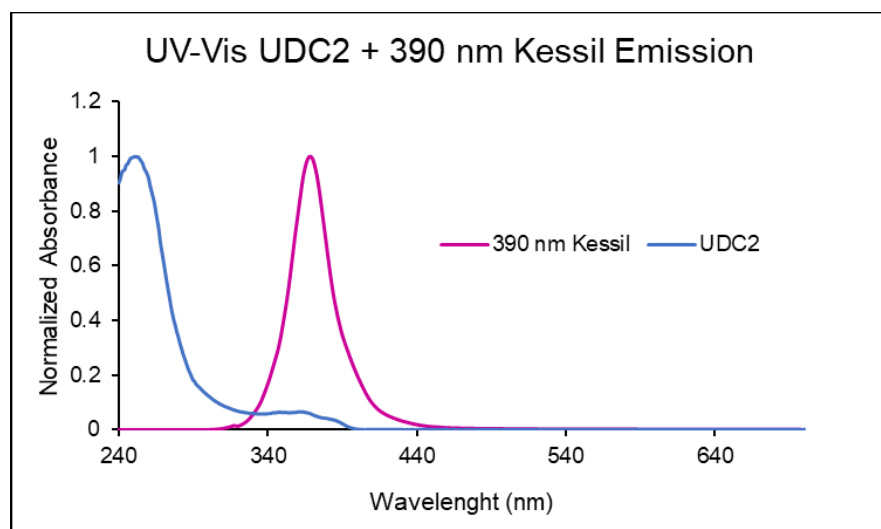


Figure S2. UV-Vis absorption profile for UDC2 (5 nM in MeCN) overlaid with 390 nm Kessil emission.

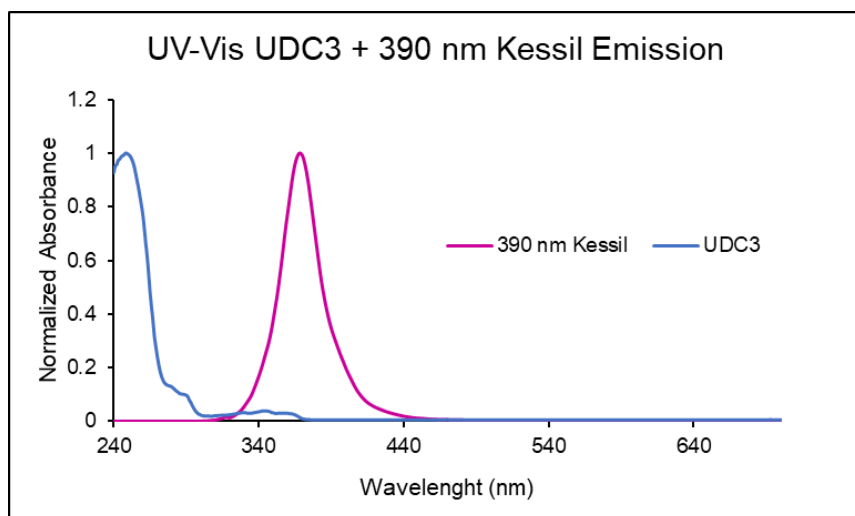
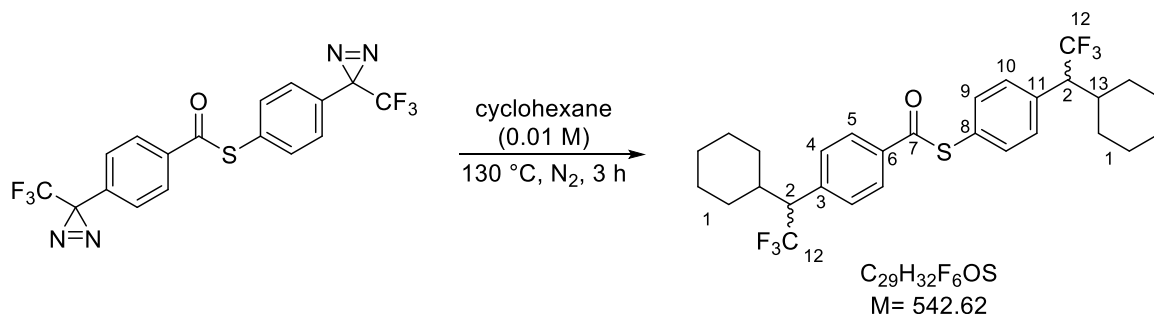


Figure S3. UV-Vis absorption profile for UDC3 (5 nM in MeCN) overlaid with 390 nm Kessil emission.

Modeled Carbene Activation and Insertion Crosslinking on Cyclohexane by UDC1, 2, and 3.

UDC1

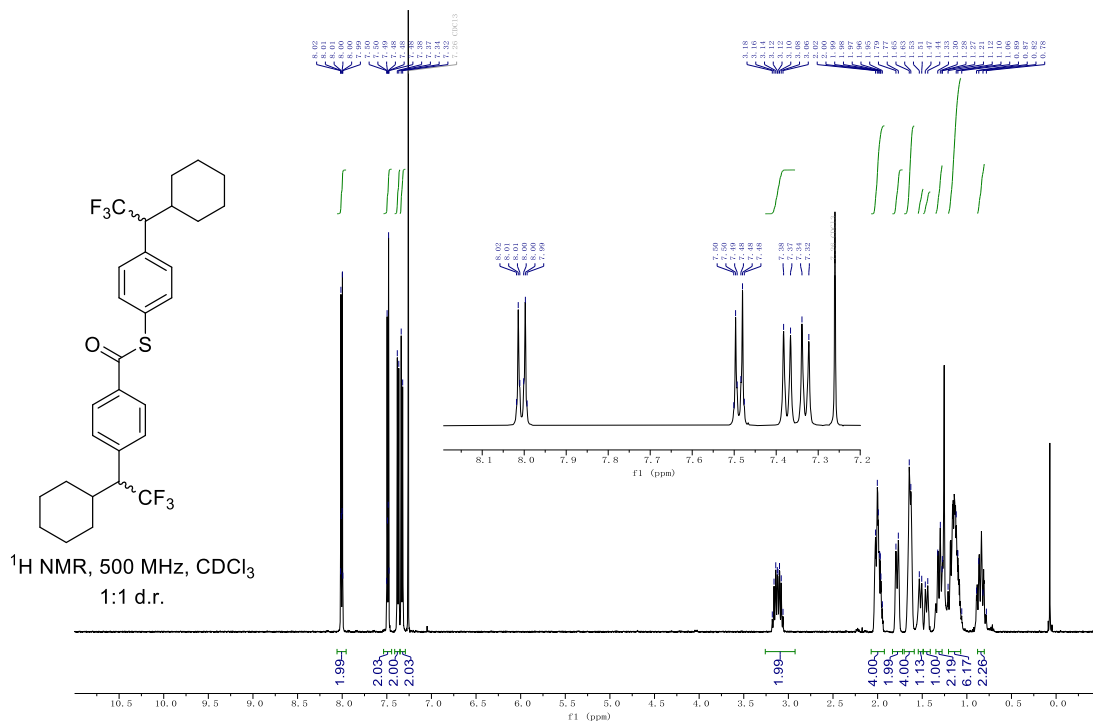


Thermal Protocol

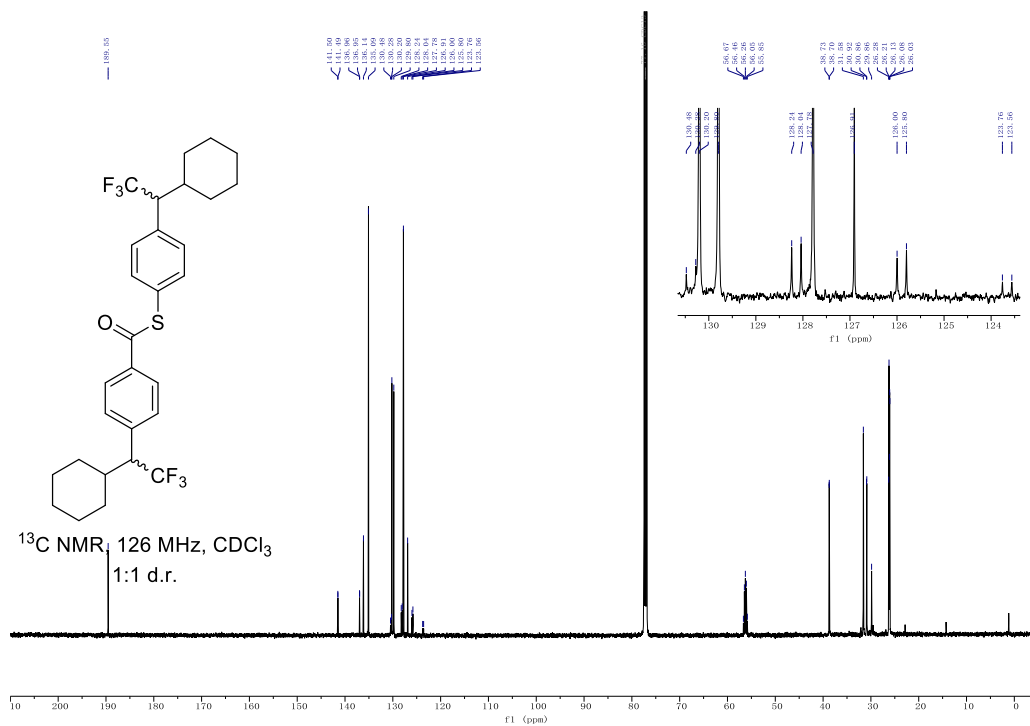
A pressure tube was charged with **UDC1** (90 mg, 0.21 mmol) under nitrogen and cyclohexane (21 ml) was added. The tube was sealed and heated to 130 °C (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the reaction mixture was concentrated. The crude reaction mixture was purified by column chromatography (12% dichloromethane in hexanes, to 20% dichloromethane in hexanes containing to give the title compound as a colorless oil (11.2 mg, 20.6 μmol , 10%) as a 1:1 mixture of diastereomers.

A similar experiment was carried out using **UDC1** (12.9 mg, 30.0 μmol) in 3.0 mL cyclohexane at 130 °C for 3h. After cooling to room temperature, 1,4-dinitrobenzene was added as an internal standard for quantification. The crude reaction mixture was concentrated and then analyzed by ^1H - and ^{19}F -NMR spectroscopy. A yield of 3.3 mg (6.07 μmol , 20%) of the crosslinked product was determined.

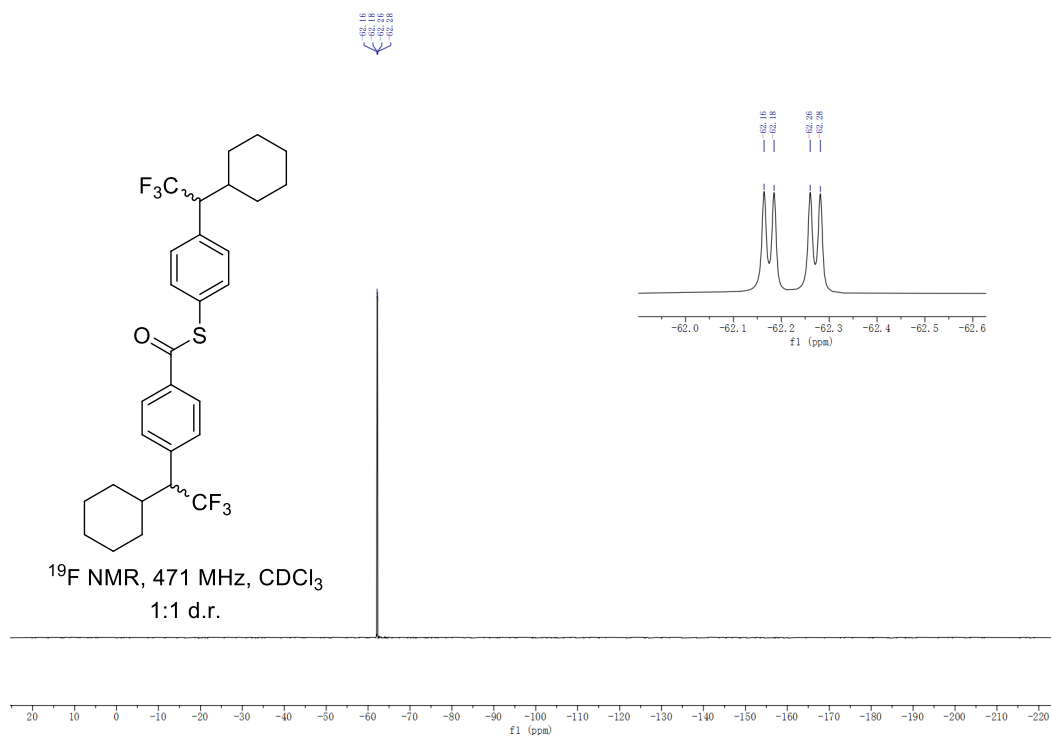
^1H NMR (500 MHz, CDCl_3) δ 8.03 – 7.99 (2H, m, H_5), 7.50 – 7.47 (2H, m, H_4), 7.37 (2 H, d, $J = 8.3$ Hz, $\text{H}_{9/10}$), 7.33 (2 H, d, $J = 8.3$ Hz, $\text{H}_{9/10}$), 3.19 – 3.04 (2H, m, H_2), 2.07 – 1.91 (4H, m, $\text{H}_{1/13}$), 1.83 – 1.74 (2H, m, $\text{H}_{1/13}$), 1.69 – 1.60 (4H, m, $\text{H}_{11/13}$), 1.52 (1 H, d, $J = 13.5$ Hz, $\text{H}_{1/13}$), 1.45 (1 H, d, $J = 13.8$ Hz, $\text{H}_{1/13}$), 1.37 – 1.27 (m, 2H, $\text{H}_{1/13}$), 1.21 – 1.06 (6H, m, $\text{H}_{1/13}$), 0.92 – 0.74 (2H, m, H_1); ^{13}C NMR (126 MHz, CDCl_3) δ 189.6 (C_7), 141.5 (q, $^3J = 2.2$ Hz, C_3), 137.0 (q, $^3J = 2.2$ Hz, C_{11}), 136.1 (C_6), 135.1 (C_5), 130.2 ($\text{C}_{4/10}$), 129.8 ($\text{C}_{4/10}$), 127.8 (C_9), 127.1 (q, $^1J = 281.6$ Hz), 126.9 (q, $^1J = 281.6$ Hz), 126.9 (C_8), 56.7 – 55.8 (m, 2C, C_{13}), 38.7 (C_1), 38.7 (C_1), 31.6 (C_1), 30.9 (C_1), 30.9 (C_1), 29.9 (C_1), 26.3 (C_1), 26.2 (C_1), 26.13 (C_1), 26.08 (C_1), 26.0 (C_1); ^{19}F NMR (471 MHz, CDCl_3) δ –62.17 (d, $J = 9.8$ Hz), –62.27 (d, $J = 9.9$ Hz); HRMS ASAP+ found $[\text{M}+\text{H}]^+$ 543.2170, $\text{C}_{29}\text{H}_{33}\text{OSF}_6^+$ requires 543.2156.

¹H NMR of UDC1-crosslinked cyclohexane (500 MHz, CDCl₃, 300 K)

¹³C NMR of UDC1-crosslinked cyclohexane (126 MHz, CDCl₃, 300 K)



^{19}F NMR of UDC1-crosslinked cyclohexane (471 MHz, CDCl_3 , 300 K)



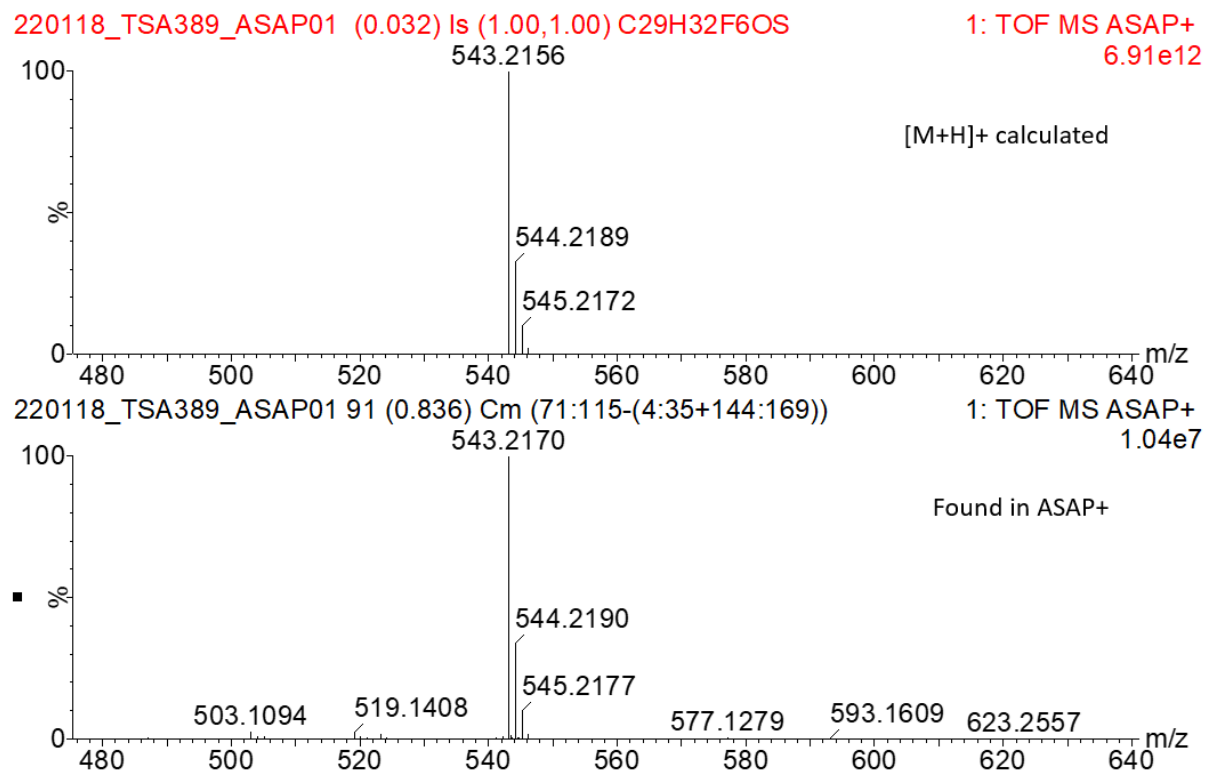
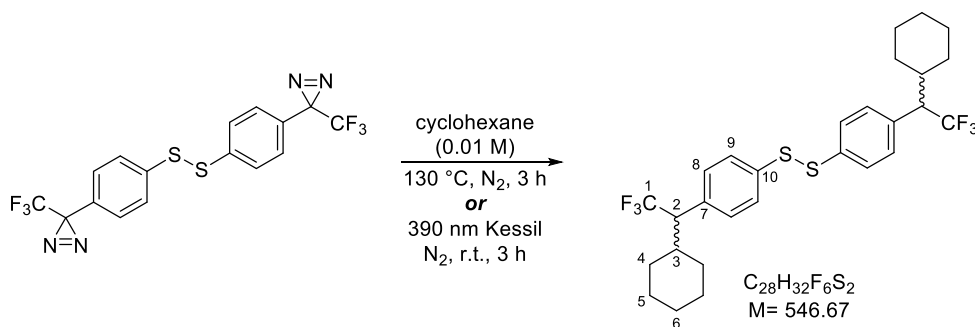


Figure S4. Mass spectrum revealing products of UDC1 thermal-initiated C-H insertion for cyclohexane.

UDC2



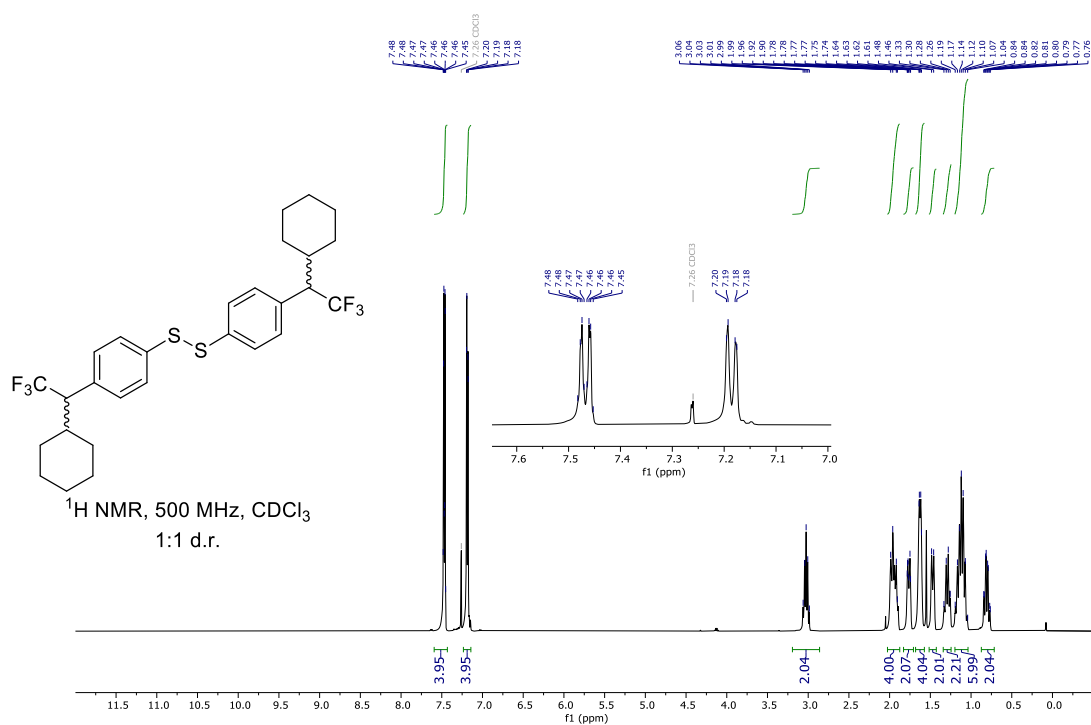
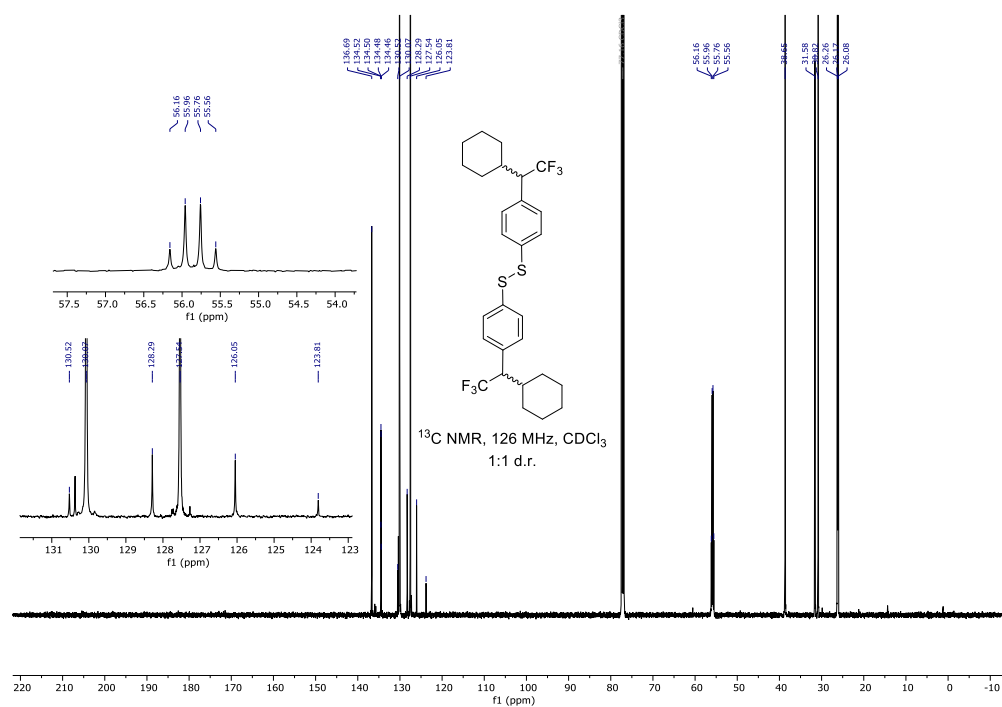
UV-Irradiation protocol

A 1.5 dram vial was charged with UDC2 (17.4 mg, 40.0 μ mol) under nitrogen and cyclohexane (4 ml) was added. The vial was sealed tightly and irradiated with a 390 nm Kessil lamp for 3 h. The reaction mixture was concentrated and 1,4-dinitrobenzene was added as an internal standard for quantification. The crude reaction mixture was then analyzed by ¹H- and ¹⁹F-NMR spectroscopy.

To obtain isolable quantities of the C-H insertion product, the protocol outlined above was set up 8 times in parallel (139 mg, 320 μ mol of UDC2 in total). Upon completion of the reactions, the crude mixtures were combined, concentrated, and purified by flash column chromatography (hexanes) to give the desired addition product (19.1 mg, 34.9 μ mol, 11%) as a colorless oil and a 1:1 mixture of diastereomers. *R_f* (hexanes): 0.61; ¹H NMR (500 MHz, CDCl₃) δ 7.52 – 7.38 (4 H, m, H₉), 7.23 – 7.14 (4 H, m, H₈), 3.02 (2 H, p, *J* = 10.1 Hz, H₂), 2.04 – 1.88 (4 H, m), 1.81 – 1.72 (2 H, m), 1.68 – 1.58 (4 H, m), 1.47 (2 H, d, *J* = 12.7 Hz), 1.36 – 1.24 (2 H, m), 1.21 – 1.03 (6 H, m), 0.80 (2 H, qd, *J* = 12.1, 3.4 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 136.7 (4 C, C₁₀), 134.5 (2 C, q, *J* = 2.7 Hz, C₇), 130.1 (4 C, C₉), 127.5 (4 C, C₈), 127.17 (2 C, q, *J* = 281.5 Hz, C₁), 55.9 (2 C, q, *J* = 25.1 Hz, C₂), 38.7 (2 C, C₃), 31.6 (2 C, C₄), 30.8 (2 C, C_{4'}), 26.3 (2 C, C_{5/6}), 26.2 (2 C, C_{5/6}), 26.1 (2 C, C_{5/6}); ¹⁹F NMR (471 MHz, CDCl₃) δ -62.45, -62.47; HRMS ASAP+ found [M+H]⁺ 547.1914, C₂₈H₃₃S₂F₆⁺ requires 547.1928; IR (film) ν_{max} : 2926, 2854, 1493, 1251, 1135, 1098, 813, 731, 518.

Thermal Protocol

A pressure tube was charged with (8.2 mg, 20.0 μ mol) under nitrogen and cyclohexane (2 ml) was added. The tube was sealed and heated to 130 °C (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. 1,4-Dinitrobenzene was added as an internal standard for quantification and the crude reaction mixture was then analyzed by ¹H- and ¹⁹F-NMR spectroscopy.

¹H NMR of UDC2-crosslinked cyclohexane (500 MHz, CDCl₃, 300 K)¹³C NMR of UDC2-crosslinked cyclohexane (126 MHz, CDCl₃, 300 K)

^{19}F NMR of UDC2-crosslinked cyclohexane (471 MHz, CDCl_3 , 300 K)

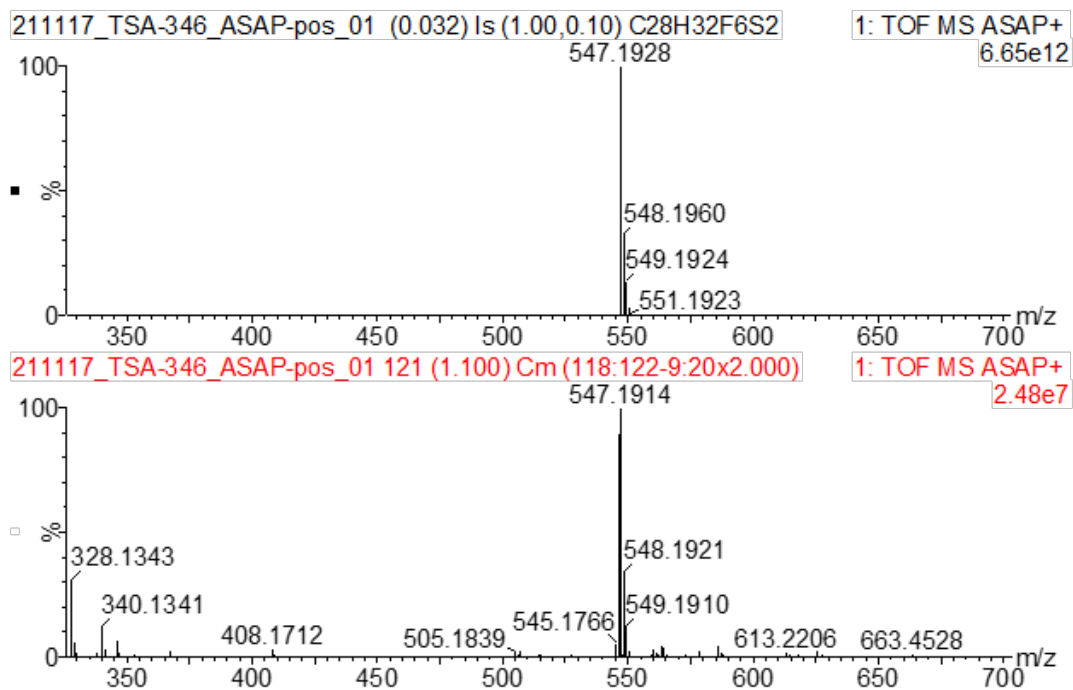
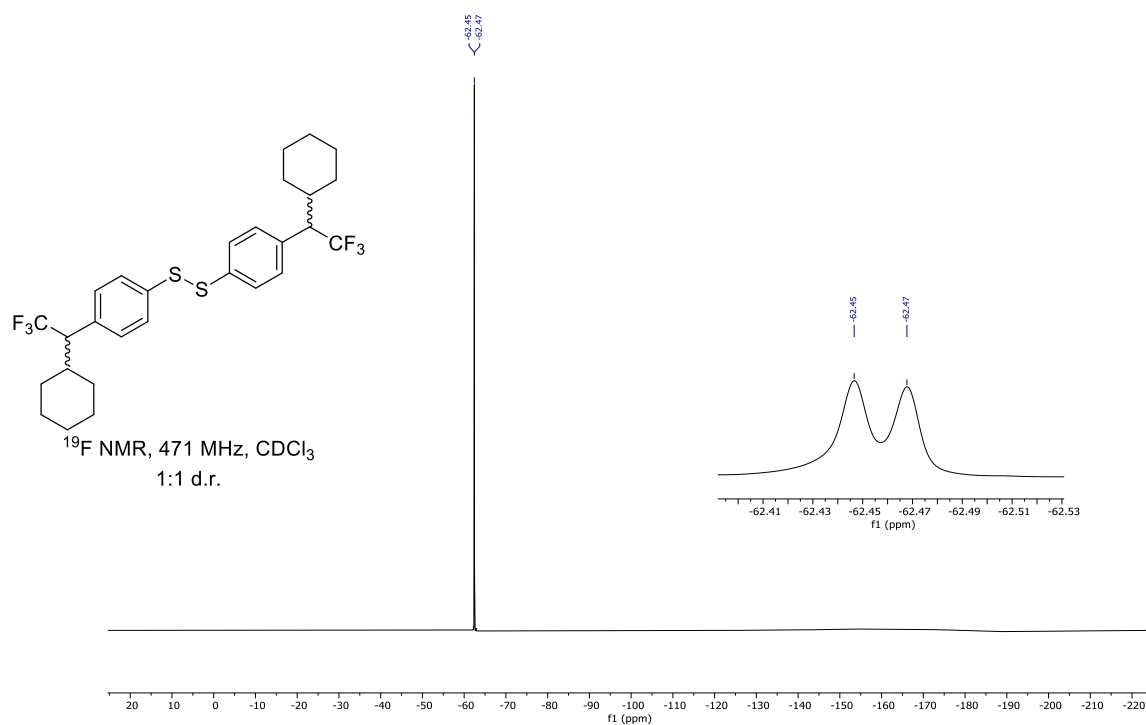
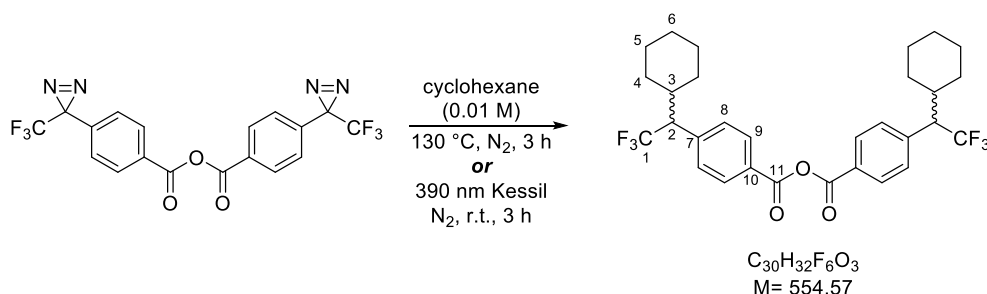


Figure S5. Mass spectrum revealing products of UDC2 thermal-initiated C-H insertion for cyclohexane.

UDC3



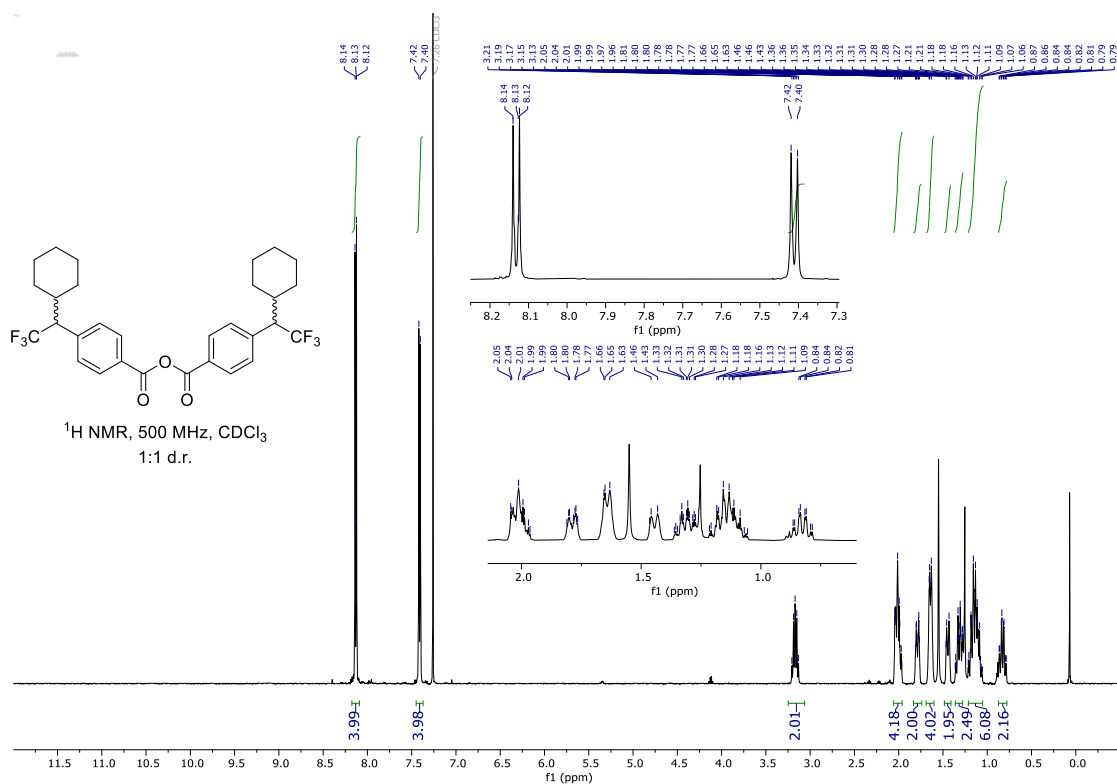
UV-Irradiation protocol

A 1.5 dram vial was charged with UDC3 (8.9 mg, 20.0 μmol) under nitrogen and cyclohexane (2 mL) was added. The vial was sealed tightly and irradiated with a 390 nm Kessil lamp for 3 h. The reaction mixture was concentrated and 1,4-dinitrobenzene was added as an internal standard for quantification. The crude reaction mixture was then analyzed by ^1H - and ^{19}F -NMR spectroscopy.

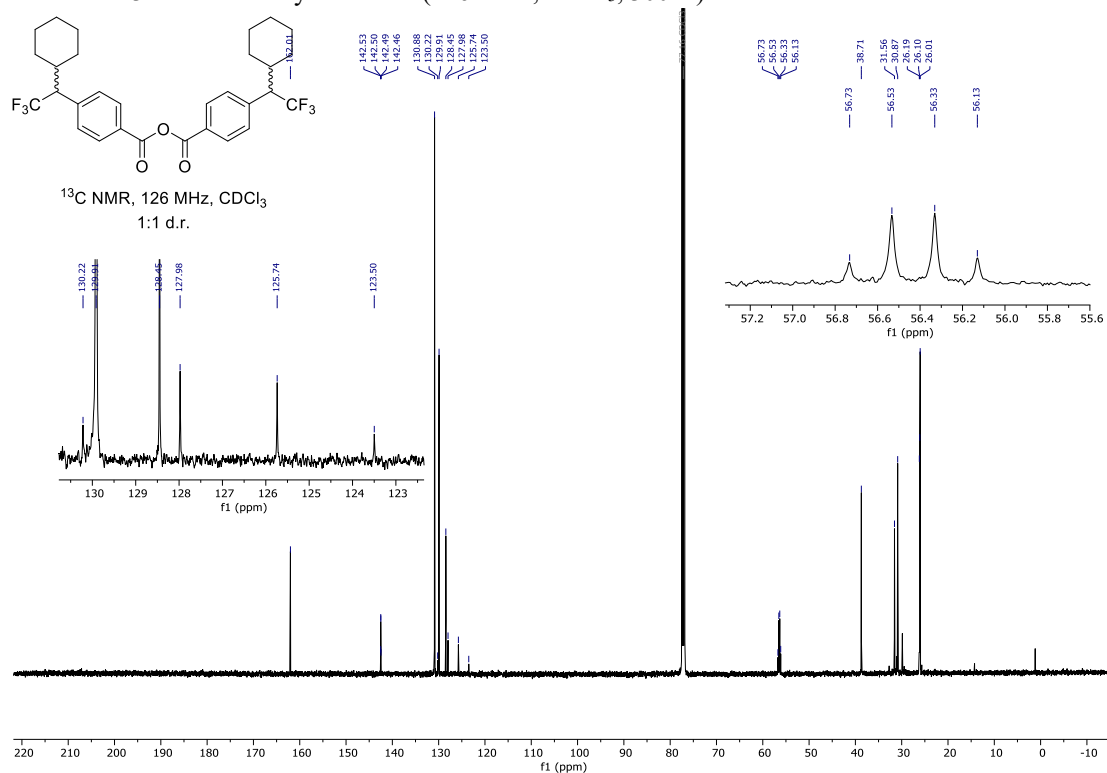
Thermal Protocol

A pressure tube was charged with (102 mg, 230.0 μmol) under nitrogen and cyclohexane (23 mL) was added. The tube was sealed and heated to 130 $^{\circ}\text{C}$ (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude reaction mixture was purified by column chromatography (1% ethyl acetate in hexanes containing 1% (v/v) HCl (2 M in Et_2O), to 2.5% ethyl acetate in hexanes containing 1% (v/v) HCl (2 M in Et_2O)) to give the title compound as a colorless oil (9.1 mg, 21.0 μmol , 9%) as a 1:1 mixture of diastereomers. R_f (3% ethyl acetate in hexanes + 1% (v/v) HCl (2 M in Et_2O)): 0.36; ^1H NMR (500 MHz, CDCl_3) δ 8.16 – 8.11 (4 H, m, H_9), 7.41 (4 H, d, $J = 8.3$ Hz, H_8), 3.17 (2 H, p, $J = 9.8$ Hz, H_2), 2.06 – 1.95 (4 H, m), 1.83 – 1.75 (2 H, m), 1.68 – 1.60 (4 H, m), 1.48 – 1.41 (2 H, m), 1.32 (2 H, qt, $J = 12.5, 2.9$ Hz), 1.22 – 1.05 (6 H, m), 0.83 (2 H, qd, $J = 12.4, 3.4$ Hz); ^{13}C NMR (126 MHz, CDCl_3) δ 162.0 (2 C, C_{11}), 142.49 (2 C, q, $J = 2.8$ Hz, C_7), 130.9 (4 C, C_9), 129.9 (4 C, C_8), 128.5 (2 C, C_{10}), 126.9 (2 C, q, $J = 281.6$ Hz, C_1), 56.4 (2 C, q, $J = 25.1$ Hz, C_2), 38.7 (2 C, C_3), 31.6 (2 C, C_4), 30.9 (2 C, C_4'), 26.2 (2 C, $\text{C}_{5/6}$), 26.1 (2 C, $\text{C}_{5/6}$), 26.0 (2 C, $\text{C}_{5/6}$); ^{19}F NMR (471 MHz, CDCl_3) δ -62.12, -62.14; HRMS ESI+ found $[\text{M}+\text{Na}]^+$ 577.2161, $\text{C}_{30}\text{H}_{32}\text{O}_3\text{NaF}_6^+$ requires 577.2153; IR (film) ν_{max} : 2934, 2857, 1790, 1728, 1612, 1252, 1221, 1003, 707.

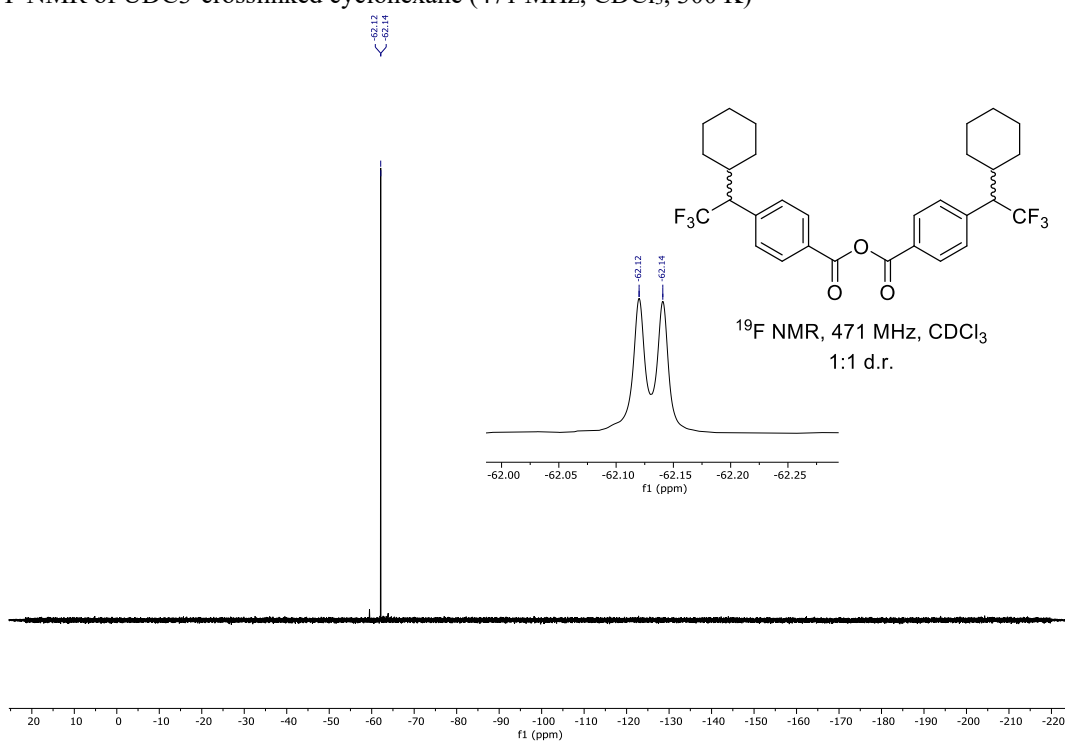
¹³C NMR of UDC3-crosslinked cyclohexane (126 MHz, CDCl₃, 300 K)



¹³C NMR of UDC3-crosslinked cyclohexane (126 MHz, CDCl₃, 300 K)



^{19}F NMR of UDC3-crosslinked cyclohexane (471 MHz, CDCl_3 , 300 K)



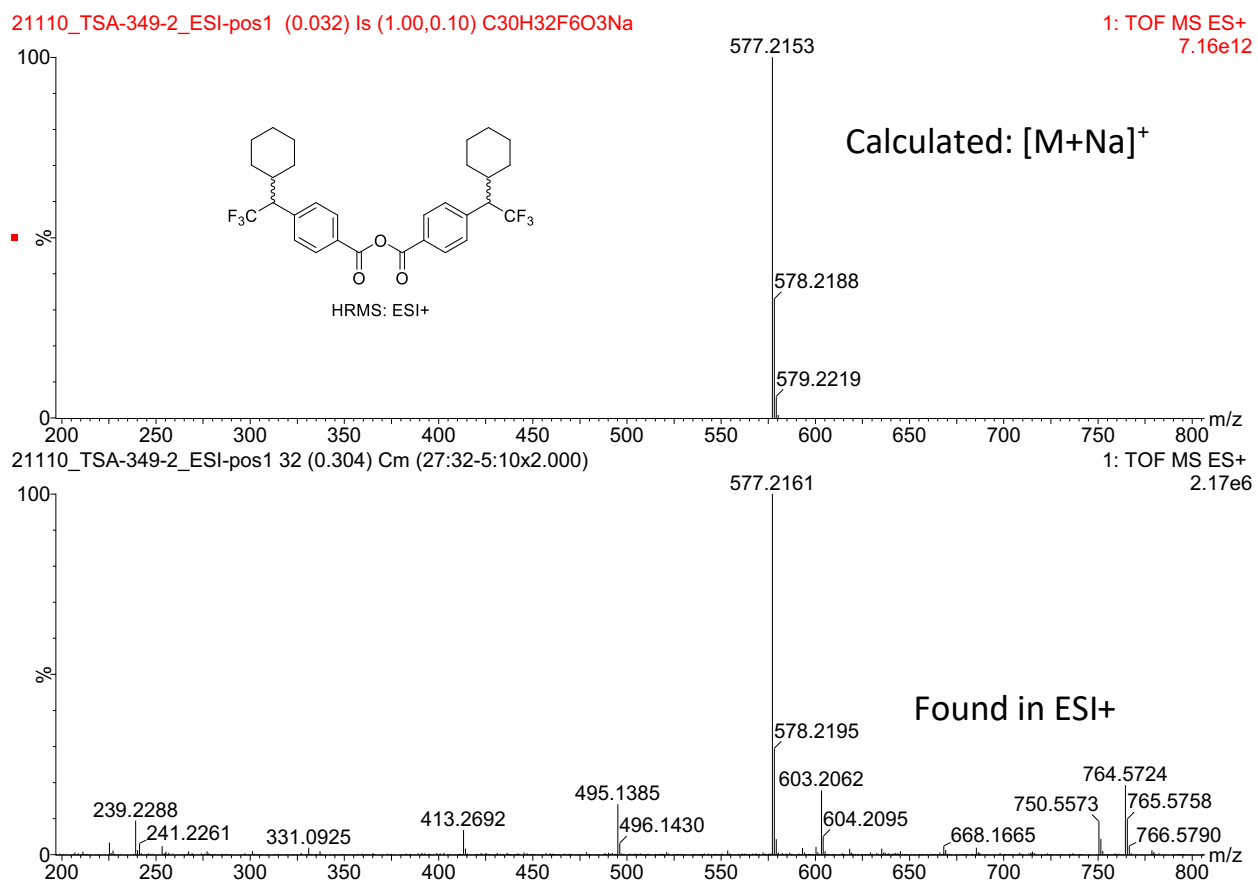


Figure S6. Mass spectrum revealing products of UDC3 thermal-initiated C-H insertion for cyclohexane.

Carbene Formation and N₂ Loss by TGA

The singular thermal degradation profile of UDC2 was not investigated, as mass loss approaching 100-110 °C led to a pungent gas escaping the TGA equipment, and thus the sample was deemed not suitable for continuing the experiment.

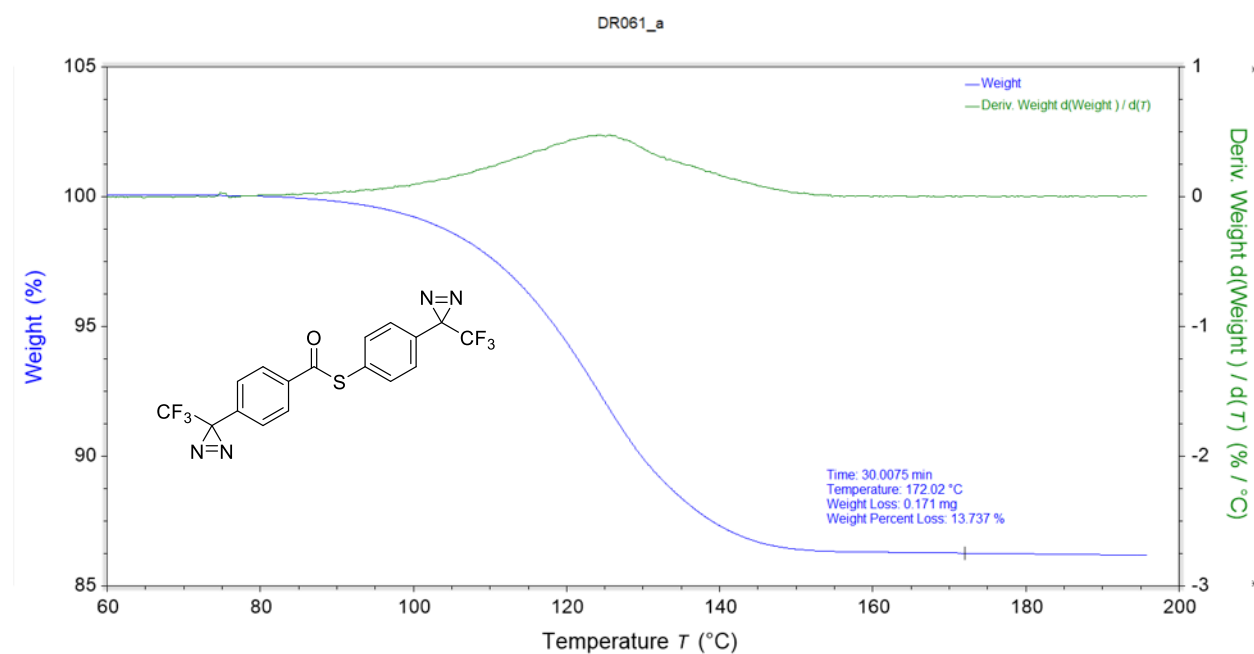


Figure S7. Weight percent loss [loss of 2 molecules of nitrogen] upon heating UDC1. Calc: 13.0 %, found 13.74%. (n = 1).

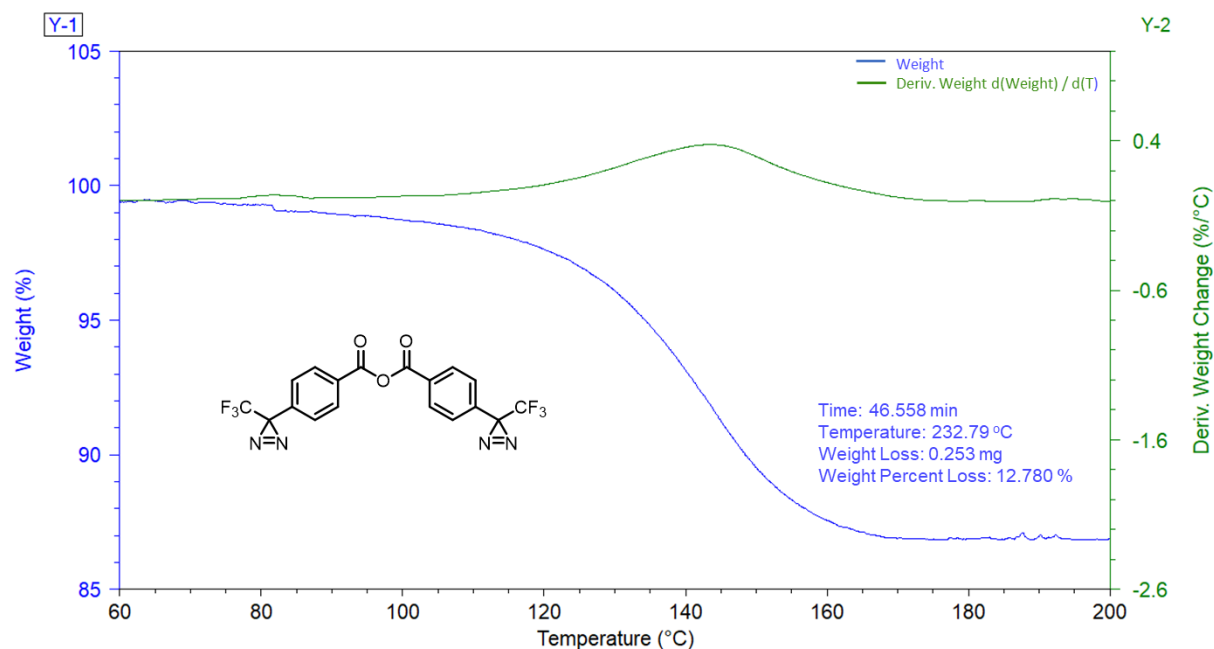


Figure S8. Weight percent loss [loss of 2 molecules of nitrogen] upon heating UDC3. Calc: 12.7 %, found 12.78%. (n = 1).

Yoshida's Correlations by DSC:

Calculations for UDC1, 2, and 3 explosivity and shock sensitivity. Note, a positive SS and EP value signify explosivity and shock sensitivity:

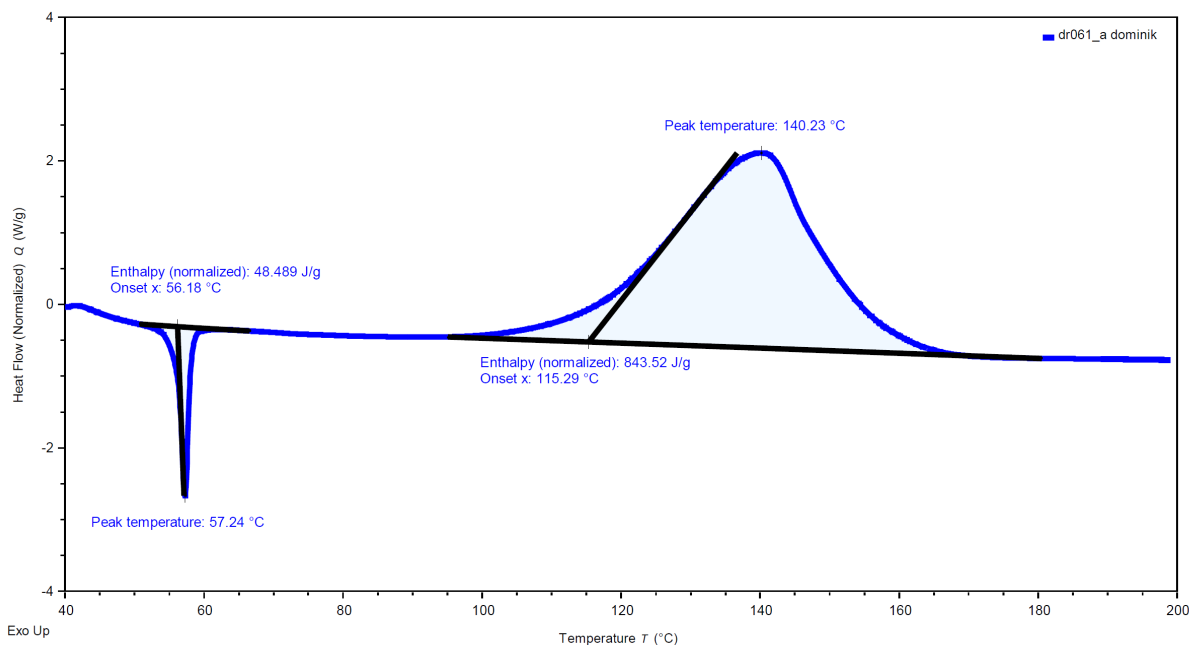


Figure S9. DSC trace for UDC1. Sample size: 0.92 mg; 40 °C – 200 °C with 5° C/min increase, Tzero pan with hermetic lid (pinholed).

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

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

$$\text{SS}_{(1)} = -0.084$$

$$\text{EP}_{(1)} = -0.109$$

In case of $\text{SS} < 0$ no shock sensitivity is expected. In case of $\text{EP} < 0$ no explosion propagation is expected.

Compound UDC1 is not likely to be explosive or shock sensitive.

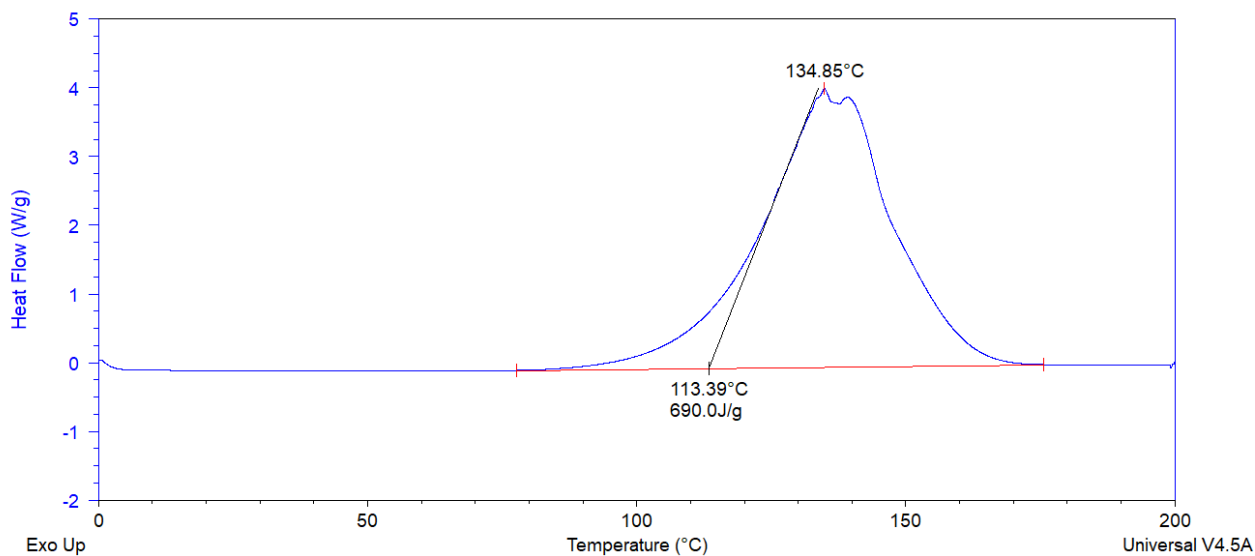


Figure S10. DSC trace for UDC2. Sample size: 10.11 mg; 0 °C – 200 °C with 5° C/min increase, Tzero pan with hermetic lid (pinholed).

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

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

$$\text{SS}_{(1)} = -0.164$$

$$\text{EP}_{(1)} = -0.193$$

In case of $\text{SS} < 0$ no shock sensitivity is expected. In case of $\text{EP} < 0$ no explosion propagation is expected.

Compound UDC2 is not likely to be explosive or shock sensitive.

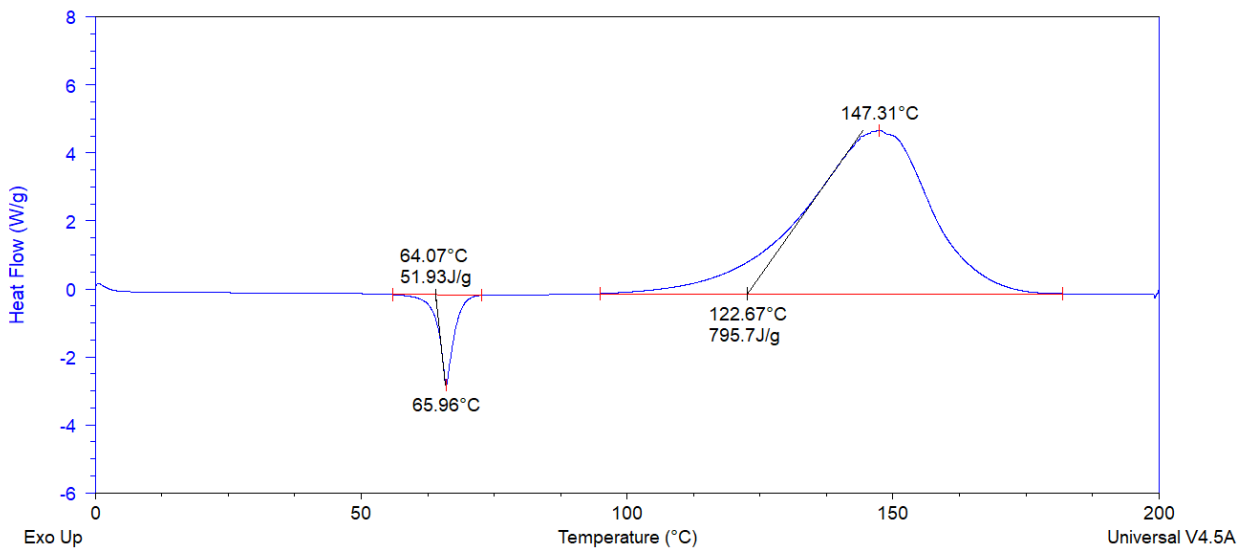


Figure S11. DSC trace for UDC3. Sample size: 5.20 mg; 0 °C – 200 °C with 5° C/min increase, Tzero pan with hermetic lid (pinholed).

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

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

$$\text{SS}_{(1)} = -0.134$$

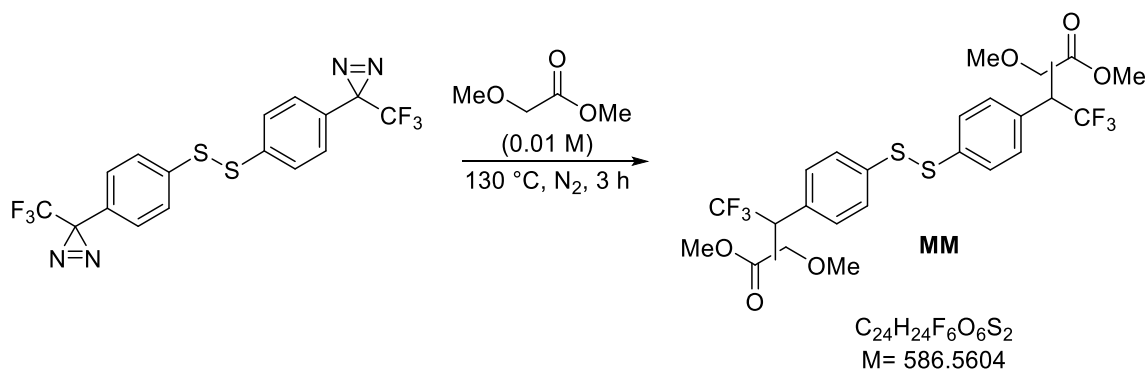
$$\text{EP}_{(1)} = -0.147$$

In case of $\text{SS} < 0$ no shock sensitivity is expected. In case of $\text{EP} < 0$ no explosion propagation is expected.

Compound UDC3 is NOT LIKELY to be explosive or shock sensitive.

Molecular Trials for Blend Compatibilisation and Mixing

Crosslinking of methyl methoxyacetate by UDC2 (reference compound)



A pressure tube was charged with (17.4 mg, 40.0 μmol) of **UDC2** under nitrogen and methyl methoxyacetate (4.0 ml) was added. The tube was sealed and heated to 130 $^{\circ}\text{C}$ (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude reaction mixture consisted of a complex mixture of regio- and diastereomers. The crude mixture was purified by preparative thinlayer chromatography (30% ethyl acetate in hexanes). All fractions were analyzed by ^1H -, ^{19}F -NMR, and HRMS. The desired product (**MM**) was unambiguously identified by HRMS: ASAP+ found $[\text{M}]^+$ 586.0913, $\text{C}_{24}\text{H}_{24}\text{O}_6\text{S}_2\text{F}_6^+$ requires 586.0919.

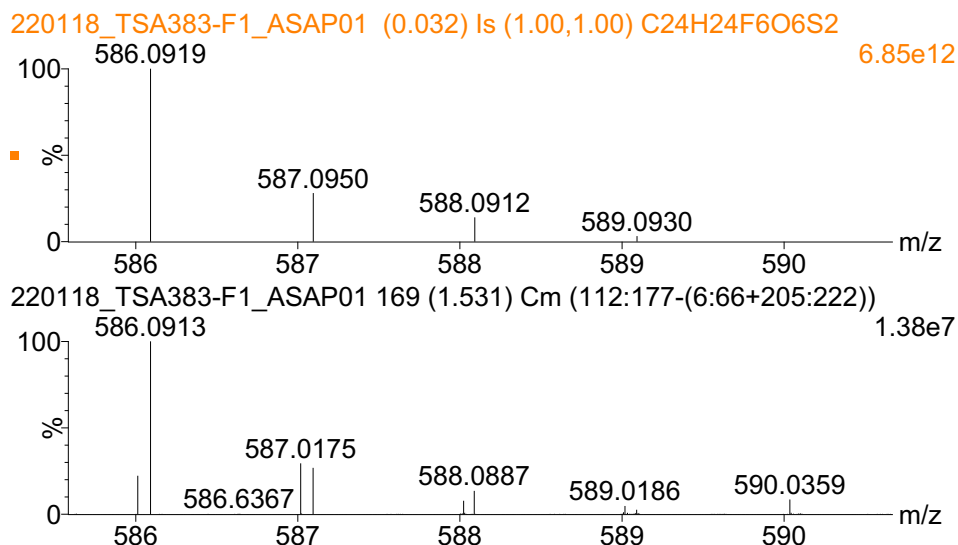
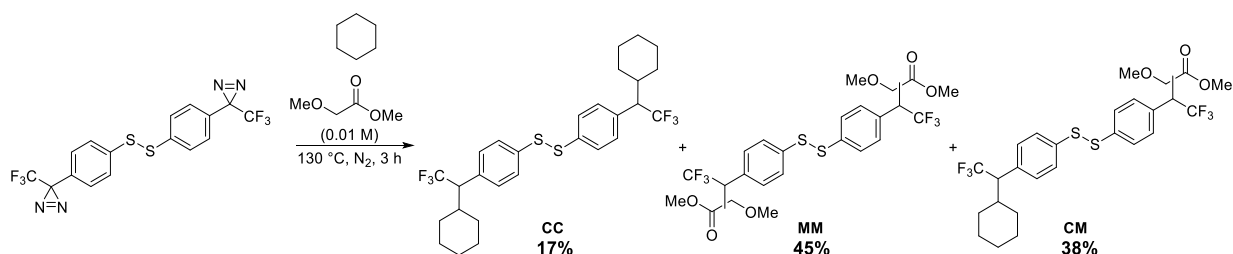


Figure S12. Mass spectrum revealing products of UDC2 thermal-initiated C-H insertion for methyl methoxyacetate.

Crosslinking of cyclohexane/methyl methoxyacetate by UDC2



A pressure tube was charged with (17.4 mg, 40.0 μmol) of **UDC2** under nitrogen. Cyclohexane (2.0 mL) and methyl methoxyacetate (4.0 ml) were added. The tube was sealed and heated to 130 $^{\circ}\text{C}$ (*careful: gas evolution, overpressure!*) for 3 h. The reaction vessel was allowed to cool to room temperature and the crude mixture was concentrated. The crude mixture was purified by preparative thinlayer chromatography (20% ethyl acetate in hexanes). All fractions were analyzed by ^1H -, ^{19}F -NMR, and HRMS. The fractions containing the mixed-crosslinked product (**CM**) were unambiguously identified by HRMS: ASAP+ found $[\text{M}]^+$ 566.1389, $\text{C}_{26}\text{H}_{28}\text{O}_3\text{S}_2\text{F}_6^+$ requires 566.1384.

The reaction protocol outlined above was repeated and the crude reaction mixture was analyzed by SFC-MS using authentic samples of **CC**, **MM**, and **CM** (see above) as reference compounds. (SFC conditions: Water BEH (Ethylene Bridged Hybrid) column, gradient elution, 0% MeCN to 5% MeCN in CO₂ over 10 min, 1.2 ml/min, 40 °C). The following relative yields were determined: **CC**: 17%, **MM**: 45% and **CM**: 38%.

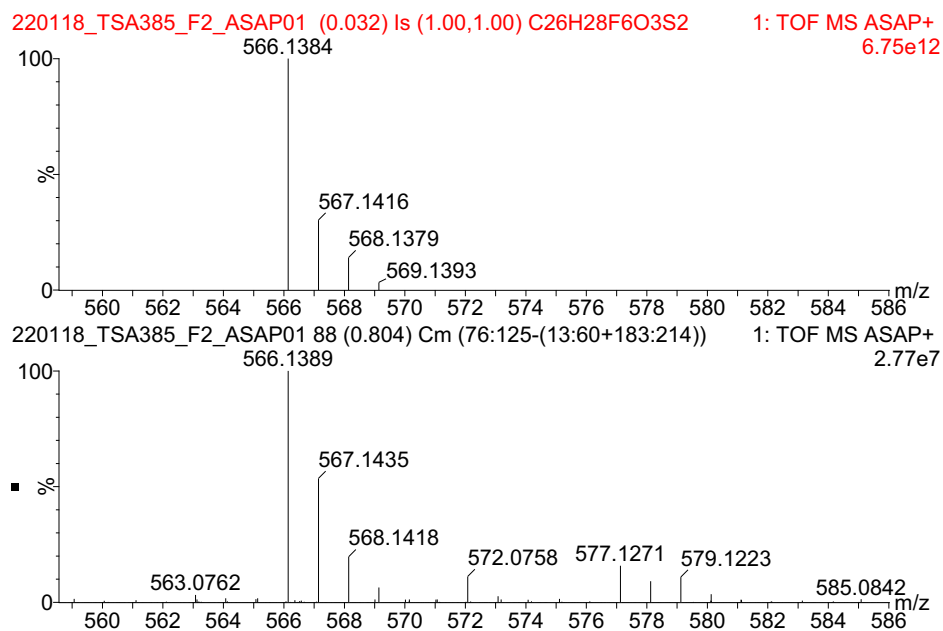


Figure S13. Mass spectrum revealing intermolecular-mixed products of UDC2 thermal-initiated C-H insertion for cyclohexane and methyl methoxyacetate.

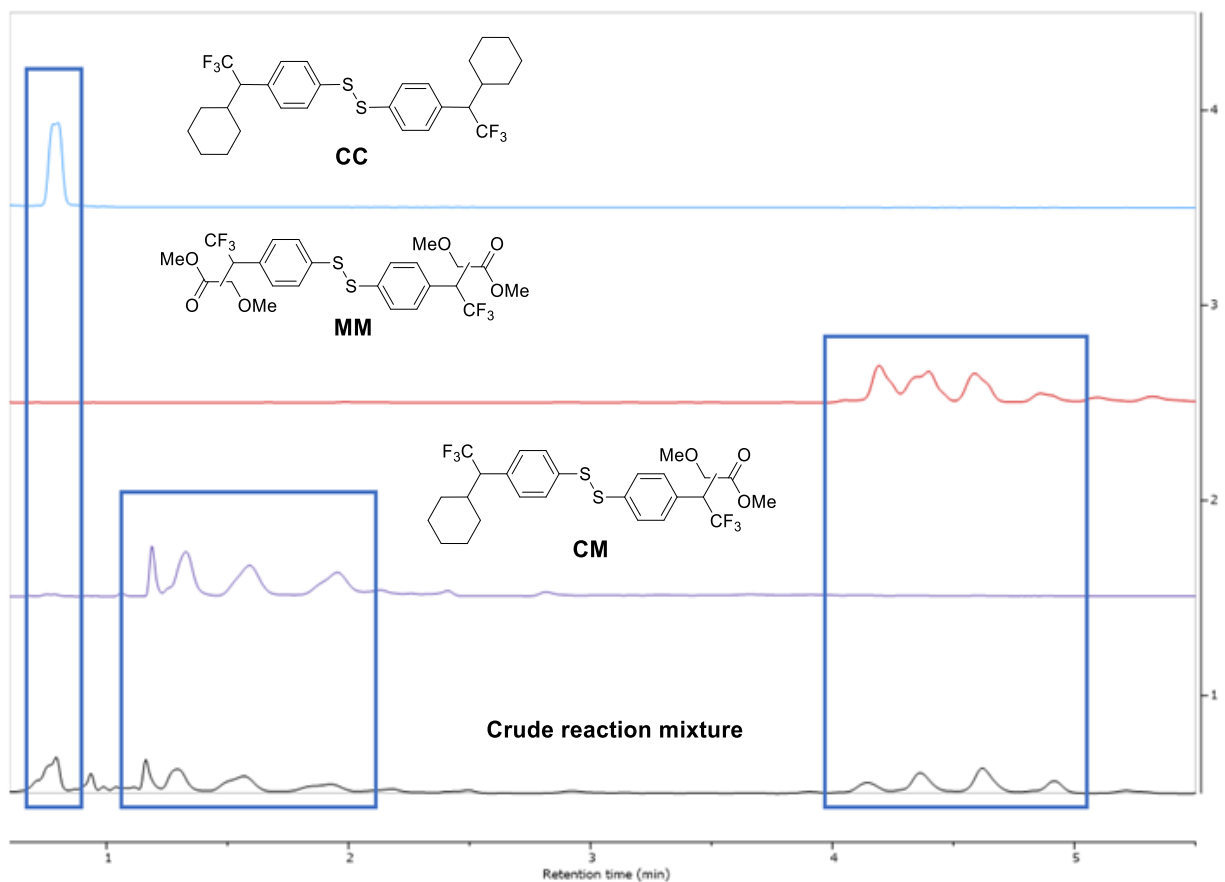


Figure S14. SFC Chromatograms of cyclohexane/methyl methoxyacetate mixed crosslinking experiments.

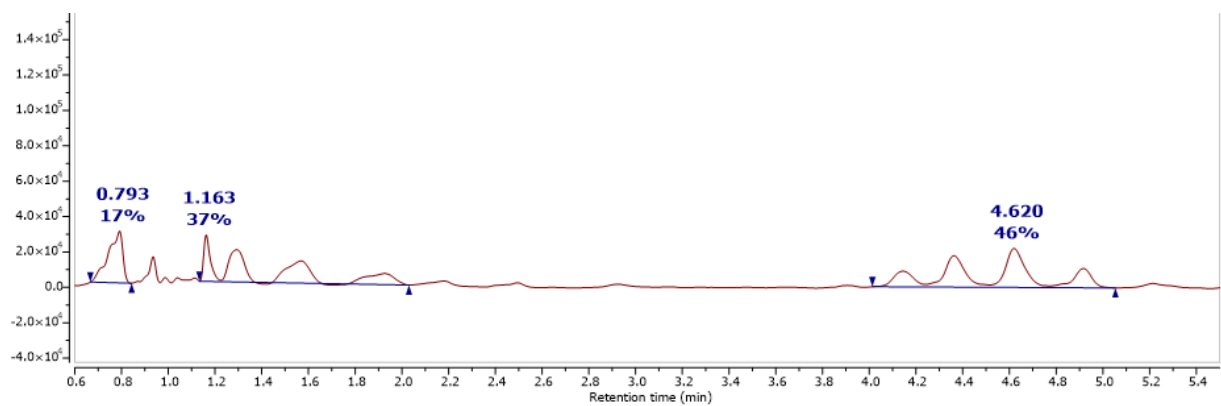
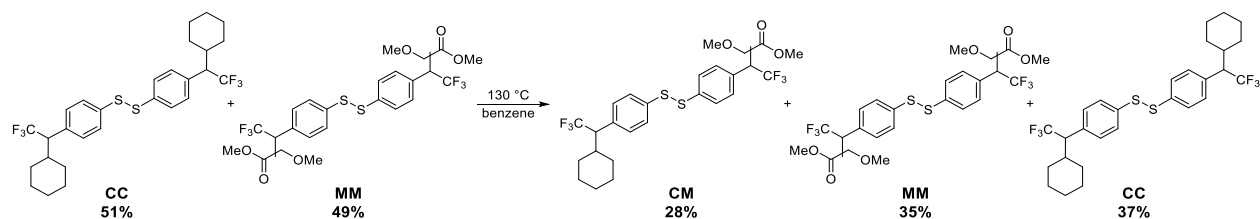


Figure S15. Quantification of cyclohexane/methyl methoxyacetate mixed crosslinking experiments by SFC-MS.

Disulfide exchange experiments



A small pressure tube was charged with **CC** (5.0 mg, 9.15 μmol) and **MM** (5.6 mg, 9.15 μmol) benzene (0.1 mL, 0.09 M) was added under argon. The vessel was sealed and heated to 130 °C for 24 h. The reaction mixture was concentrated and analyzed by SFC-MS. The following relative product distribution was determined: **CC**: 37%, **MM**: 35% and **CM**: 28%.

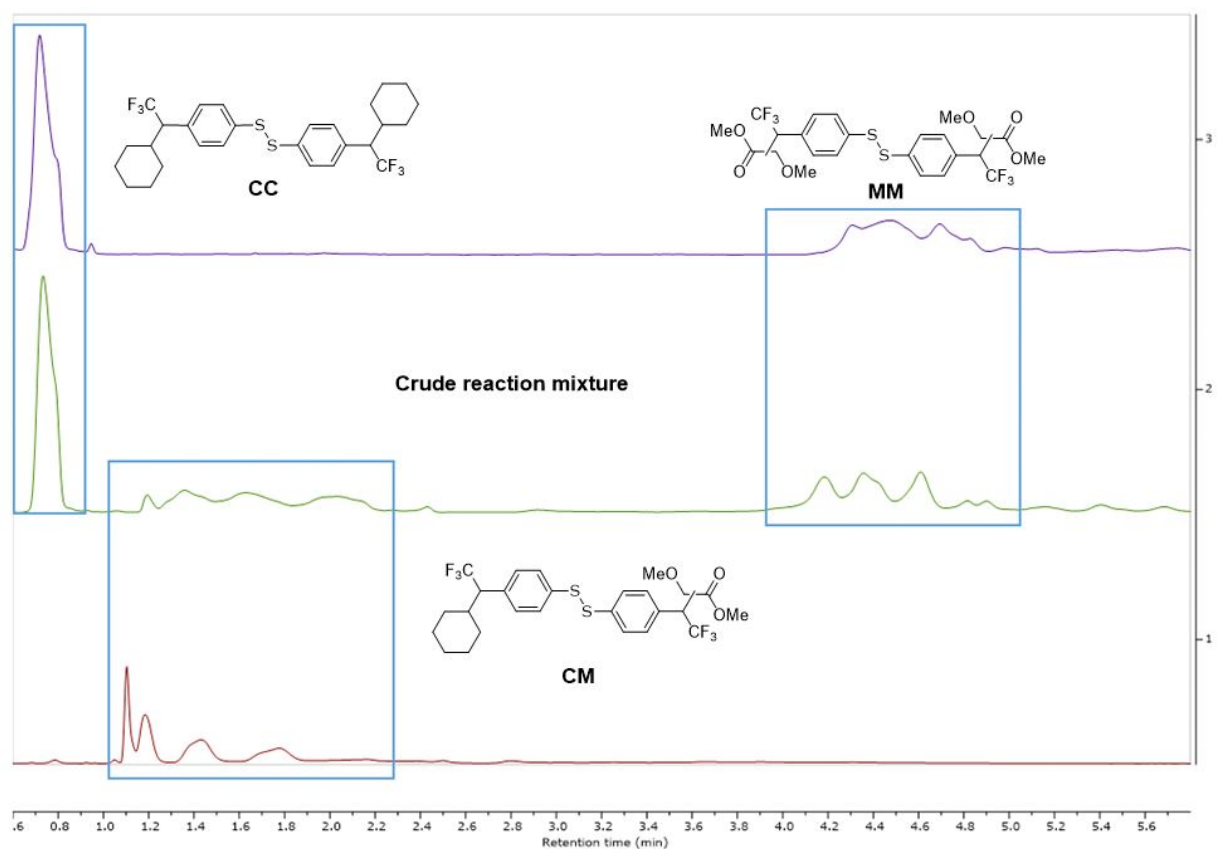


Figure S16. SFC Chromatograms of disulfide-metathesis experiments.

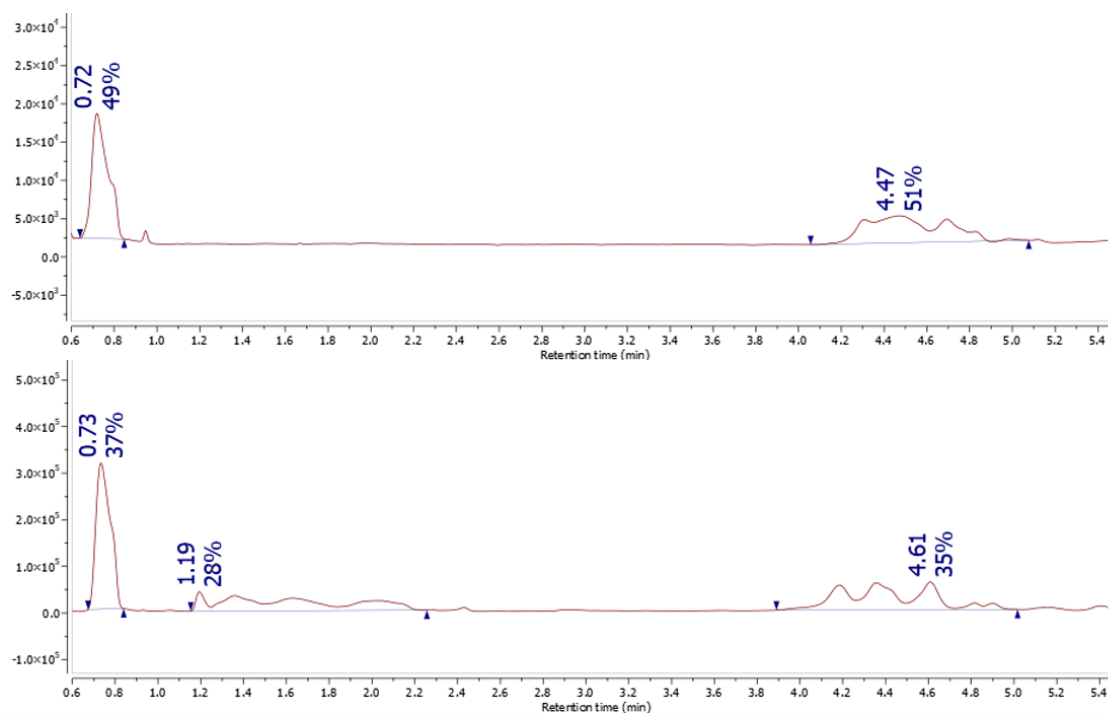
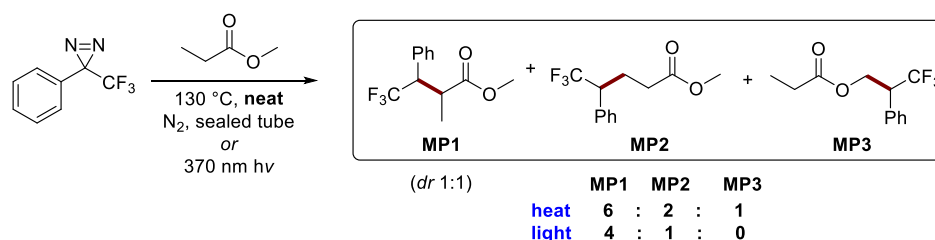


Figure S17. Quantification of disulfide-metathesis experiments by SFC-MS.

Determination of C-H insertion selectivity for polyesters

Methyl propionate was used as a model substrate to investigate the regioselectivity of the C-H insertion of aryl-trifluoro diazirines into polyesters.



A small pressure tube was charged with commercially available 3-phenyl-3-(trifluoromethyl)-3H-diazirine (7.2 μ l, 7.5 mg, 40.0 μ mol) and methyl propionate. (4.0 mL, 0.01 M). The vessel was sealed and heated to 130 °C for 3 h. The reaction mixture was cooled to room temperature and the volatiles were removed by rotary evaporation. The thus obtained crude mixture was analyzed by ¹H-NMR spectroscopy. **MP1**⁵ and **MP2**⁶ are literature-known compounds. An authentic sample of **MP3** was obtained through chemical synthesis (*vide infra*). Using NMR spectroscopic data and reference spectra, a ratio of **MP1:MP2:MP3** of **6:2:1** was determined. This is in agreement with earlier literature reports⁷ concluding preferential insertion of phenyl-trifluoro diazirine-derived carbenes into α -carbonyl C-H bonds of ethyl acetate.

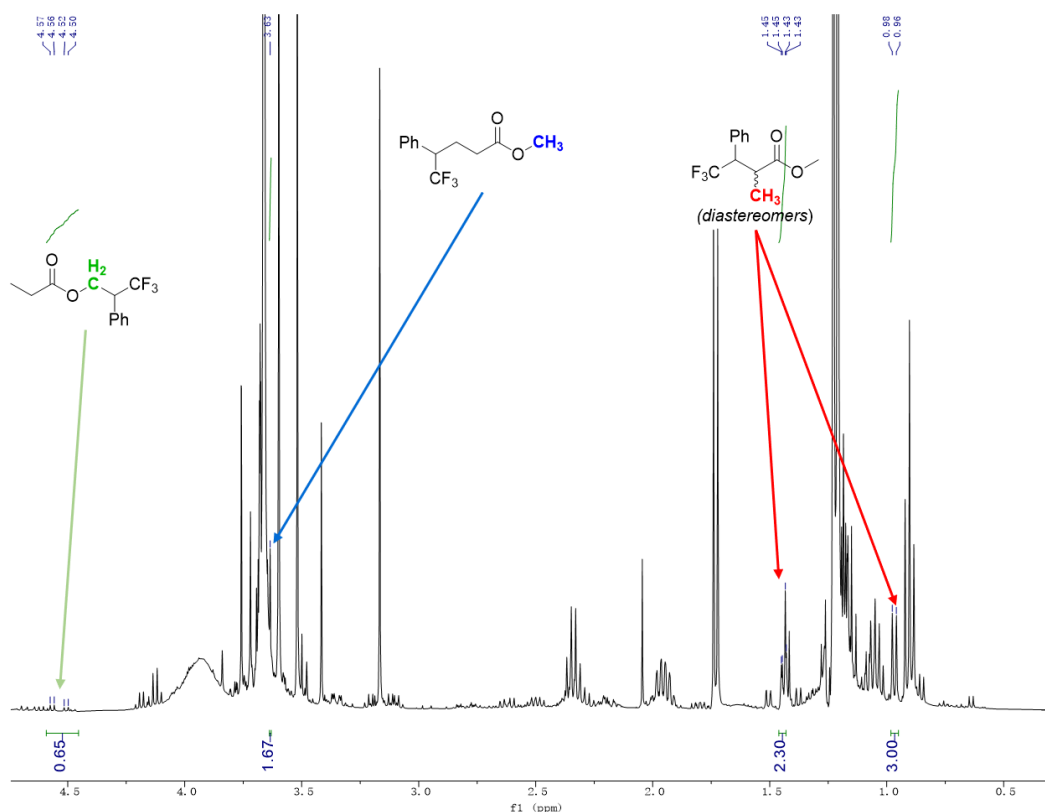
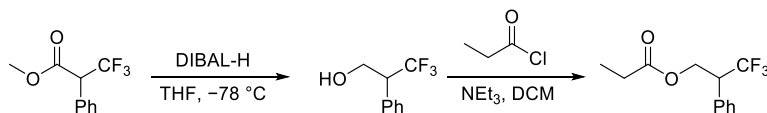


Figure S18. Quantification of disulfide-metathesis experiments by SFC-MS.

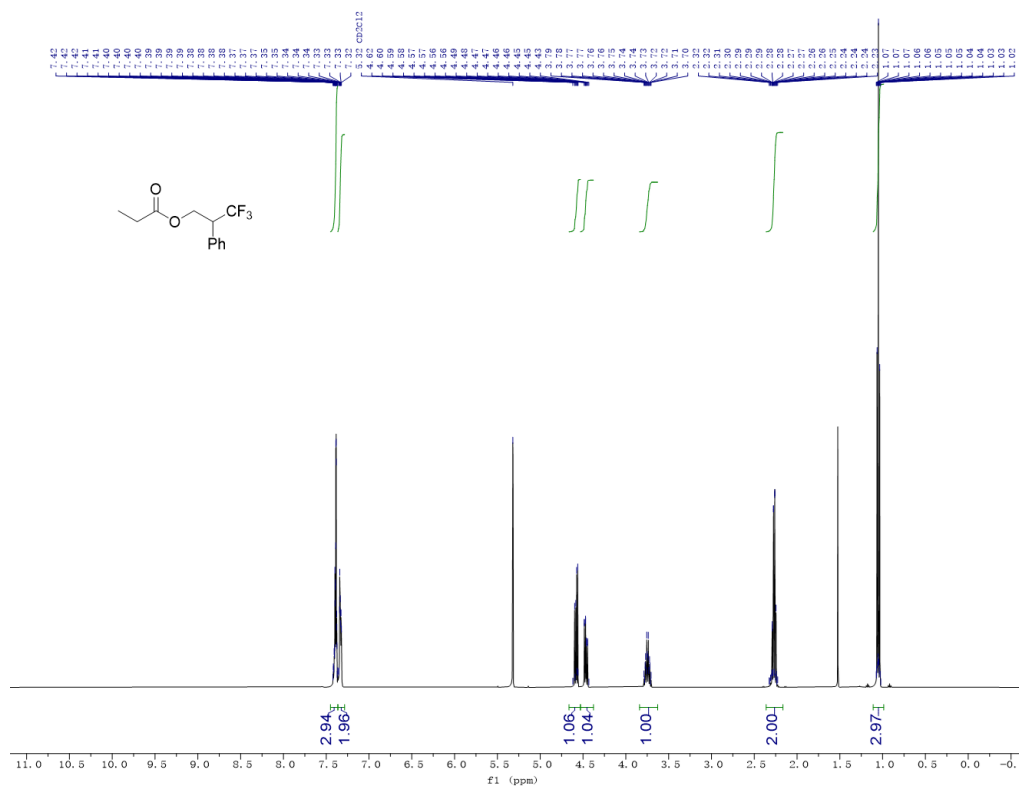
Synthesis of 3,3,3-trifluoro-2-phenylpropyl propionate (MP3, reference compound)



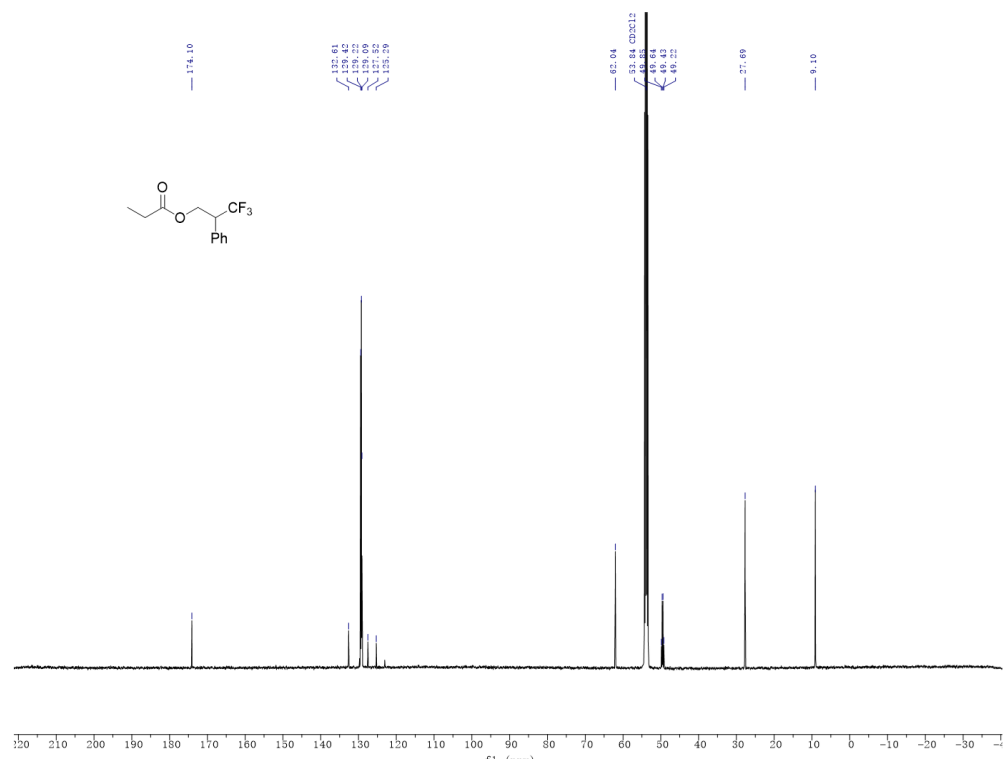
Methyl 3,3,3-trifluoro-2-phenylpropanoate (150 mg, 0.67 mmol, 1.0 equiv.) was dissolved in THF (5 mL) under nitrogen and cooled to $-78\text{ }^{\circ}\text{C}$. DIBAL-H (1.0 M in DCM, 3.30 mL, 3.30 mmol, 5.0 equiv.) was added dropwise. The reaction mixture was allowed to stir at room temperature for 3h and then cooled to $-78\text{ }^{\circ}\text{C}$. MeOH (0.48 mL) was added dropwise followed by aq. NaOH (1 M, 0.42 mL). The mixture was allowed to warm to room temperature and stirred overnight. The thus obtained suspension was filtered through Celite[®] to obtain crude 3,3,3-trifluoro-2-phenylpropan-1-ol which was directly used in the subsequent step.

A 10 mL flask was charged with crude 3,3,3-trifluoro-2-phenylpropan-1-ol (126 mg, 0.66 mmol, 1.0 equiv.), CH_2Cl_2 (3.3 mL, 0.2 M), and triethylamine (120 μL , 0.86 mmol, 1.3 equiv.). The reaction mixture was cooled to $0\text{ }^{\circ}\text{C}$ and a solution of propionyl chloride (88 μL , 0.99 mmol, 1.5 equiv.) in CH_2Cl_2 (0.6 mL) was added dropwise. The mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 40 min and then allowed to warm to room temperature overnight. The reaction was quenched by addition of sat. aq. NaHCO_3 (6.6 mL) and diluted with CH_2Cl_2 (6.6 mL). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 6.6 mL). The combined organic phases were dried over MgSO_4 , filtered and concentrated. The crude product was purified by flash column chromatography (5% EtOAc in hexanes) to give 3,3,3-trifluoro-2-phenylpropyl propionate (55.8 mg, 34%) as a colorless oil. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.43 – 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 4.58 (dd, $J = 11.6, 6.8\text{ Hz}$, 1H), 4.50 – 4.43 (m, 1H), 3.75 (qt, $J = 9.2, 6.9\text{ Hz}$, 1H), 2.33 – 2.22 (m, 2H), 1.05 (t, $J = 7.6\text{ Hz}$, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 174.10, 132.61, 129.42, 129.22, 129.09, 126.41 (q, $J = 280.0\text{ Hz}$), 62.03 (d, $J = 3.1\text{ Hz}$), 49.53 (q, $J = 26.6\text{ Hz}$), 27.69, 9.10; ^{19}F NMR (470 MHz, CD_2Cl_2) δ -68.07 (d, $J = 9.2\text{ Hz}$).

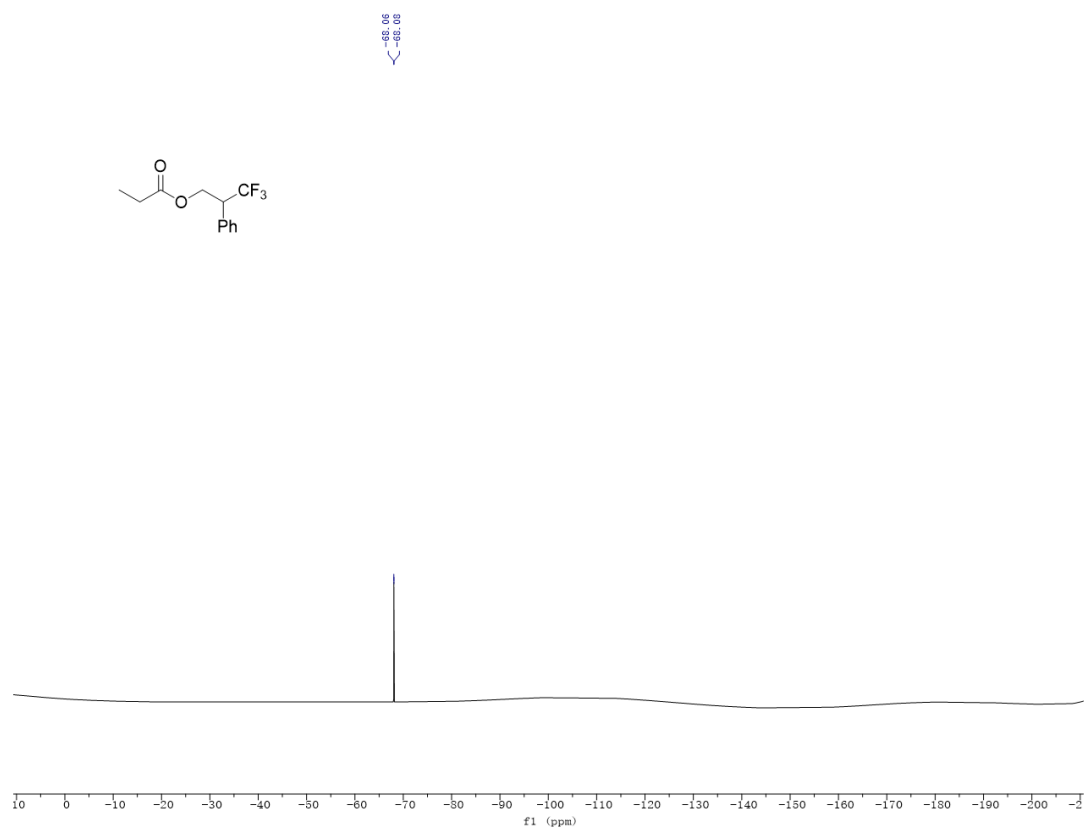
^1H NMR of 3,3,3-trifluoro-2-phenylpropyl propionate (500 MHz, CD_2Cl_2 , 300 K)



^{13}C NMR of 3,3,3-trifluoro-2-phenylpropyl propionate (126 MHz, CD_2Cl_2 , 300 K)



^{19}F NMR of 3,3,3-trifluoro-2-phenylpropyl propionate (470 MHz, CD_2Cl_3 , 300 K)



General Polymer Crosslinking Procedures/Considerations (Method 1)

Typical polymer crosslinking by UDC1, 2, and 3 was performed on the dissolved target polymer in a suitable solvent (toluene or CHCl_3) at or below 85 °C in a round bottom flask. Selected UDC (5 wt.%) was added to the polymer mixture in a toluene solution and allowed to mix briefly before being removed from heat and cooled in an ice bath (0 °C). Careful monitoring of temperature is critical to avoiding pre-mature UDC activation. Solvent was removed under vacuum, which yielded a white powder that was placed in a vacuum oven at 50 °C until a constant mass was achieved. The powder was moved into an oven at 125 °C for 3 h, during which time the polymer was crosslinked by activated carbenes, visibly confirmed by powder yellow tint. The following strategy, based on discussed thermal/solubility/performance results among similar literature precedent, was deemed effective for homogeneous dispersion of and crosslink by UDC. This procedure was the full requirement for UDCs 2 and 3. UDC1 CANs were further diluted (swelled) in heated (85 °C) toluene for 4 h. Then 3 % base catalyst (DBU) and free tetra-thiol source PETMP (equimolar to UDC) was added to the mixture and stirred briefly, after which the sample was cooled using an ice bath (0 °C) and the toluene was removed under vacuum at 60 °C. Polymer-UDC1 was then dried in a 60 °C vacuum oven overnight or until a constant mass was achieved. Dried samples were stored in sealed containers at ambient conditions. Small-scale initial trials were performed at 50 mg polymer loading, while large-scale trials were performed at 5.0 g polymer loading. Procedure deviations for blended samples are discussed in the supplemental materials and tables.

Example Homopolymer Small-Scale Crosslinking Procedure (0, 5, 10 wt.% UDC)

Applicable Polyesters:

PLA, P3HB

The specified polyester (50 mg) was mixed with chloroform (15 mL) in a 20 mL glass scintillation vial and placed in an 85 °C automatic heating and orbiting shaker until fully dissolved. Upon full or near-full solubility, a solution of selected UDC (2.5 mg) dissolved in chloroform (1 mL) was added quantitatively to the stirring mixture. The UDC was briefly mixed into the polymer solution before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed (50 °C) by rotovap, and the sample was left to dry in a vacuum oven (60 °C) overnight or until a constant mass was achieved. The obtained white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbene precursors. Crosslinked polymers appeared light yellow, a visual signal of successful installment.

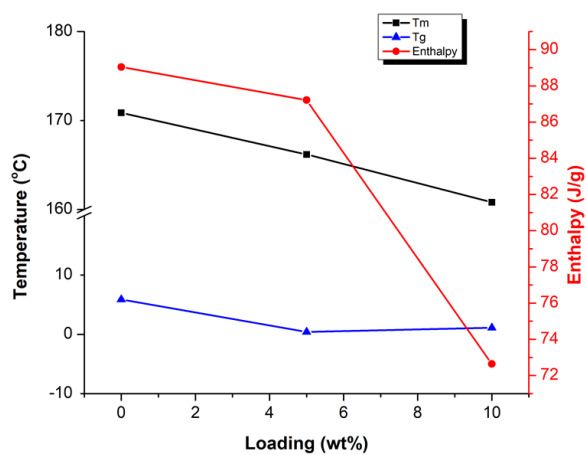
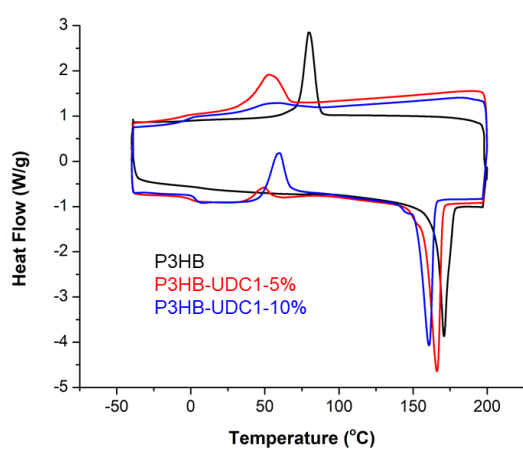


Figure S19. Thermal behavior and trends for P3HB at 0, 5, and 10 wt.% loading of UDC1.

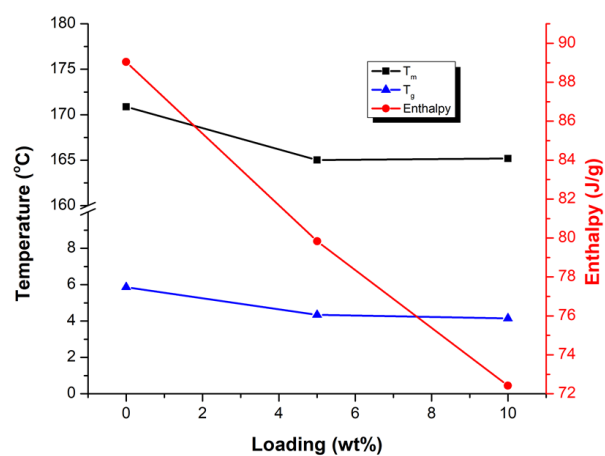
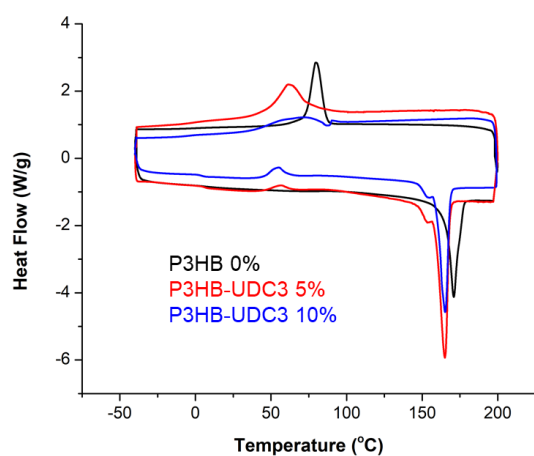


Figure S20. Thermal behavior and trends for P3HB at 0, 5, and 10 wt.% loading of UDC3.

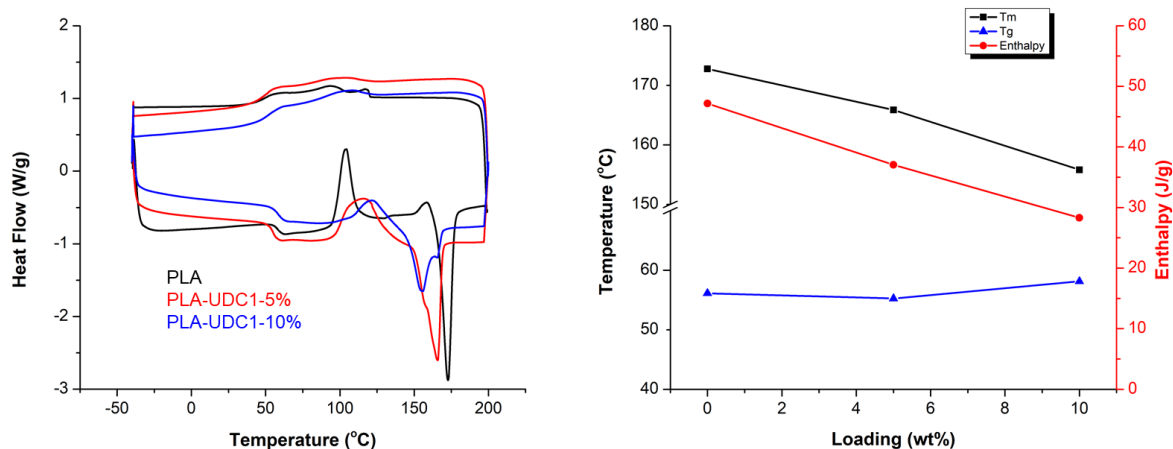


Figure S21. Thermal behavior and trends for PLA at 0, 5, and 10 wt.% loading of UDC1.

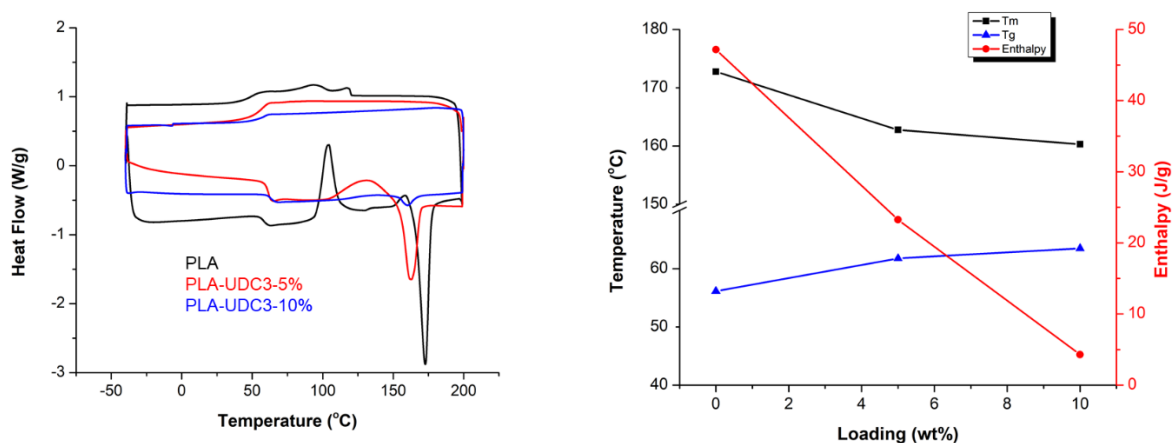


Figure S22. Thermal behavior and trends for PLA at 0, 5, and 10 wt.% loading of UDC3.

Applicable Polyolefins:

LMWPE, LDPE, HDPE, UHMWPE, *it*-PP

The specified polymer (50 mg) was mixed with toluene (15 mL) in a 20 mL glass scintillation vial and placed in an 85 °C automatic heating and orbiting shaker until fully dissolved. Upon full solubility, a solution of selected UDC (2.5 mg) dissolved in toluene (1 mL) was added quantitatively to the stirring mixture. The UDC is briefly mixed into the polymer solution before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed (60 °C) by rotovap, and the sample was left to dry in a vacuum oven (60 °C) overnight or until a constant mass was achieved. The obtained white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbene precursors. Crosslinked polymers appeared light yellow, a visual sign of successful installment.

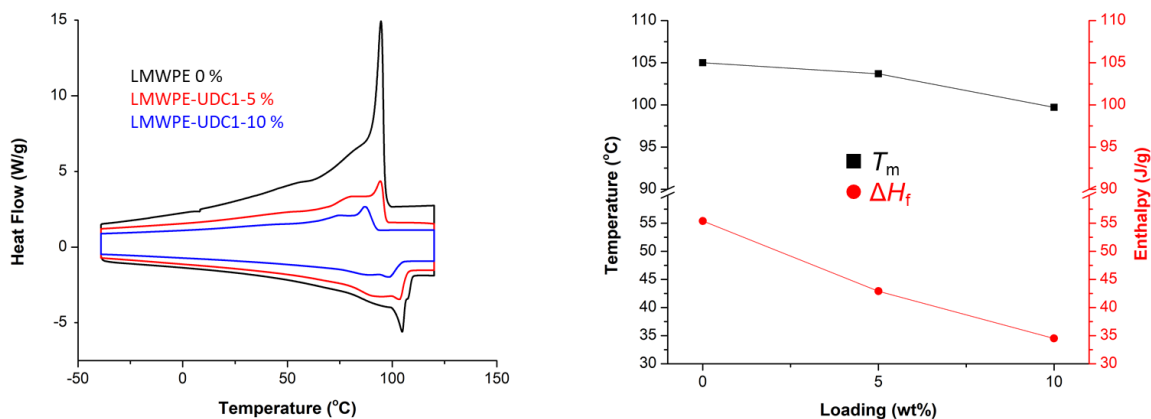


Figure S23. Thermal behavior and trends for LMWPE at 0, 5, and 10 wt.% loading of UDC1.

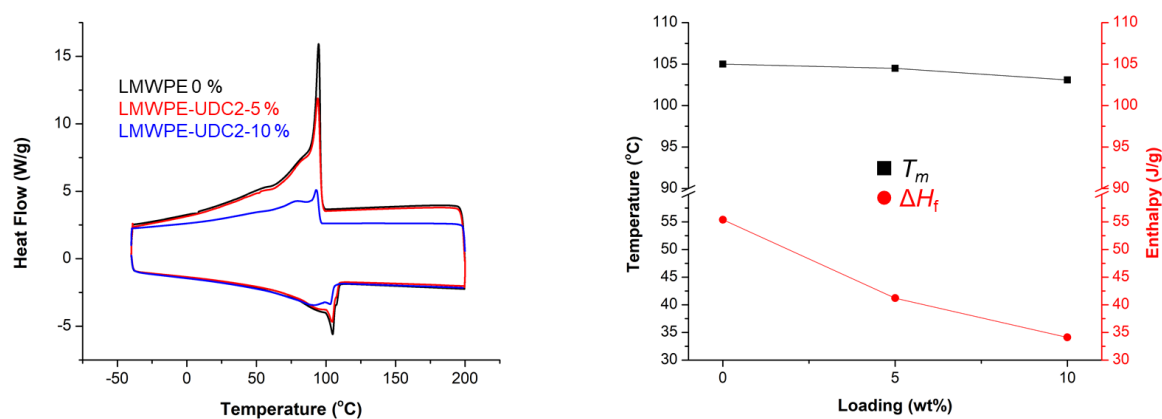


Figure S24. Thermal behavior and trends for LMWPE at 0, 5, and 10 wt.% loading of UDC2.

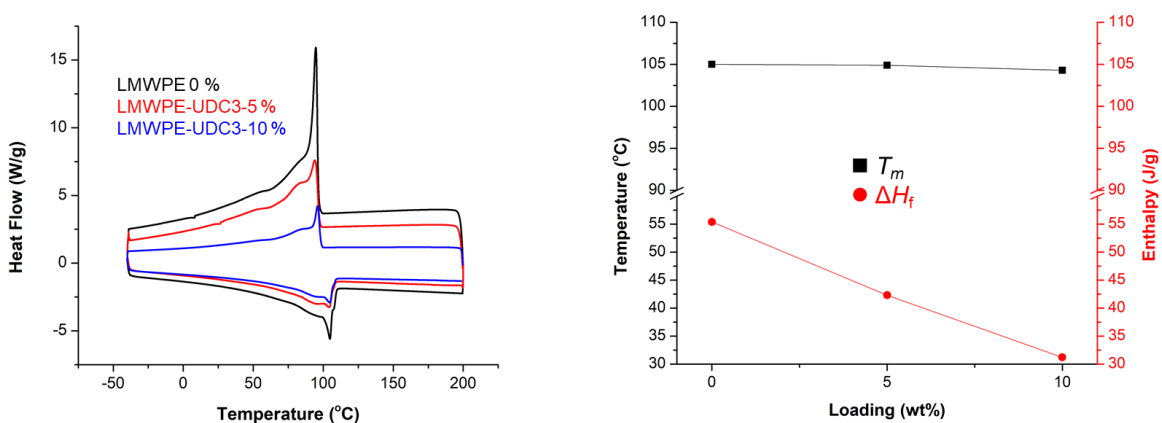


Figure S25. Thermal behavior and trends for LMWPE at 0, 5, and 10 wt.% loading of UDC3.

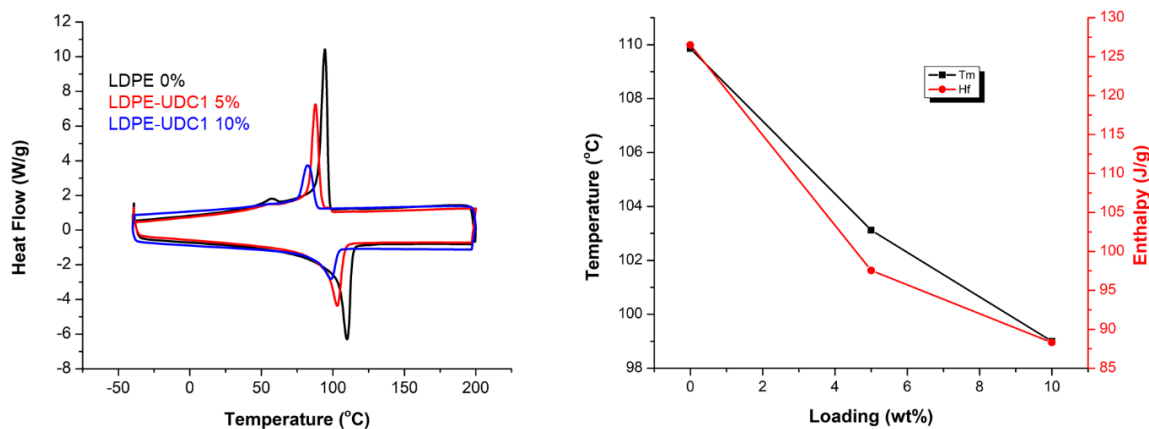


Figure S26. Thermal behavior and trends for LDPE at 0, 5, and 10 wt.% loading of UDC1.

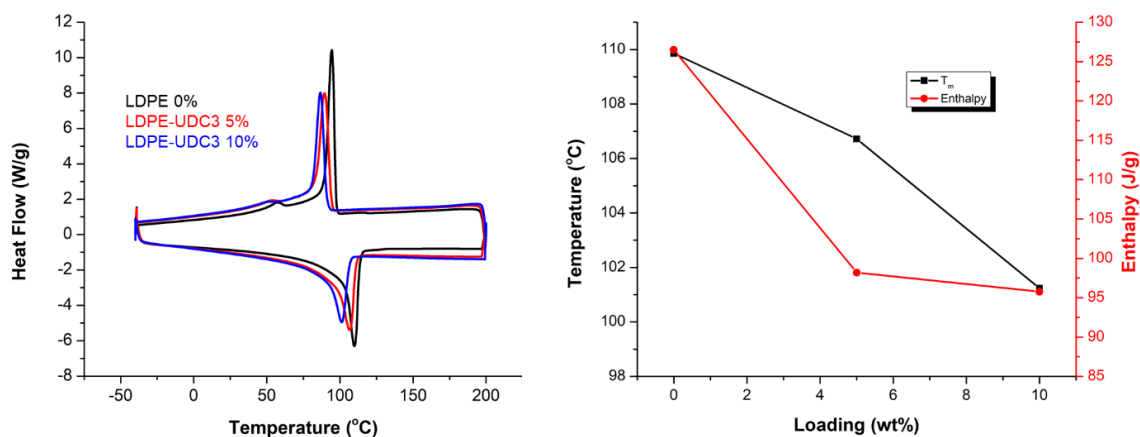


Figure S27. Thermal behavior and trends for LDPE at 0, 5, and 10 wt.% loading of UDC3.

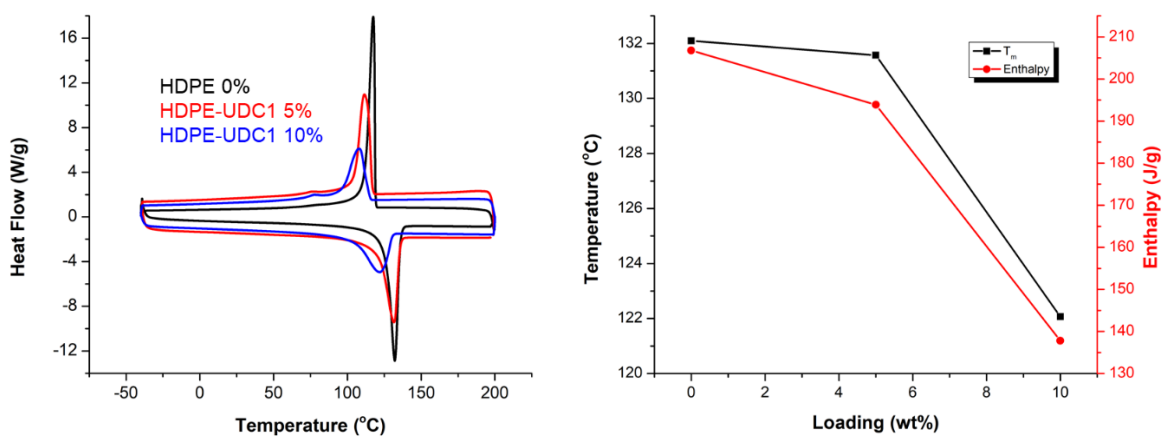


Figure S28. Thermal behavior and trends for HDPE at 0, 5, and 10 wt.% loading of UDC1.

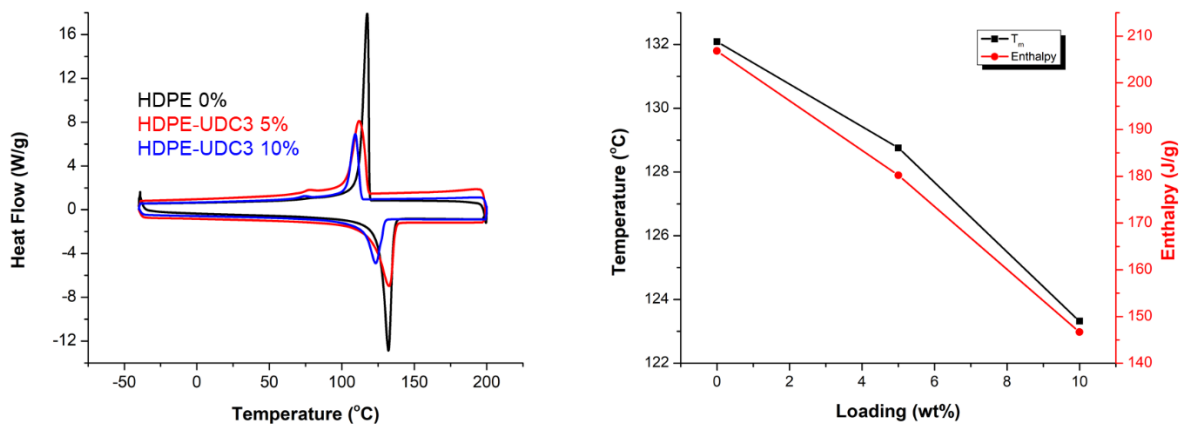


Figure S29. Thermal behavior and trends for HDPE at 0, 5, and 10 wt.% loading of UDC3.

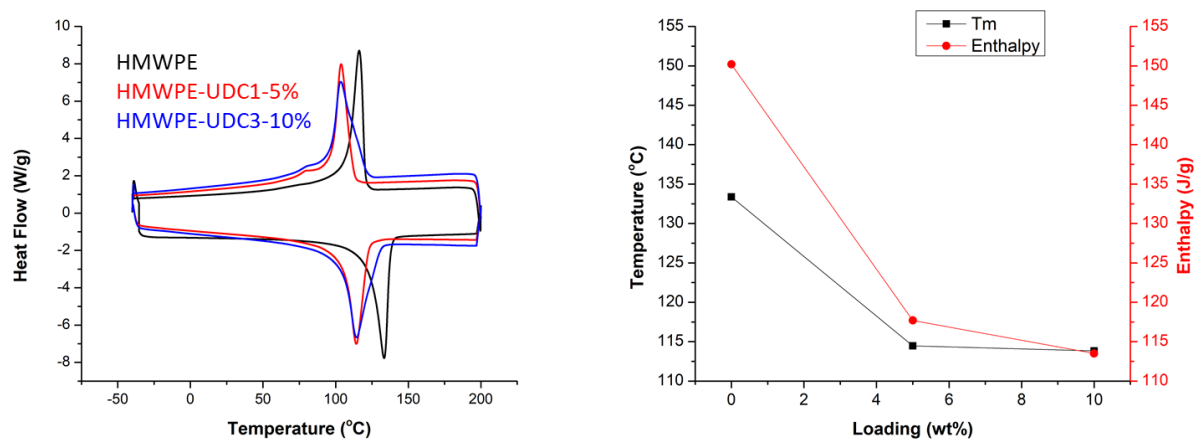


Figure S30. Thermal behavior and trends for UHMWPE at 0, 5, and 10 wt.% loading of UDC1.

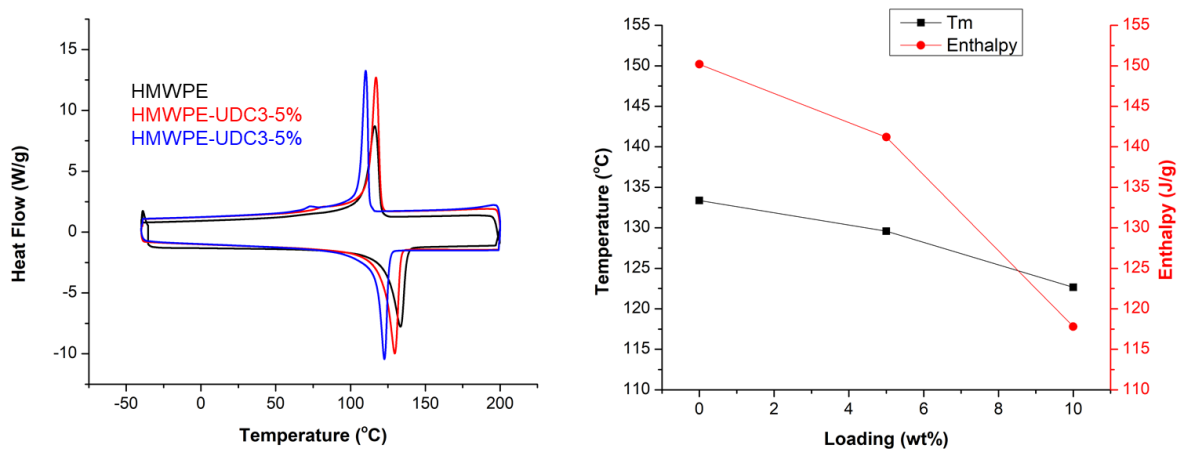


Figure S31. Thermal behavior and trends for UHMWPE at 0, 5, and 10 wt.% loading of UDC3.

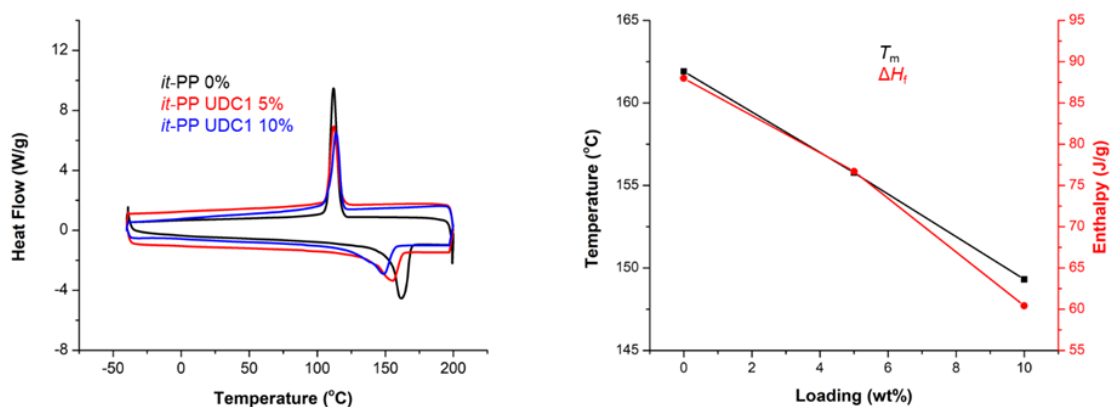


Figure S32. Thermal behavior and trends for *it*-PP at 0, 5, and 10 wt.% loading of UDC1.

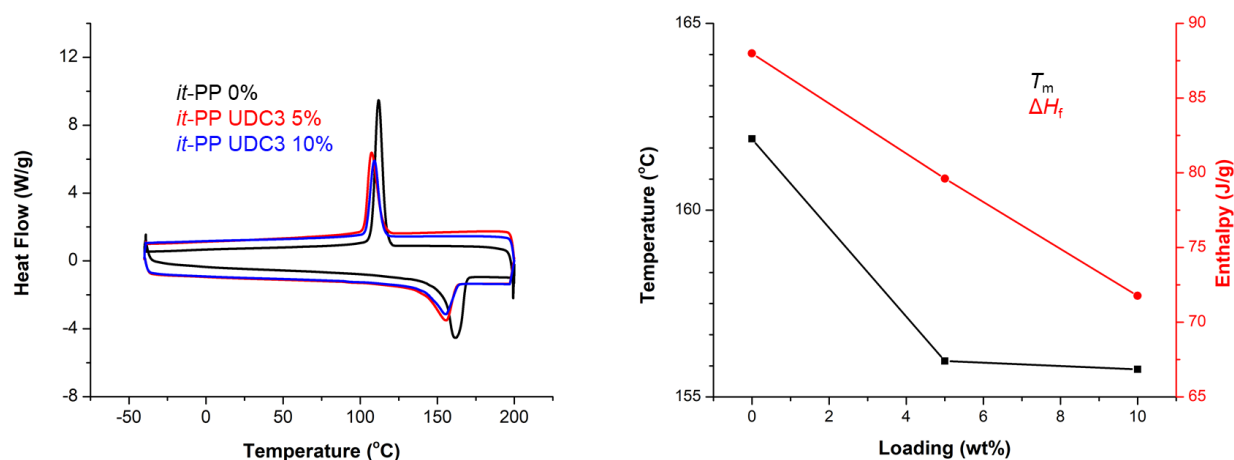


Figure S33. Thermal behavior and trends for *it*-PP at 0, 5, and 10 wt.% loading of UDC3.

Example Homopolymer Crosslinking Procedure (5 wt.% UDC)

Applicable Polymers:

HDPE, LDPE, LMWPE

A 500 mL round bottom flask was charged with toluene (100 mL), specified polymer powder or pellets (5.0 g), and a stir bar. The mixture was heated to 85 °C and allowed to stir until partial or full solubility was observed, at which point selected UDC (0.25 g, 5.0 wt.%) in a separate toluene solution (5 mL) was added into the solution. (Note: PMMA and others may not require heating to achieve solubility). The mixture was stirred briefly before cooling over an ice bath (0 °C), which yielded a gelatinous white precipitate. Toluene was then removed under vacuum at 60 °C and the precipitated UDC-imbedded-polymer was dried under vacuum at 60 °C overnight or until a constant mass was achieved. The resulting white powder was then placed in a 125 °C oven for 3 h

to crosslink via thermal activation of UDC carbenes. Crosslinked polymers appeared light yellow, a visual sign of successful installment.

Example 50/50 wt.% Polyolefin/Polyester Blend Small-Scale Crosslinking Procedure

Applicable Polymers:

LMWPE, LDPE, PLA, and P3HB

In a 20 mL glass scintillation vial polyethylene (25 mg) was mixed with toluene (10 mL) and placed in an 85 °C automatic heating and orbiting shaker until fully dissolved. Separately, a 20 mL scintillation vial was charged with the specified polyester (25 mg, 50 wt.%), 10 mL of chloroform, and a stir bar and mixed until full solubility was observed. The polyester solution was added to the heated toluene mixture, and allowed to mix for 30 minutes, at which time a solution of selected UDC (2.5 mg) dissolved in toluene (1 mL) was added quantitatively to the stirring mixture. The solution blend of all three components was briefly mixed before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed (60 °C) by rotovap, and the sample was left to dry in a vacuum oven (60 °C) overnight or until a constant mass was achieved. The obtained white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbene precursors. Crosslinked blends appeared light yellow, a visual sign of successful installment.

Example 50/50 wt.% Polyolefin/Polyester Blend Crosslinking Procedure

Applicable Polymers:

LMWPE, LDPE, PLLA, and P3HB

In a 250 mL round bottom flask polyethylene (2.5 g) was vigorously stirred in toluene (100 mL) at 85 °C until full solubility was observed. In a separate 250 mL round bottom flask, specified PLLA or P3HB pellets (2.5 g, 50 wt.%) were vigorously stirred in chloroform (50 mL) until full solubility was observed. The polyester solution was then quickly added to the polyethylene solution. Additional stirring at 85 °C was carried out for 30 min, which achieved stable solution-blended polymers. Selected UDC (0.25 g) was then dissolved in toluene (5 mL) and added quantitatively to the stirring mixture. The UDC-blend was stirred briefly before cooling over an ice bath (0 °C), which yielded a white gelatinous precipitate. Solvents were removed under vacuum at 60 °C and the received UDC-blend was dried under vacuum at 60 °C overnight or until a constant mass was achieved. The white powder was moved to a 125 °C oven for 3 h to crosslink via thermal activation of UDC carbene precursors. Crosslinked blends appeared light yellow, a visual sign of successful installment.

Virgin (0 %) blends of LMWPE and PLLA/P3HB were prepared by the above procedures, without the steps of UDC addition.

General Crosslinked Polymer Characterizations

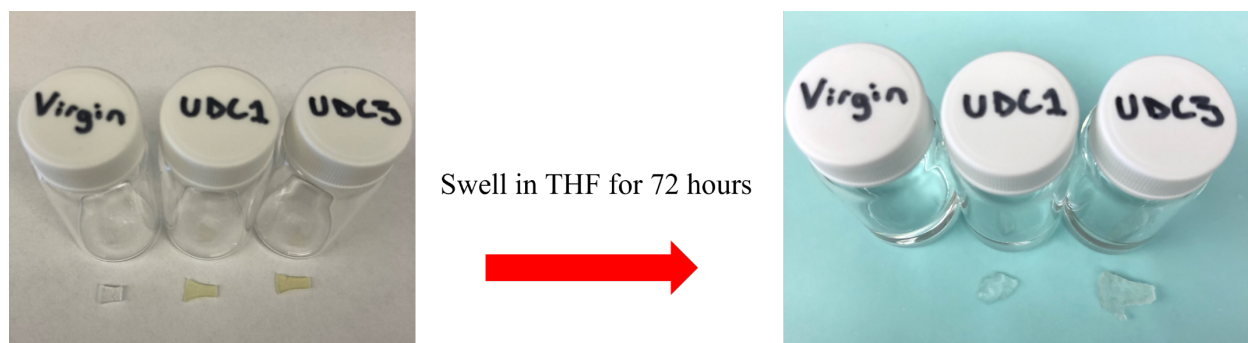


Figure S34. Solubility test on amorphous PMMA-UDC1 and -UDC3 at 5 wt.% loading (THF, 72 h, 50 °C).

Tensile Testing, Photos, and FTIR: Reprocessing Studies

Reprocessability experiments were carried out on LMWPE and LDPE:

1. Melt compression reprocessed film homogeneity. Film processing conditions are reported in materials & methods.
2. Tensile pulling experiments (stress/strain, ~23 °C, 5 mm/min) on both virgin materials and re-compression molded films to study performance enhancements and retention following use. Tensile curves are an average of 3-4 individual ASTM D638 samples with error margins reported in the supplemental tables (~23 °C, 5 mm/min until fail).
3. FTIR spectral analysis for signs of decomposition or structural differences following reprocessing, and anticipated bond exchange events, at high temperature. No noticeable changes were observed in any of the samples, supporting clean network reprocessing.

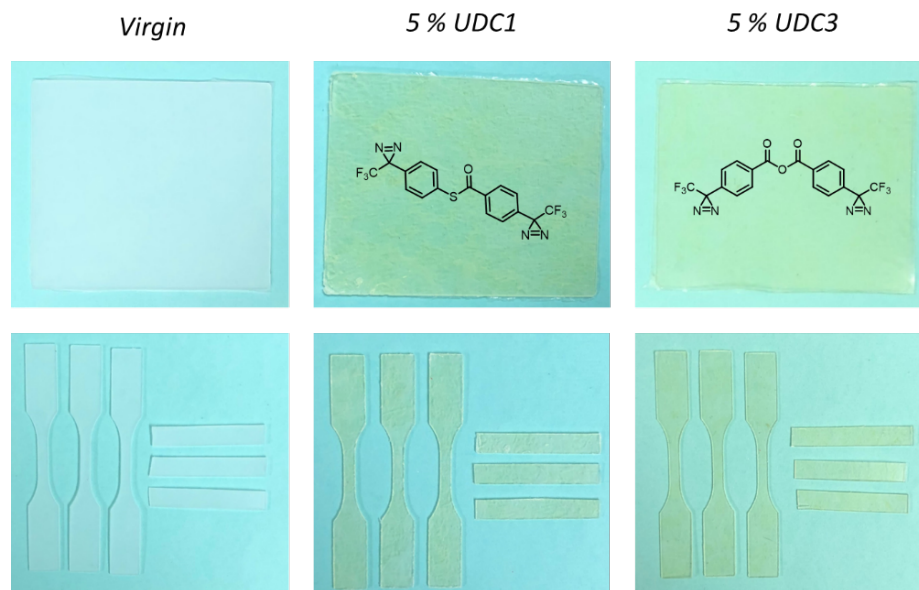


Figure S35. Photos of UDC1 and 3 crosslinked (labeled, 5 wt.%) LDPE films and corresponding tensometer/DMA samples.

LDPE-UDC3 5% Reprocessed

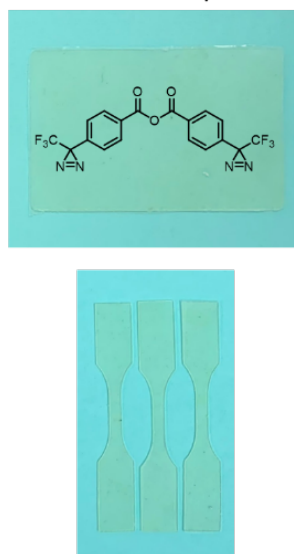


Figure S36. Photos of UDC3 crosslinked (labeled, 5 wt.%) LDPE film and corresponding tensometer/DMA samples following one melt-reprocessing step.

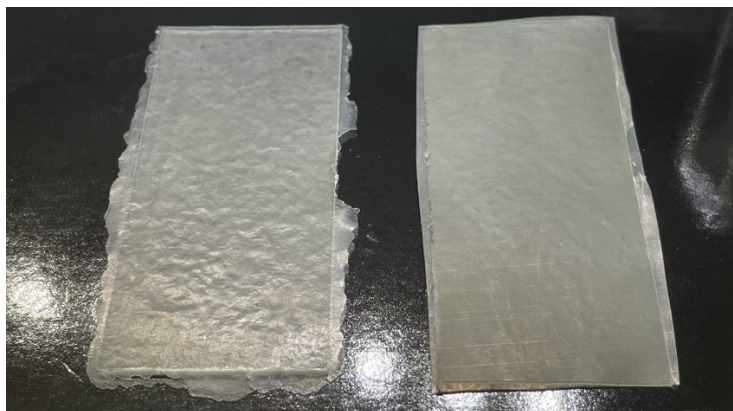
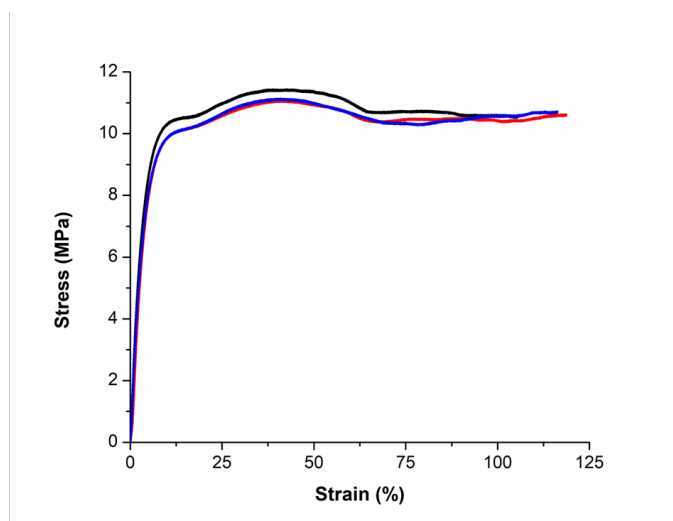


Figure S37. Photos of USC (left) and UDC3 (right) crosslinked films of LDPE at an angle highlighting the distinctions in surface homogeneity, a pre-text for subsequent mechanical performance, upon reprocessing.



Sample	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
1	10.4	105.4	354	11.4
2	10.5	118.7	333	12.9
3	10.6	116.2	330	13.0
Average	10.5 ± 0.1	113 ± 5.8	345 ± 14	12.4 ± 0.7

Figure S38. Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE (MFI = 26).

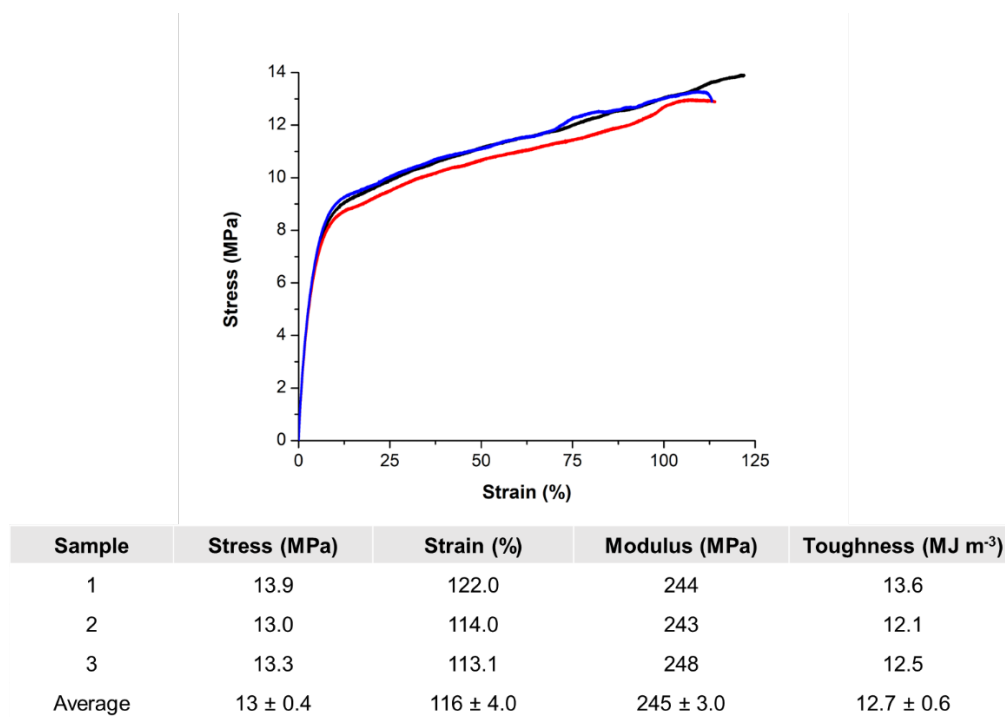


Figure S39. Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for LDPE-UDC3.

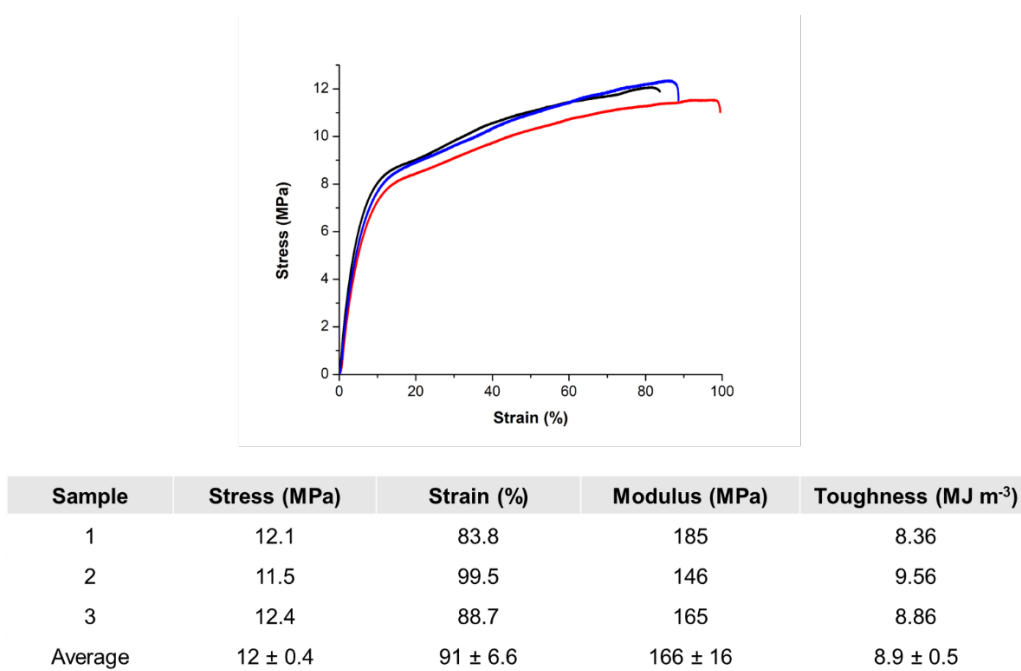
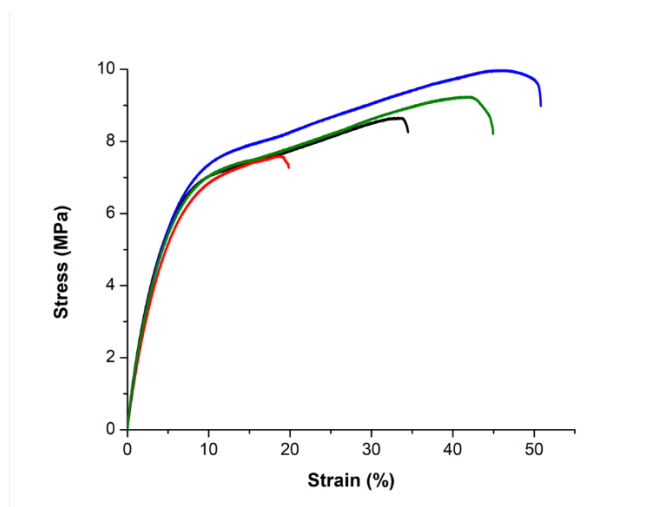
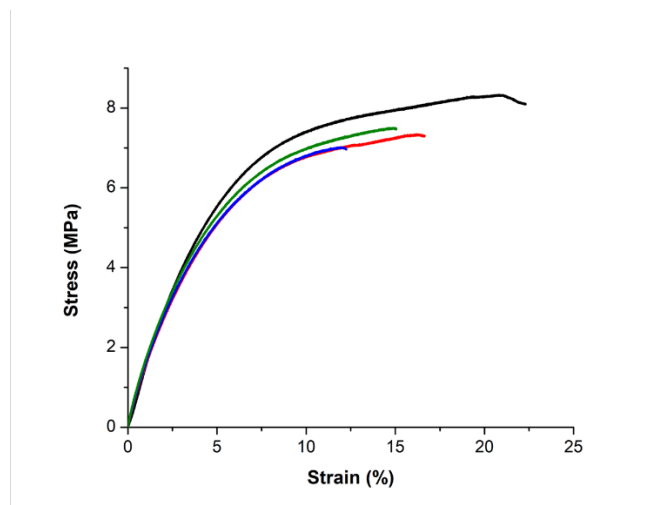


Figure S40. Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE-UDC3 after reprocessing.



Sample	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
1	8.66	34.5	180	2.43
2	7.60	19.8	153	1.18
3	9.98	50.8	163	4.15
4	9.24	44.9	167	3.39
Average	8.9 ± 1.0	38 ± 12	166 ± 10	2.8 ± 1.1

Figure S41. Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE-USC.



Sample	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
1	8.33	16.3	169	1.48
2	7.34	22.3	151	0.93
3	7.02	12.3	160	0.61
4	7.50	15.0	159	0.84
Average	7.5 ± 0.5	16 ± 3.7	160 ± 6.4	1.0 ± 0.3

Figure S42. Individual tabulated and plotted tensile trials (5 mm/min, ~23 °C) for LDPE-USC after reprocessing.

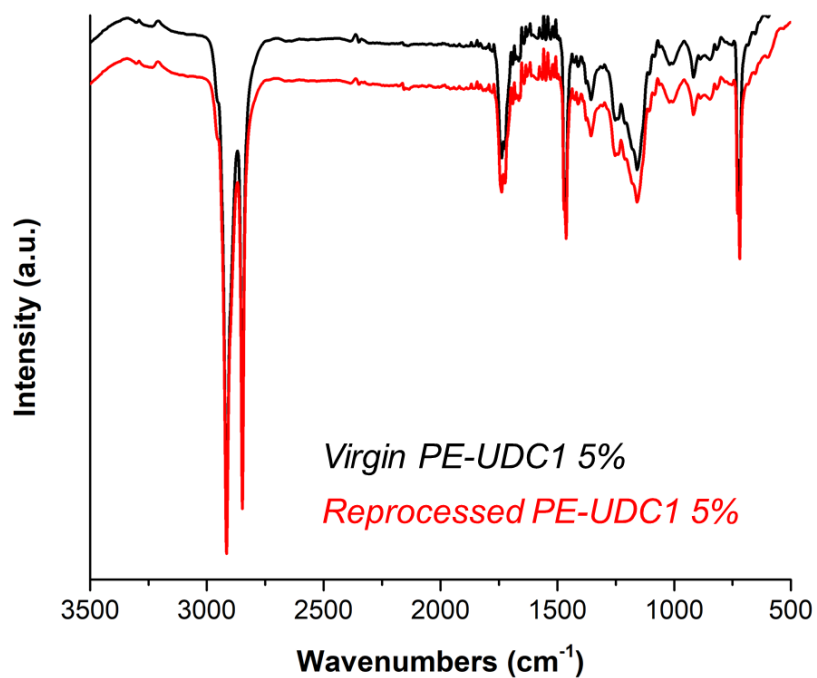


Figure S43. Overlaid FTIR spectra for virgin quality (black) and reprocessed (red) PE-UDC1 (5 wt.%)

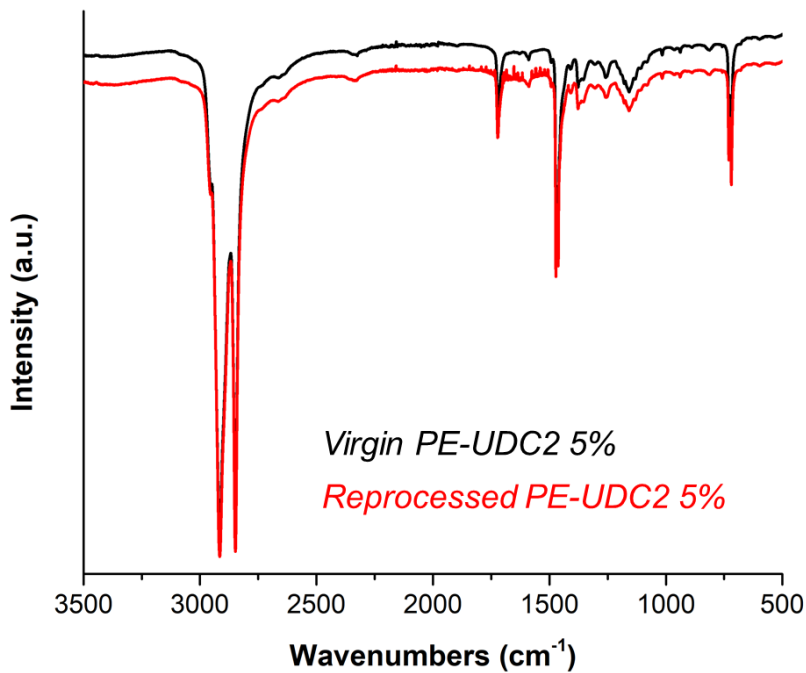


Figure S44. Overlaid FTIR spectra for virgin quality (black) and reprocessed (red) PE-UDC2 (5 wt.%)

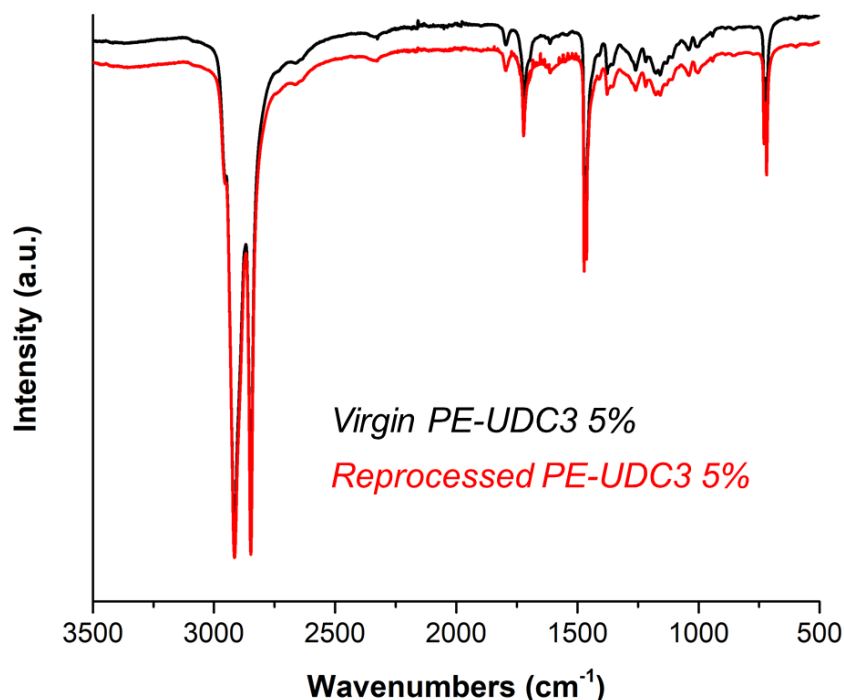


Figure S45. Overlaid FTIR spectra for virgin quality (black) and reprocessed (red) PE-UDC3 (5 wt.%)

Dynamic Mechanical Analysis

Tension-film mode experiments were performed on the above-referenced DMA on LMWPE, LDPE, and HDPE dynamic thermosets.

Thermomechanical frequency sweeps were performed between -50 – 200 °C at a heating rate of 5 °C/min, 0.3 % strain, and an oscillation frequency of 1 Hz. Creep-recovery experiments were performed at a constant stress of 2 MPa for HDPE and LDPE samples, and 5 MPa for UHMWPE. Prolonged creep-recovery experiments on HDPE samples were run for 240 minutes (4 h) with constant load at 40 °C followed by 30 minutes of recovery time. Elevated temperature (80 – 110 °C) creep-recovery tests for LDPE and HDPE were run under similar 2 MPa stress loading for 600 sec (10 min), with 300 sec (5 min) allotted for strain recovery.

1. Frequency sweeps were performed between -50 – 200 °C at consistent 5 °C/min heat ramp rate, 0.1 – 0.3 % strain, and an oscillation frequency of 1 Hz. DMA curves are a reported average of 2-3 samples and further reported in the supplementary tables.
2. Low-Temperature Creep-Recovery experiments were performed below the melt transition temperature to exhibit working behavior upon addition of dynamic crosslinks. A 2 MPa stress was applied for 600 s (10 min) at specified temperatures, following which the

recovered strain (non-permanent deformation) was tracked for 300 s (5 min). In the case of HDPE at 40 °C, performed to mimic possible prolonged working conditions, operated on 240 min (4 h) of creep, and 30 min (0.5 h) of recovery. Strain loss was converted to creep recovery (%) by inverse-normalizing and reversing the strain values immediately upon entering the recovery phase in the main text, for clarification, though the original plots are reported herein below.

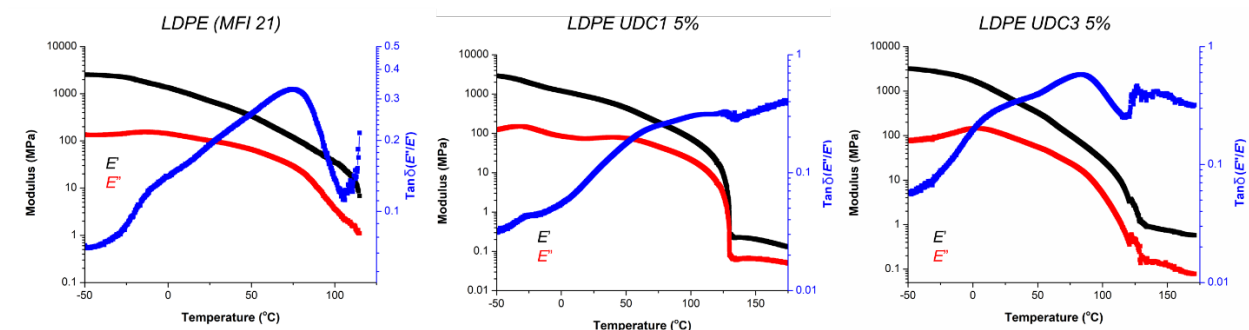


Figure S46. Representative DMA temperature-ramp frequency-sweeps for LDPE (MFI 21) samples treated with 5 wt.% UDC1 and 3 as specified (-50 to 175 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).

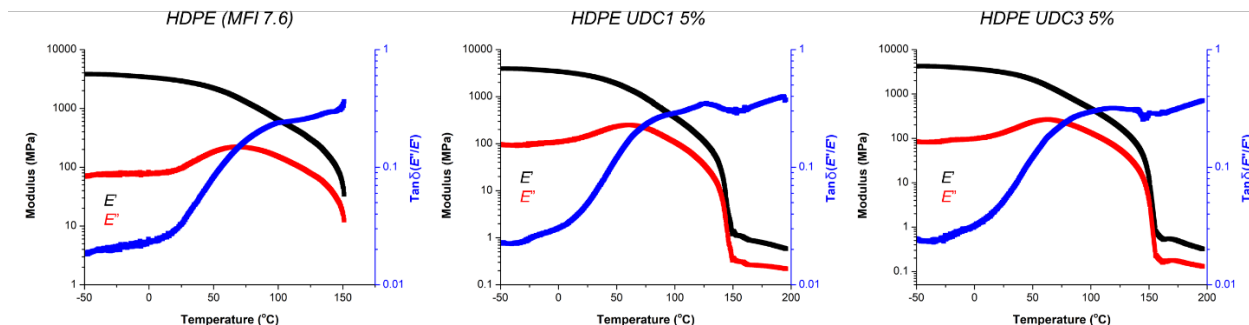


Figure S47. Representative DMA temperature-ramp frequency-sweeps for HDPE (MFI 7.6) samples treated with 5 wt.% UDC1 and 3 as specified (-50 to 200 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).

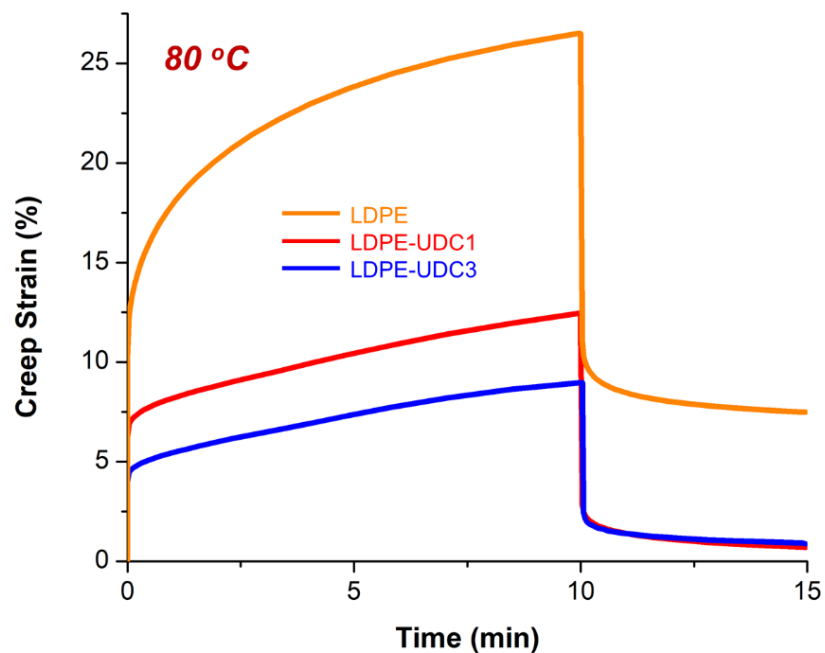


Figure S48. Prolonged creep-recovery plots for virgin LDPE (orange), and LDPE treated with UDC1 and UDC3 (5 wt.%; red, blue respectively) (2 MPa, 80 °C, 600 s creep, 300 s recovery).

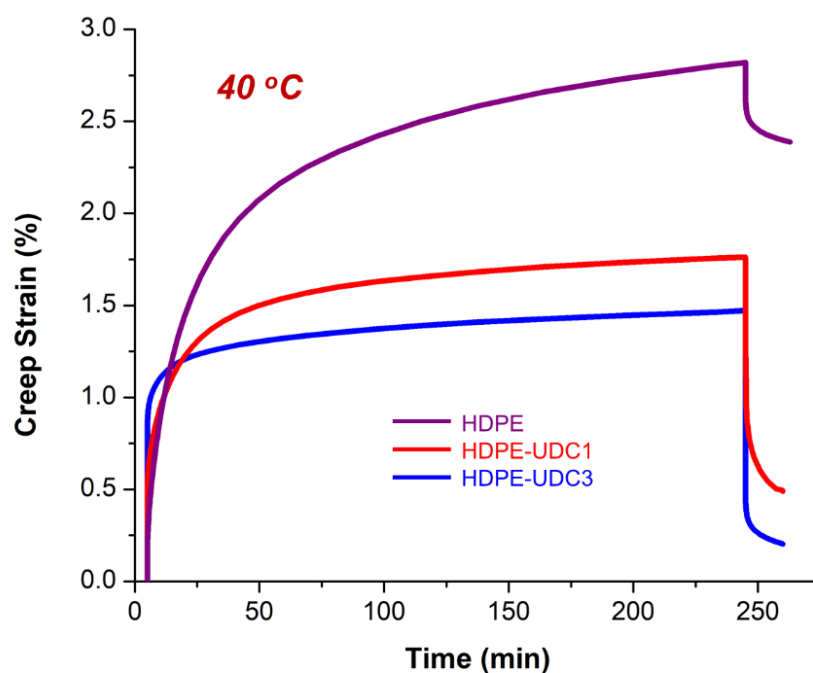


Figure S49. Near-ambient-condition creep-recovery plots for virgin HDPE (purple), and HDPE treated with UDC1 and UDC3 (5 wt.%; red, blue respectively) (2 MPa, 40 °C, 240 min creep, 30 min recovery).

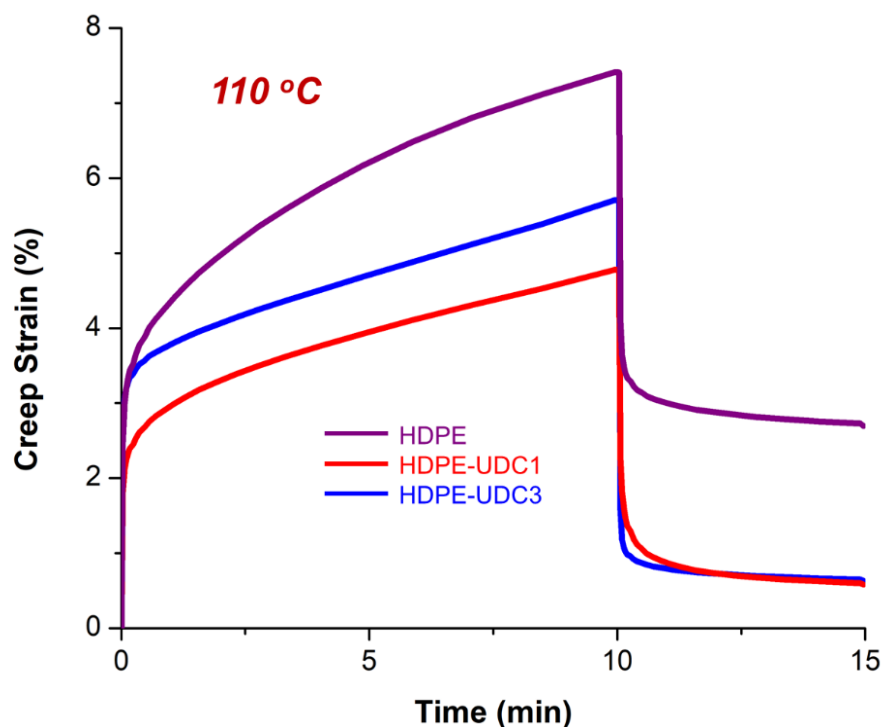


Figure S50. High-temperature creep-recovery plots for virgin HDPE (purple), and HDPE treated with UDC1 and UDC3 (5 wt.%; red, blue respectively) (2 MPa, 110 °C, 240 min creep, 30 min recovery).

Bulk-Shearing Oscillation Rheology

As our dynamic thermosets retained the capacity for flow behavior, we were able to further observe chain behavior under rheological testing conditions. Similarly, nuances between exchange mechanisms in various UDCs highlighted material performance tunability.

1. Creep-recovery was carried out for 600 s under 2.5 kPa shear stress (creep) and additionally 300 s with removed shear stress (recovery). Strain was applied with a 1 s rise time. Temperature listed above.
2. High-temperature frequency sweeps and crosslink density were carried out in the rubbery plateau and above the melt temperature of LDPE. The sample was oscillated to 0.1 % shear strain at angular frequencies between 0.5 to 100 rad/s. Values for the average storage moduli (G' , Pa) at each temperature are averaged from the plateau at frequencies 0.5 – 5.0 rad/s.

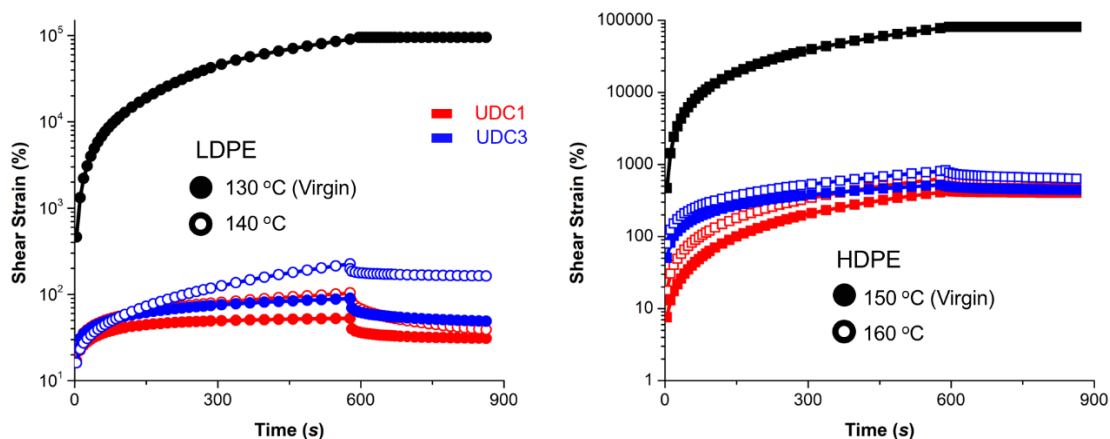


Figure S51. Rheological creep-recovery overlays for LDPE (130 °C) and HDPE (150 °C, black) thermoplastics against UDC1 (red) and UDC3 (blue) crosslinked counterparts (2.5 kPa, 600 s creep, 300 s recovery).

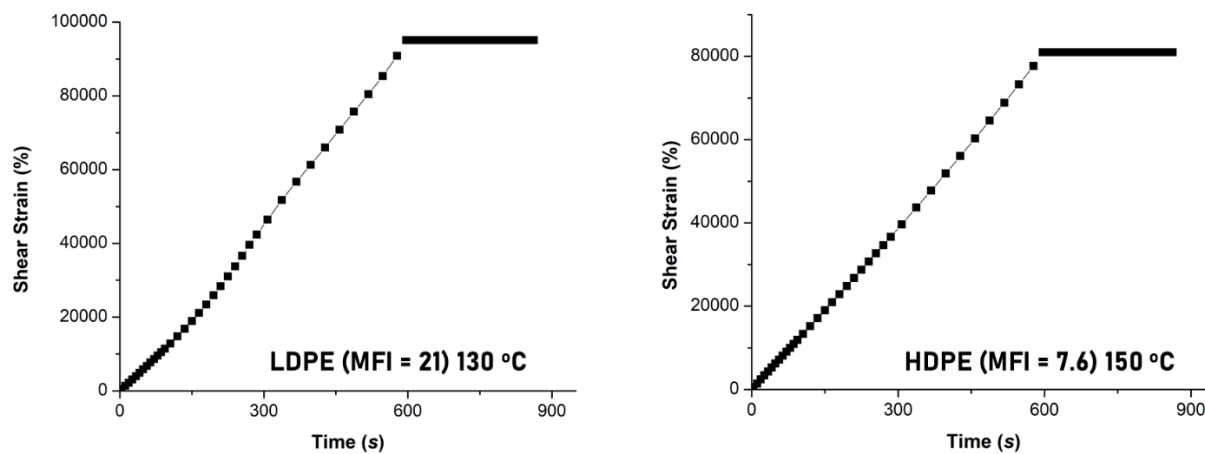


Figure S52. Rheological creep-recovery for virgin thermoplastics LDPE (left, 130 °C) and HDPE (right, 150 °C) (2.5 kPa shear stress, 600 s creep, 300 s recovery).

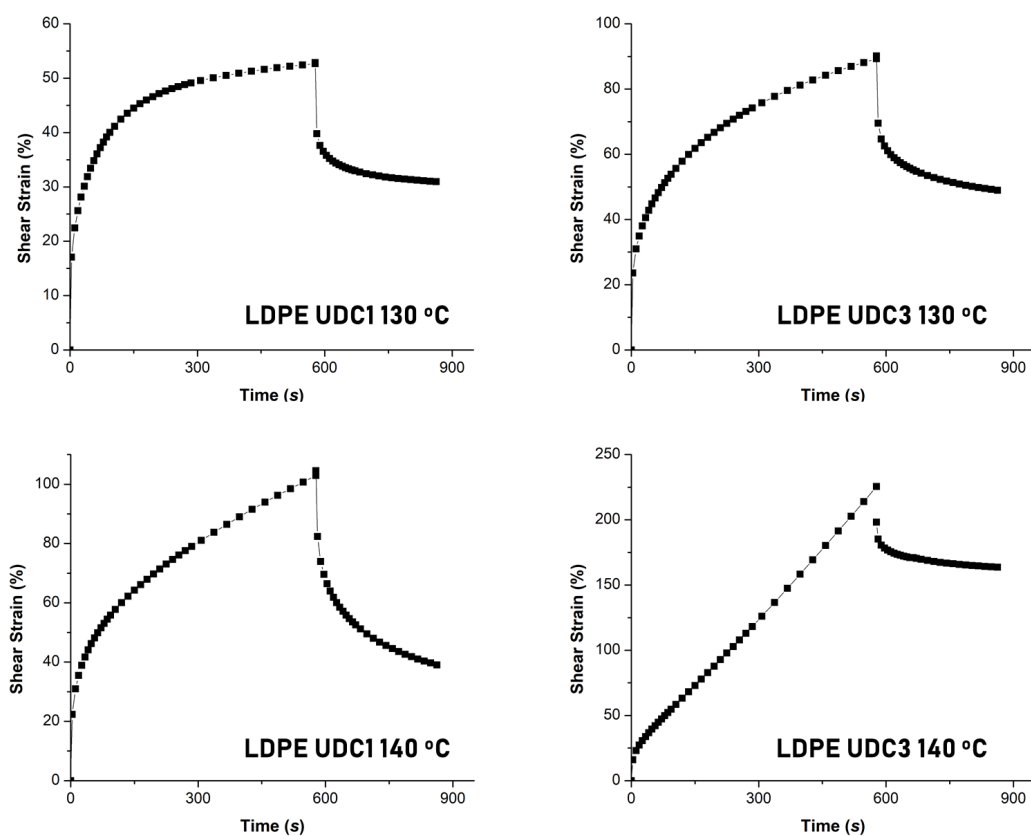


Figure S53. Rheological creep-recovery plots from LDPE with 5 wt.% UDC1 (left) and UDC3 (right) at 130 °C (top) and 140 °C (bottom) (2.5 kPa shear stress, 600 s creep, 300 s recovery).

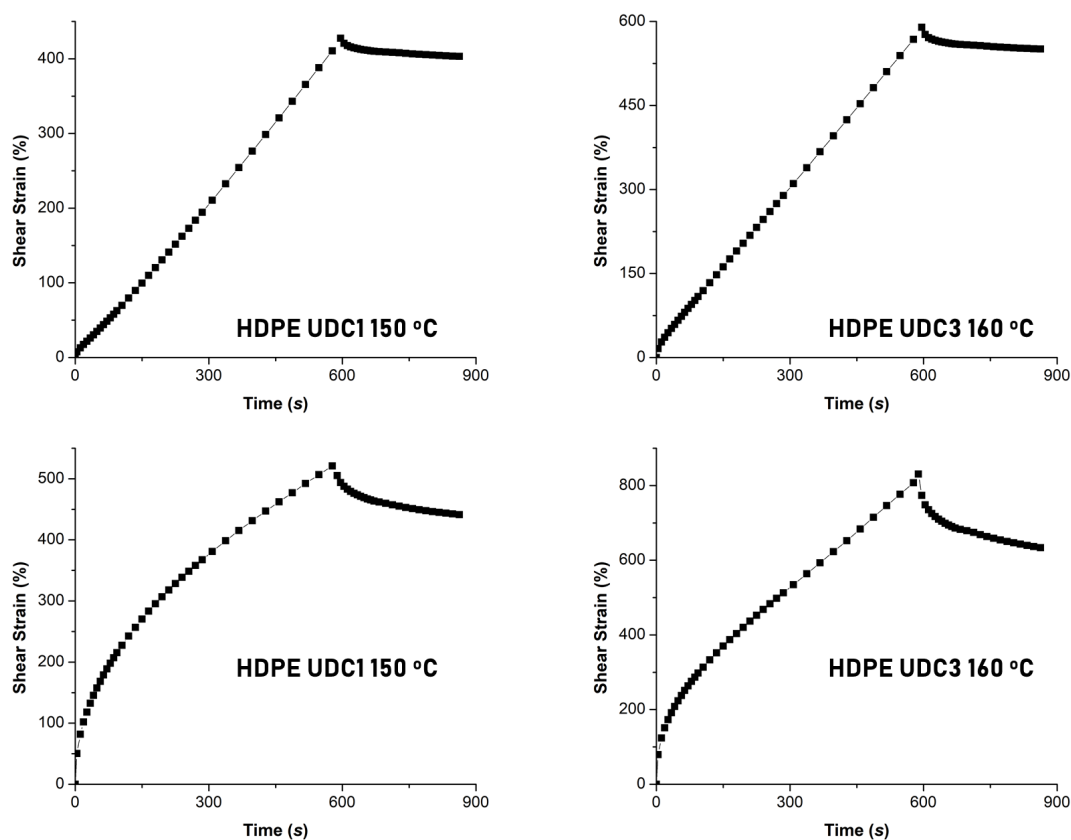


Figure S54. Rheological creep-recovery for HDPE with 5 wt.% UDC1 (red) and UDC3 (blue) at 130 °C (solid) and 140 °C (dashed) (5 kPa shear stress, 600 s creep, 300 s recovery).

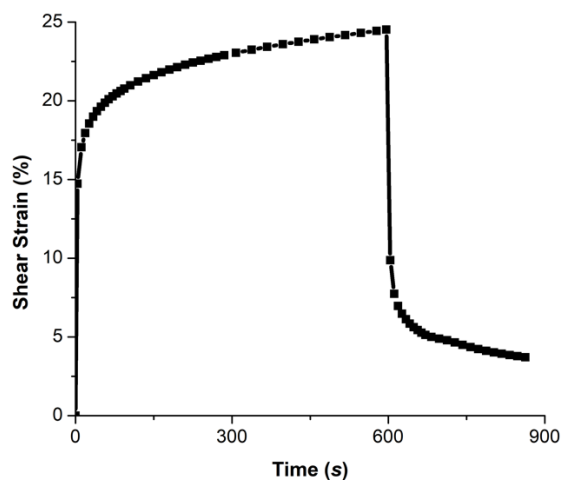


Figure S55. Rheological creep-recovery for LDPE with 5 wt.% USC at 130 °C highlighting the most flow/creep suppression (2.5 kPa shear stress, 600 s creep, 300 s recovery).

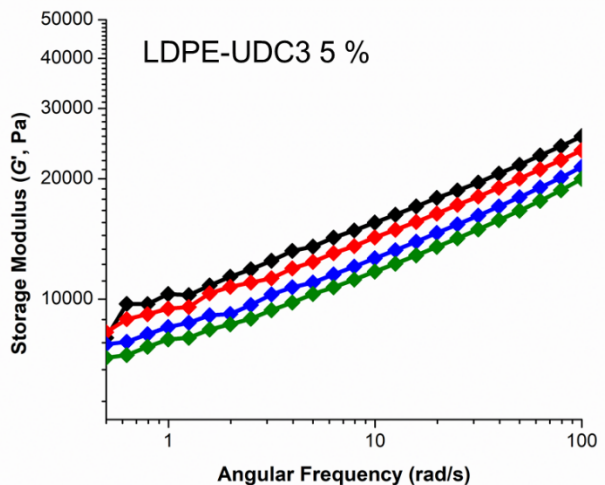
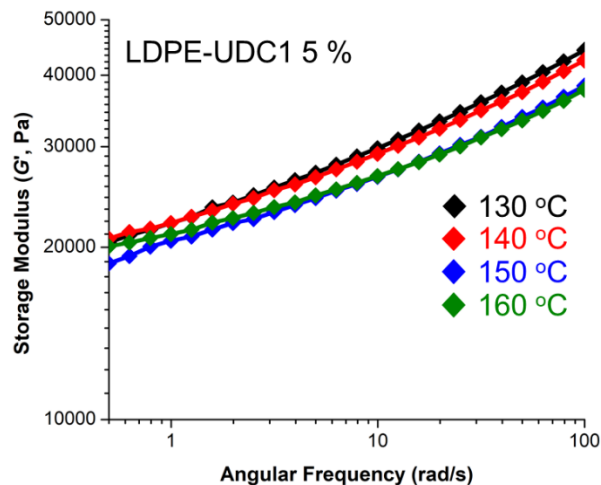


Figure S56. High temperature frequency sweeps for LDPE with 5 wt.% UDC1 and UDC3 (130 – 160 °C, 0.1 % shear strain, 0.5 – 100 rad/s).

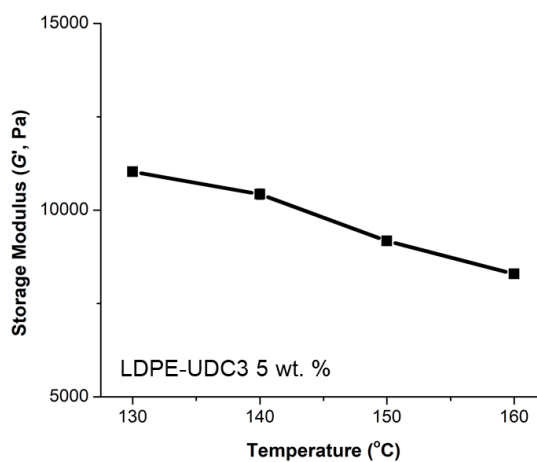
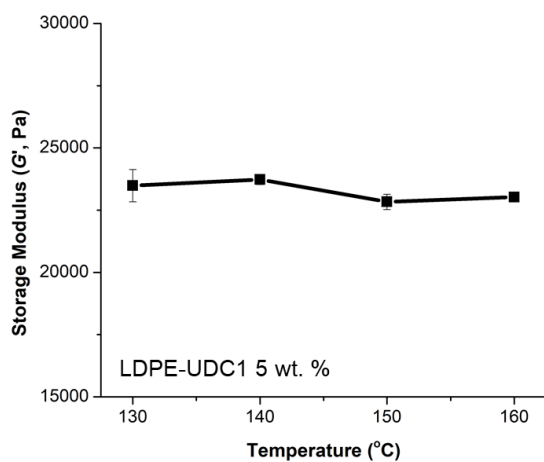


Figure S57. Frequency sweep values tracing the rubbery plateau storage modulus with varied temperature (G' , Pa).

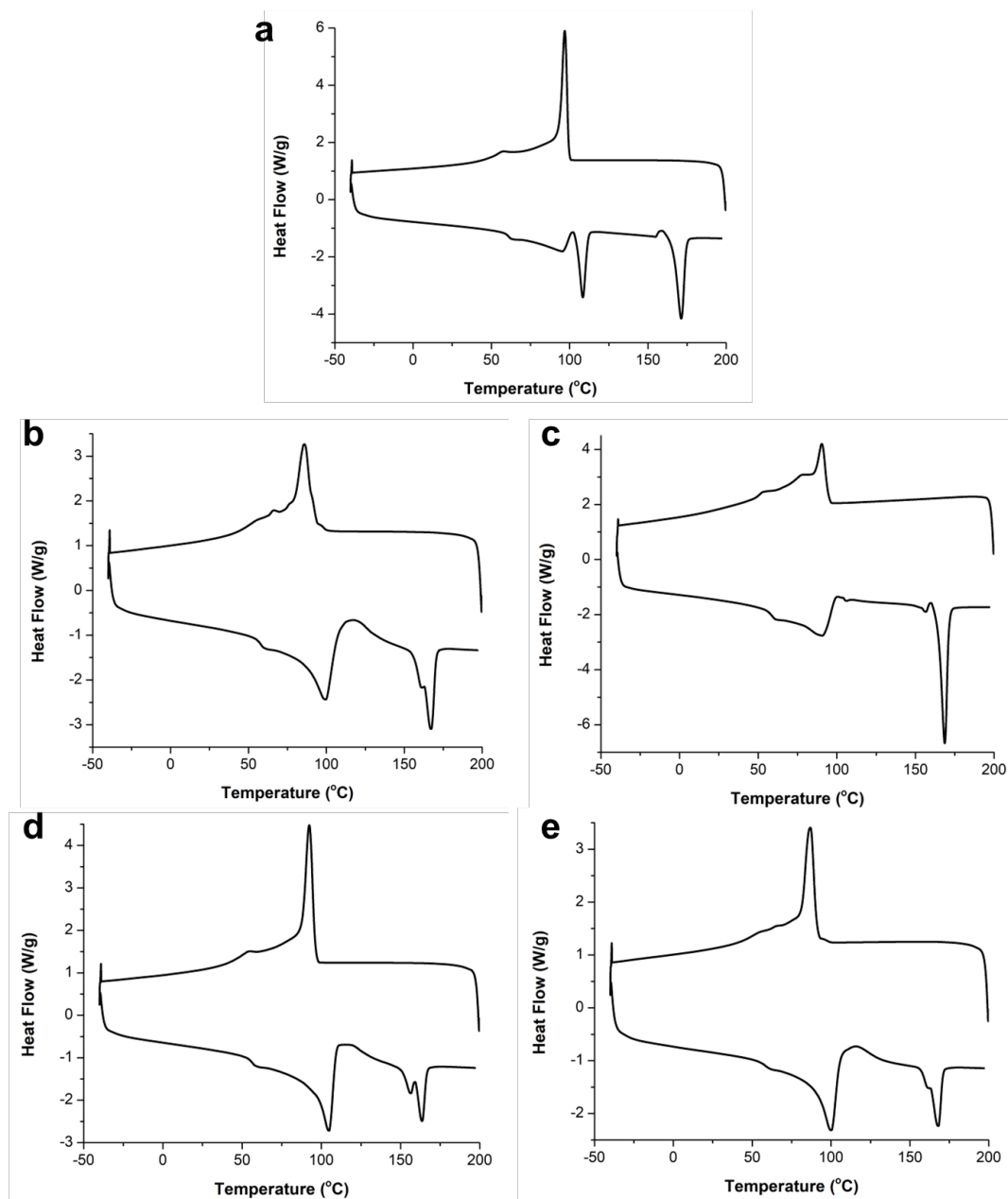


Figure S58. DSC trials for blends of LMWPE-PLA with **a)** no crosslinks, **b)** 5 wt.% UDC1, **c)** 5 wt.% UDC2, **d)** 5 wt.% UDC3, and **e)** 5 wt.% USC (10 °C/min heating and cooling, second heating scan).

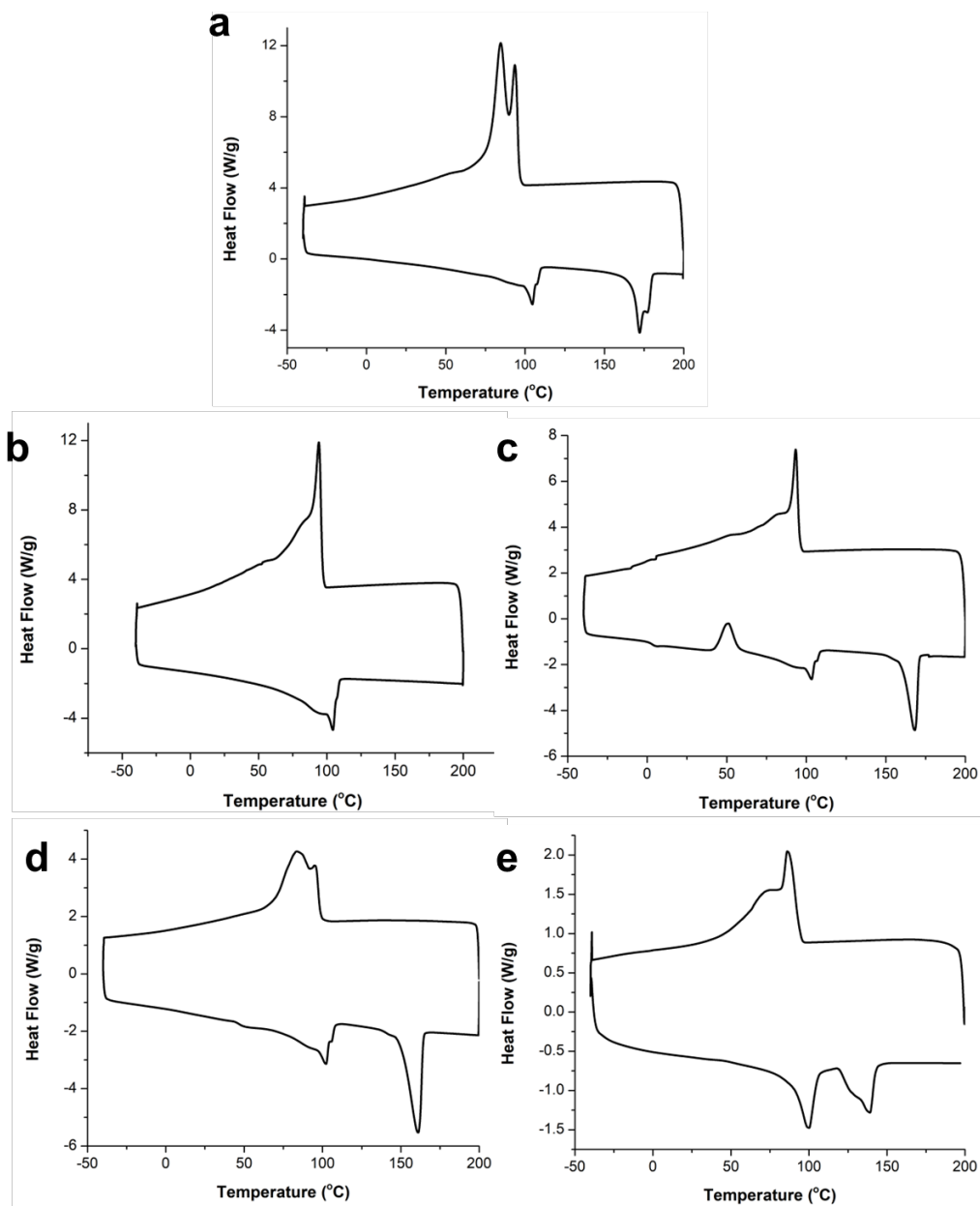


Figure S59. DSC trials for blends of LMWPE-P3HB with **a)** no crosslinks, **b)** 5 wt.% UDC1, **c)** 5 wt.% UDC2, **d)** 5 wt.% UDC3, and **e)** 5 wt.% USC (10 °C/min heating and cooling, second heating scan).

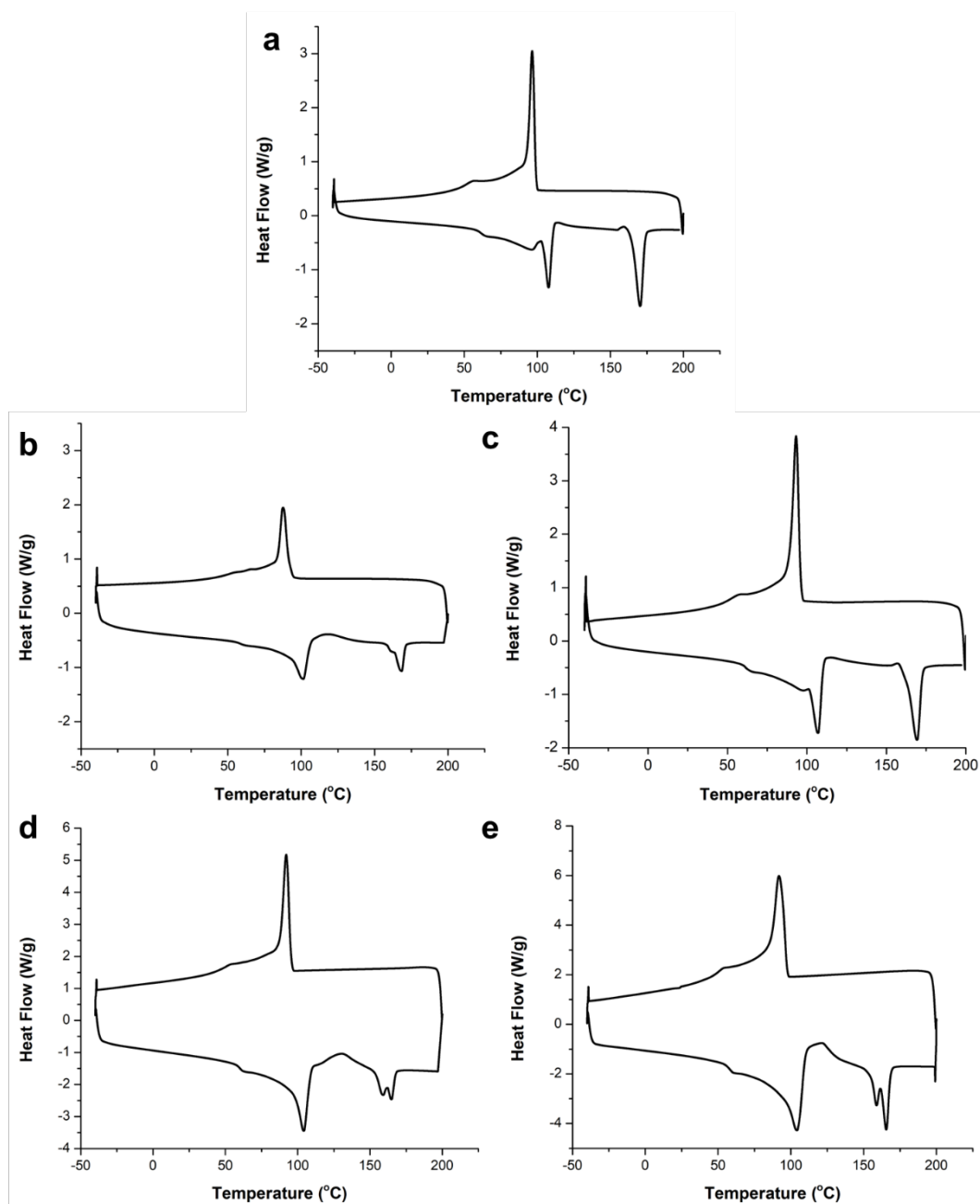


Figure S60. DSC trials for blends of LDPE-PLA with **a)** no crosslinks, **b)** 5 wt.% UDC1, **c)** 5 wt.% UDC2, **d)** 5 wt.% UDC3, and **e)** 5 wt.% USC (10 °C/min heating and cooling, second heating scan).

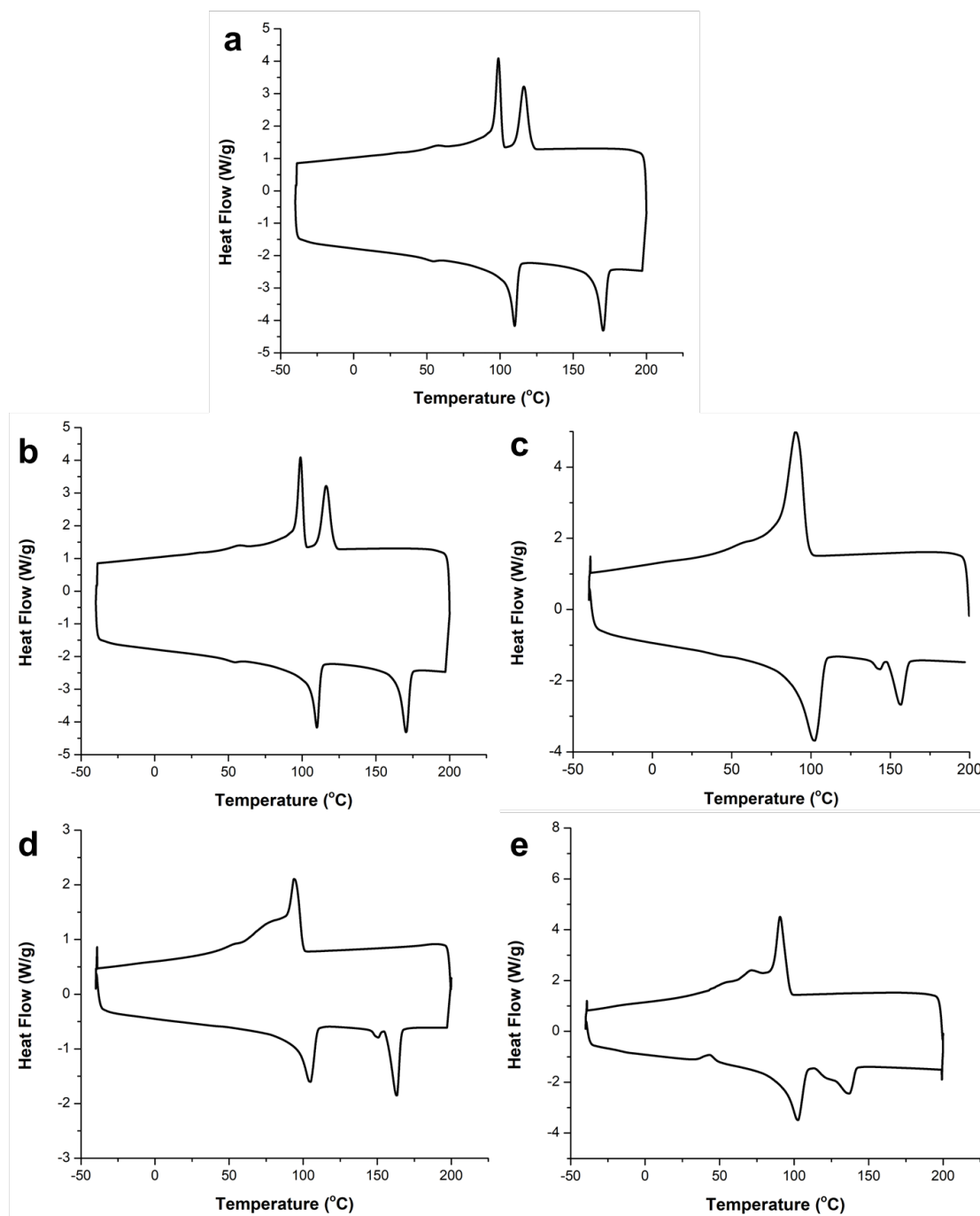


Figure S61. DSC trials for blends of LDPE-P3HB with **a)** no crosslinks, **b)** 5 wt.% UDC1, **c)** 5 wt.% UDC2, **d)** 5 wt.% UDC3, and **e)** 5 wt.% USC (10 °C/min heating and cooling, second heating scan).



Figure S62. Digital images of LDPE-PLLA (50/50 wt%) + UDC3 (5 wt%) blend extrudate flakes (left) and dogbone tensile specimens generated from reprocessing post-tensile test specimens (right). The original blend of LDPE-PLLA (50/50 wt%) + UDC3 (5 wt%) was first compounded via melt-extrusion, and the blend extrudate was reprocessed via compression molding into dogbone specimens for initial tensile tests. After these tensile tests, the broken pieces were mixed with 50 wt% virgin LDPE and melt-extruded, and the resulting blend extrudate (now 75/25 wt% LDPE-PLLA + 2.5 wt% UDC3) was once again compression-molded to the reprocessed/recycled dogbone specimens (right image) for additional tensile tests. The results were reported in Figure S65.

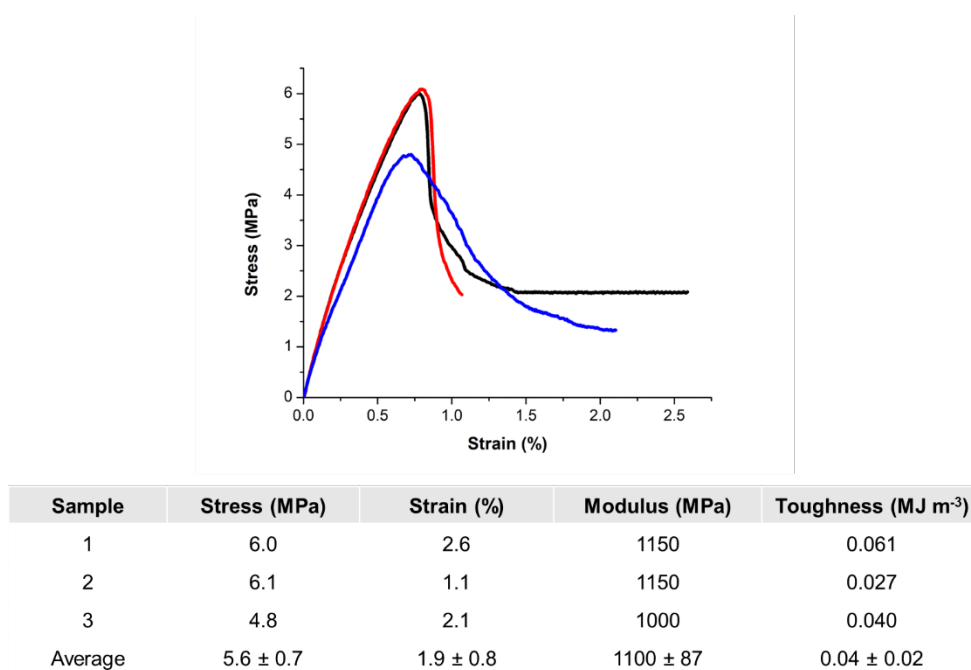
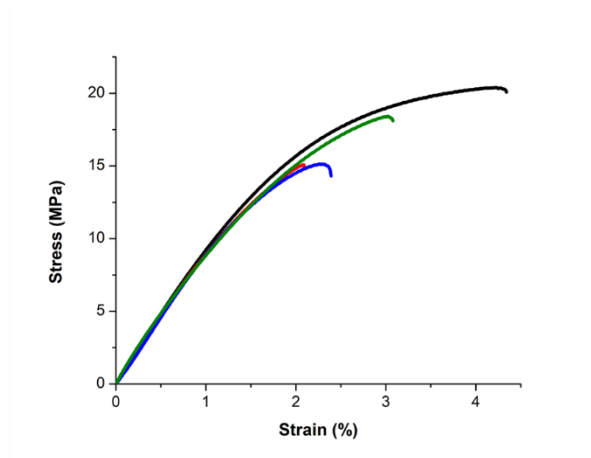
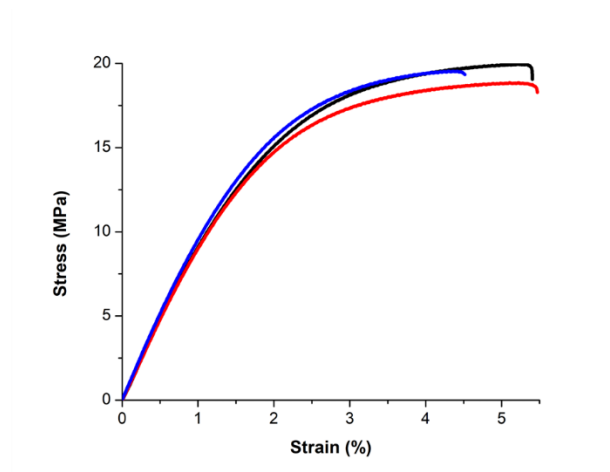


Figure S63. Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for virgin LDPE-PLA.



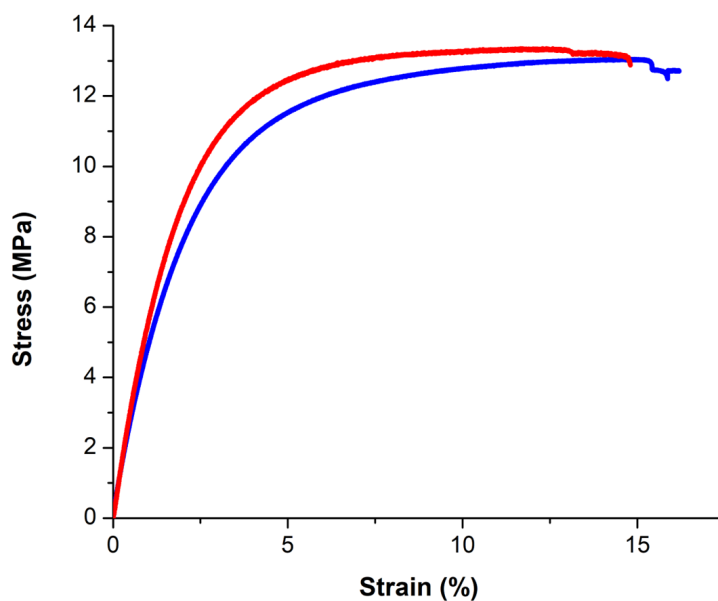
Sample	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
1	20.4	4.3	991	0.62
2	15.1	2.1	983	0.18
3	15.1	2.4	951	0.22
4	18.4	3.1	988	0.35
Average	17 ± 2.6	3.0 ± 1.0	978 ± 18	0.34 ± 0.2

Figure S64. Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for LDPE-PLA 5 % UDC3 processed by melt extrusion.



Sample	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
1	20.0	5.4	997	0.81
2	18.8	5.5	972	0.79
3	19.5	4.5	1040	0.64
Average	19.4 ± 0.6	5.1 ± 0.5	1003 ± 34	0.74 ± 0.1

Figure S65. Tabulated and plotted individual tensile trials (5 mm/min, ~23 °C) for reprocessed LDPE-PLA 5 % UDC3 specimens reprocessed by melt extrusion.



Extruded LDPE-PLA-UDC3 75:25 Blend Seeded with 50 wt. % Virgin LDPE				
Sample	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
1	12.7	17.7	508	1.95
2	12.8	15.9	567	1.75
3	13.6	15.4	589	1.79
Average	13.0 ± 0.5	16.3 ± 1.2	555 ± 42	1.83 ± 0.1
Reprocessed Average	13.4 ± 0.07	14.0 ± 1.2	642 ± 15	1.62 ± 0.15

Figure S66. Tensile overlay (5 mm/min, ~23 °C) and tabulated data for UDC3 (2.5wt%) compatibilised LDPE-PLLA (75:25) blend, prepared by melt-extrusion of added 50 wt% LDPE to 50 wt% LDPE-PLLA (50:50) compatibilised by UDC3 (5 wt%) (red) and melt-extrusion reprocessed resulting LDPE-PLLA-UDC3 blend (blue). More details were provided in Figure S62.

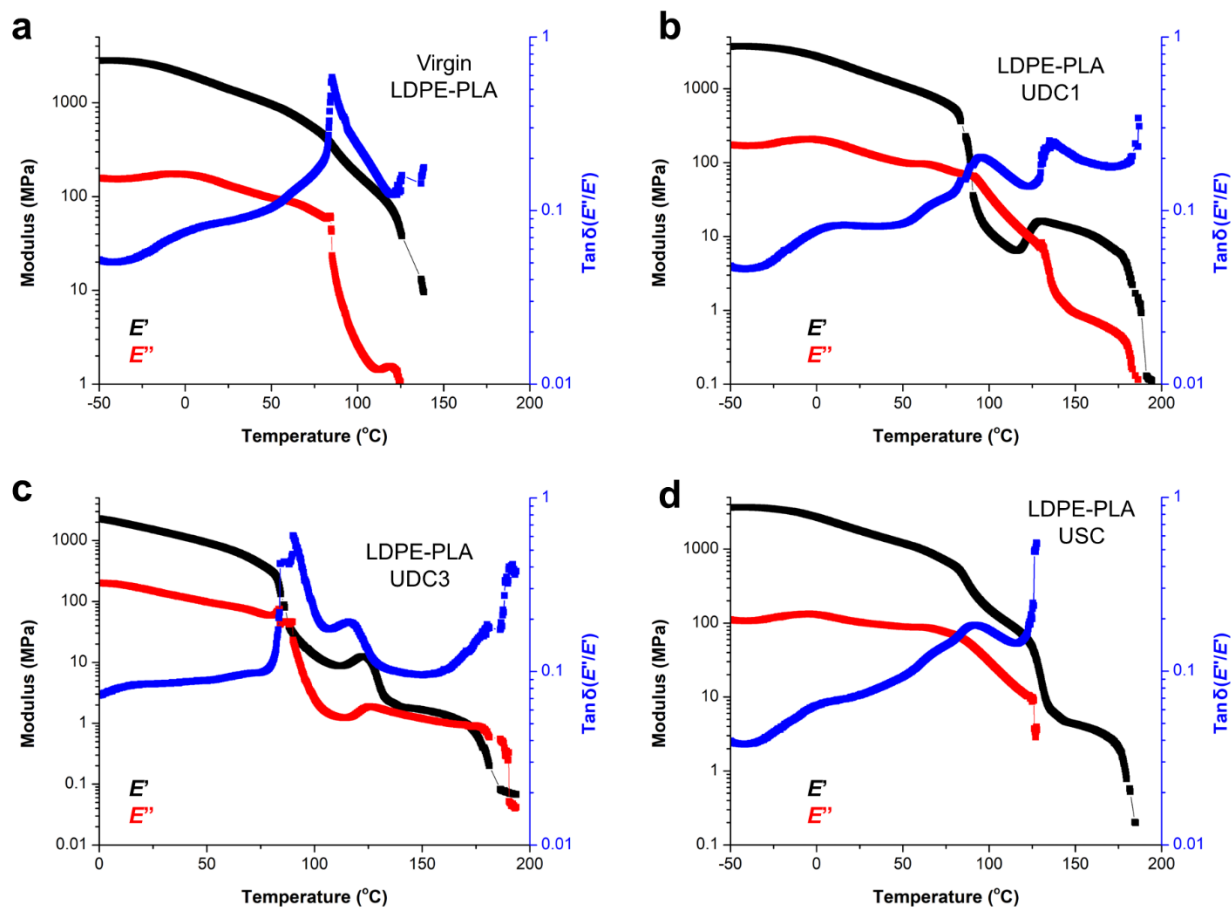


Figure S67. Representative DMA temperature-ramp frequency-sweeps for blends of LDPE-PLLA **a**, virgin, **b**, with 5 wt.% UDC1, **c**, with 5 wt.% UDC3, and **d**, with 5 wt.% USC (-50 to 200 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).

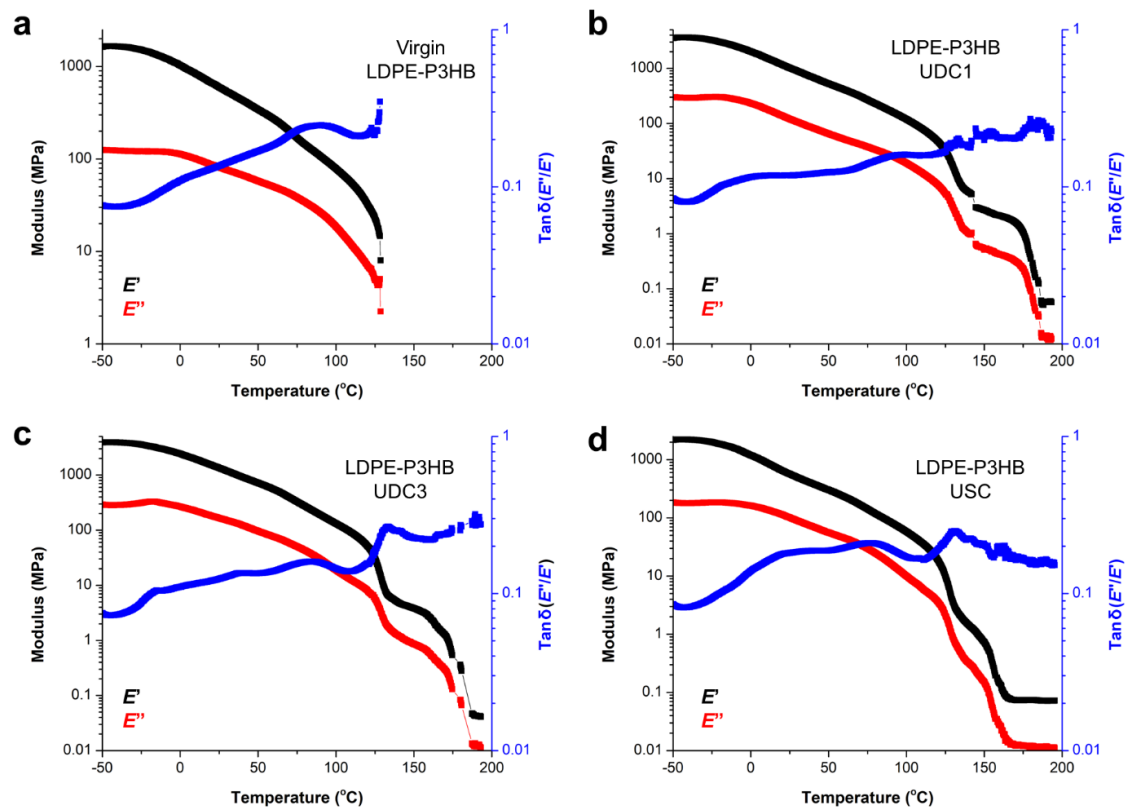


Figure S68. Representative DMA temperature-ramp frequency-sweeps for blends of LDPE-P3HB **a**, virgin, **b**, with 5 wt.% UDC1, **c**, with 5 wt.% UDC3, and **d**, with 5 wt.% USC (-50 to 200 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).

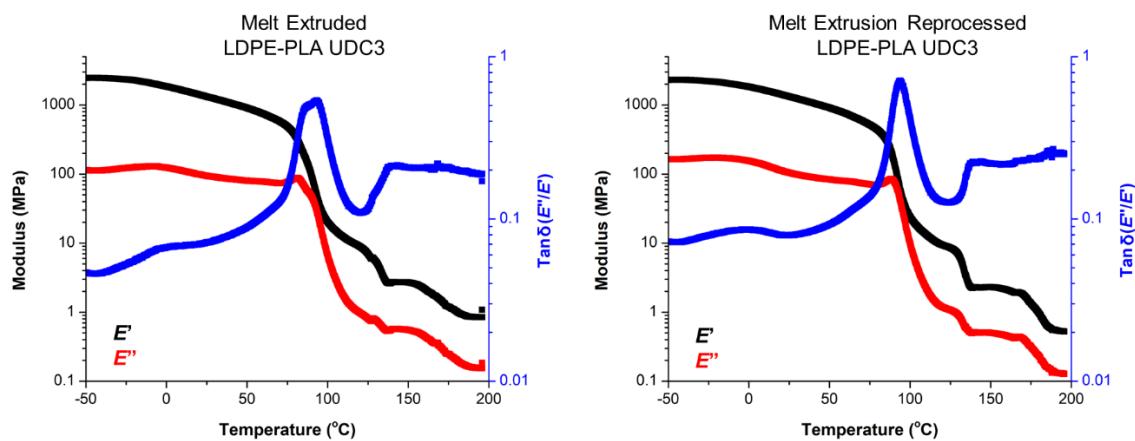


Figure S69. Representative DMA temperature-ramp frequency-sweep for blends of LDPE-PLA with 5 wt.% UDC3 prepared by reactive melt extrusion (left) and the reprocessed cycle by melt extrusion (right) (-50 to 200 °C or failure, 5 °C/min, 0.3 % strain, 1 Hz).

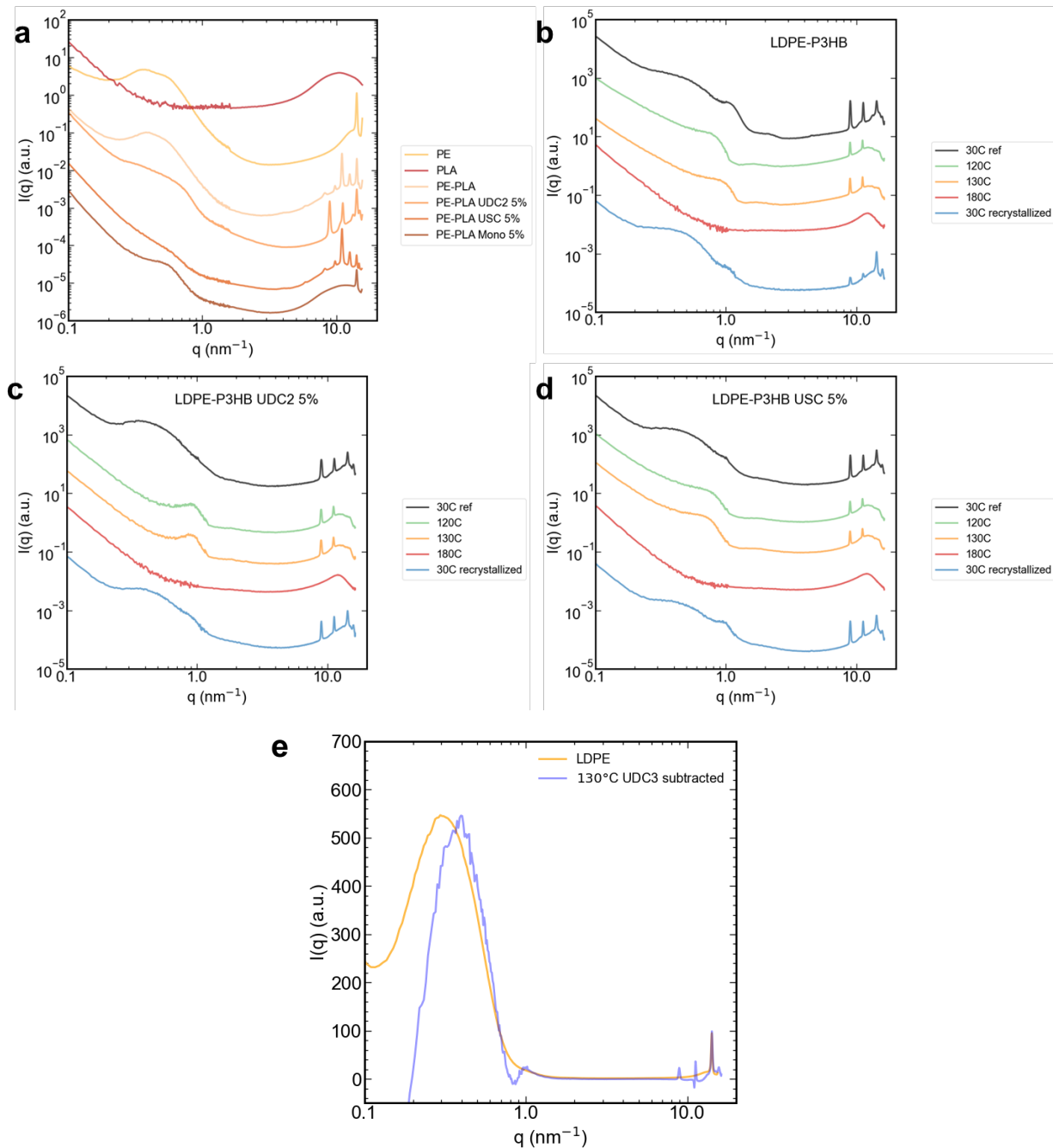


Figure S70. Additional SAXS/WAXS Curves. **a**, SAXS/WAXS comparison curves for cross-linked PE-PLA blends relative to virgin blend and reference homopolymers. **b**, Effect of temperatures above the component T_m s on domain-averaged combination SAXS/WAXS curves for non-cross-linked LDPE-P3HB blend. **c**, Effect of temperatures above the component T_m s on domain-averaged combination SAXS/WAXS curves for UDC2 compatibilised LDPE-P3HB blend. **d**, Effect of temperatures above the component T_m s on domain-averaged combination SAXS/WAXS curves for USC compatibilised LDPE-P3HB blend. **e**, SAXS/WAXS pattern of P3HB subtracted from LDPE-P3HB compatibilised UDC3 blend heated to 130 °C; determination of structure of the melted component (i.e., LDPE). LDPE at 30 °C given as reference.

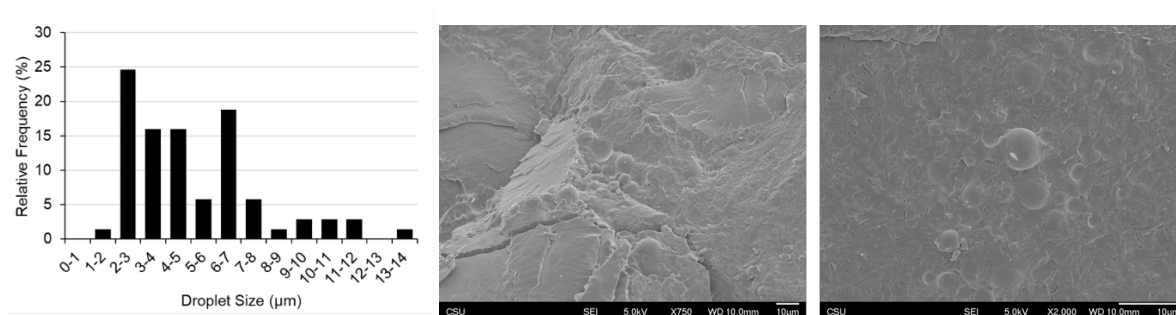


Figure S71. Additional cross-section SEM images of the virgin LDPE-P3HB blend with cross-section droplet diameter size analysis.

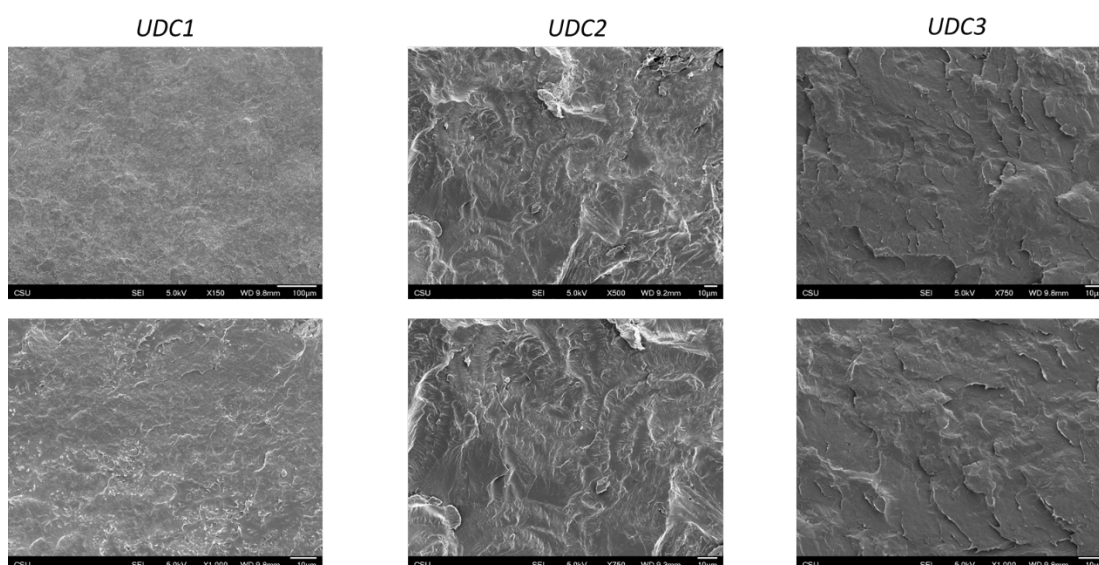


Figure S72. Additional cross-section SEM images of LDPE-P3HB blends compatibilised with UDCs 1 (left), 2 (middle), and 3 (right).

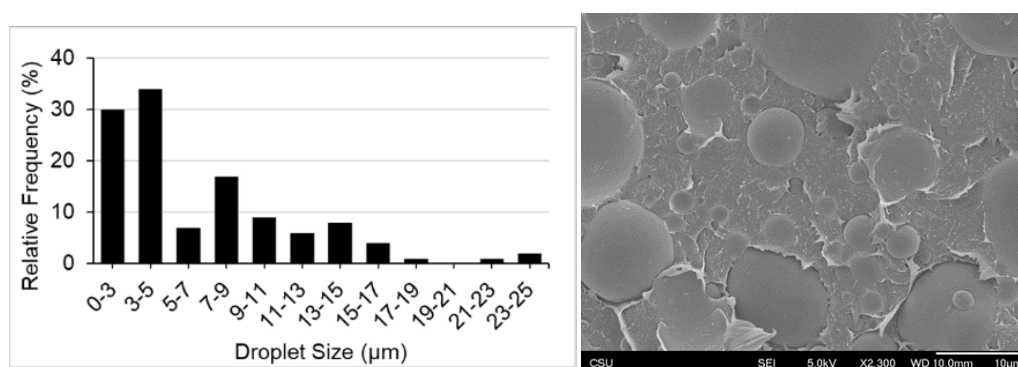


Figure S73. Additional cross-section SEM images of the virgin LDPE-PLLA blend with cross-section droplet diameter size analysis.

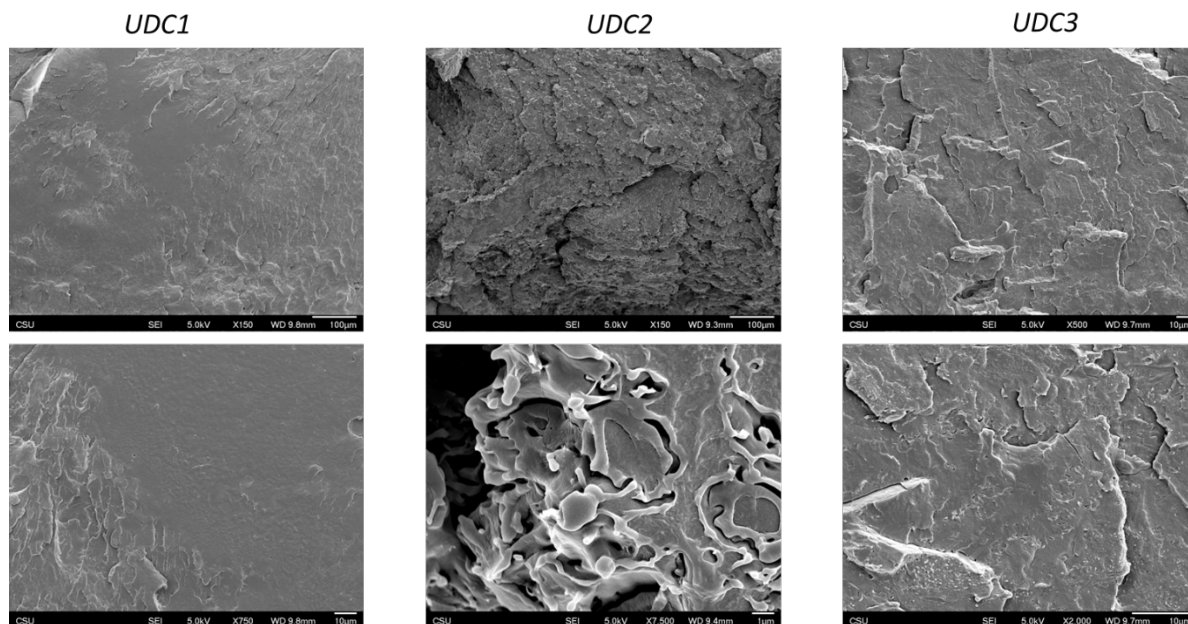


Figure S74. Additional cross-section SEM images of LDPE-PLLA blends compatibilised with UDCs 1 (left), 2 (middle), and 3 (right).

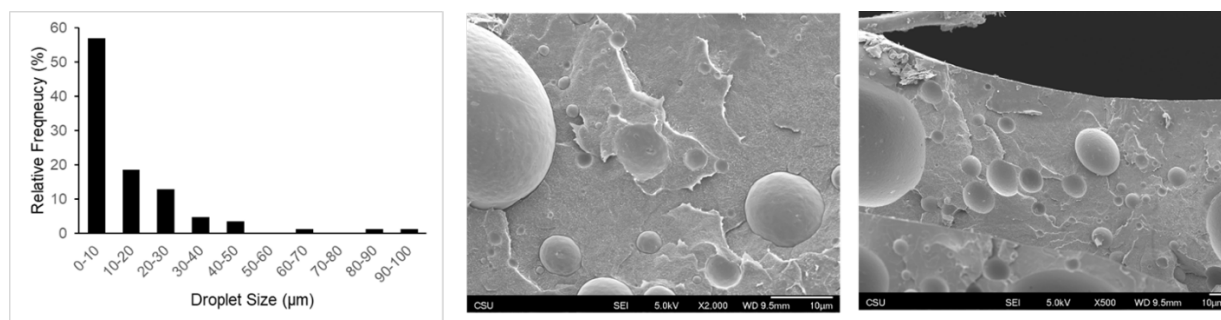


Figure S75. Additional cross-section SEM images of the virgin post-consumer LDPE-PLLA blend with cross-section droplet diameter size analysis.

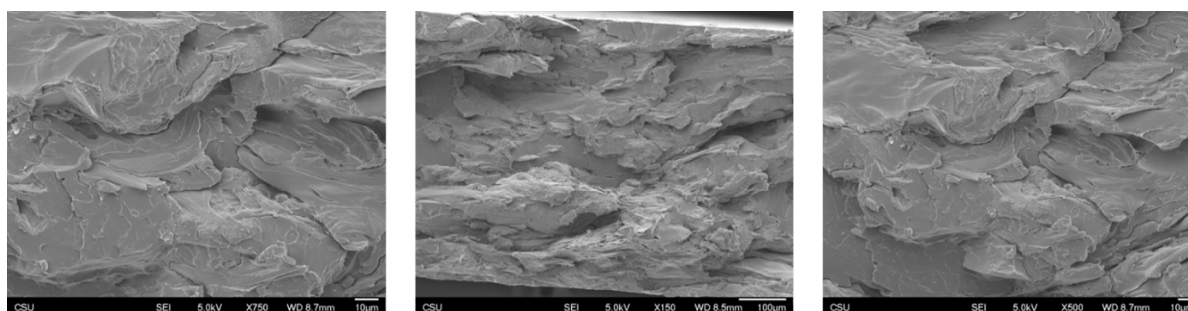


Figure S76. Additional cross-section SEM images of the post-consumer LDPE-PLLA blends compatibilised with UDC3.

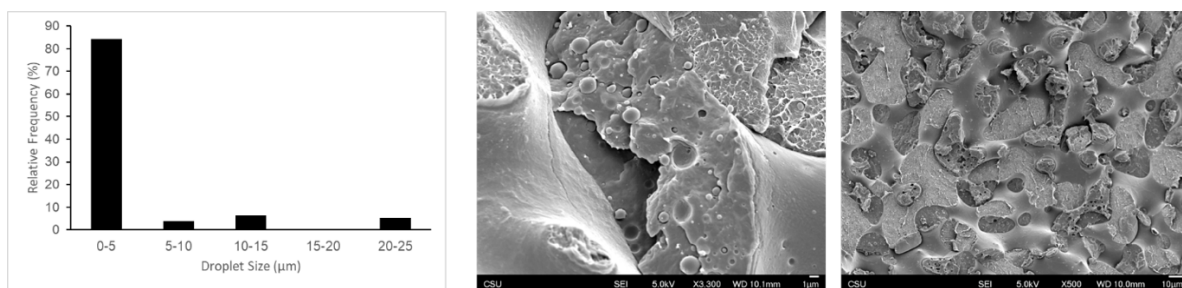


Figure S77. Additional cross-section SEM images of the virgin LDPE-*i*PP blend with cross-section droplet diameter size analysis.

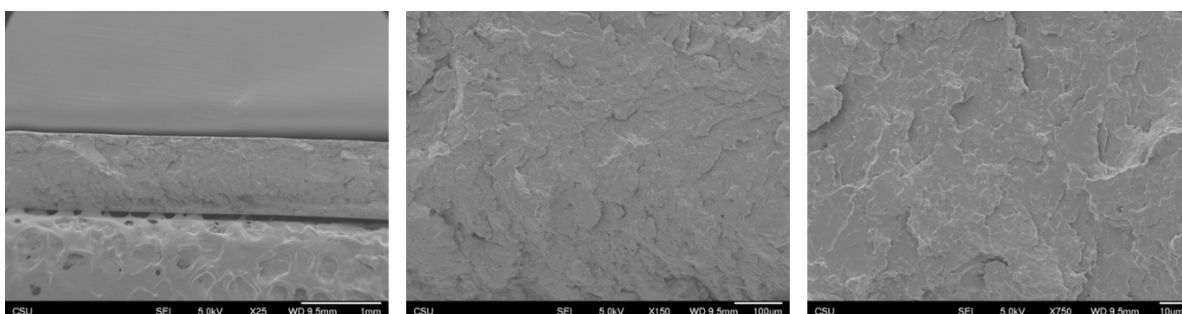


Figure S78. Additional cross-section SEM images of the LDPE-*i*PP blends compatibilised with UDC3.

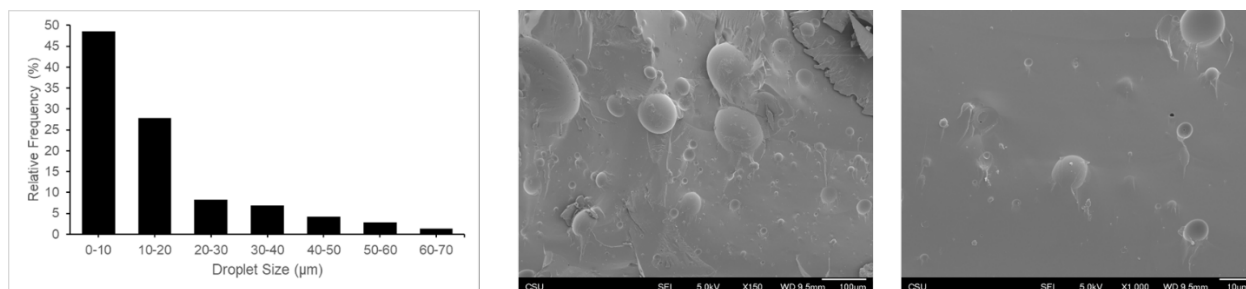


Figure S79. Additional cross-section SEM images of the virgin PS-PLLA blend with cross-section droplet diameter size analysis.

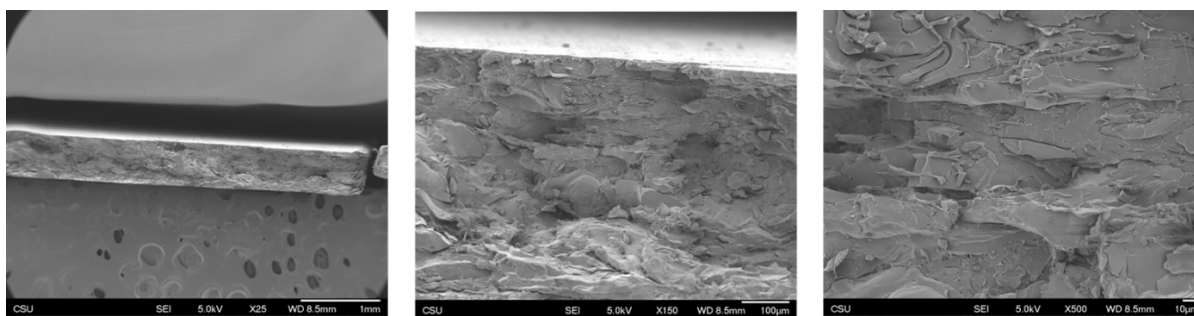


Figure S80. Additional cross-section SEM images of the PS-PLLA blends compatibilised with UDC3.

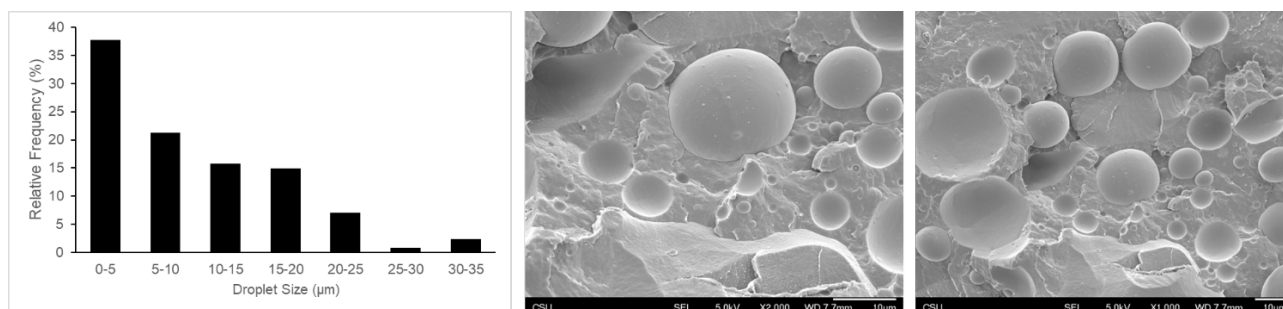


Figure S81. Additional cross-section SEM images of the virgin LDPE-*i*PP-PLLA ternary blend with cross-section droplet diameter size analysis.

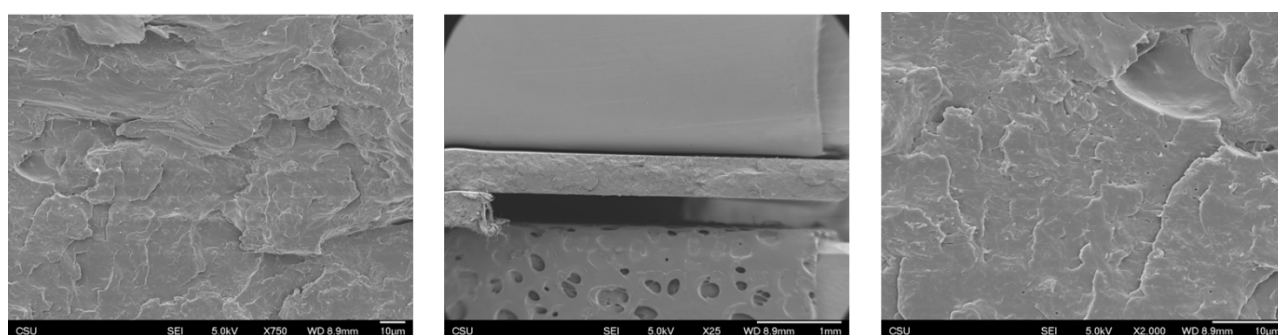
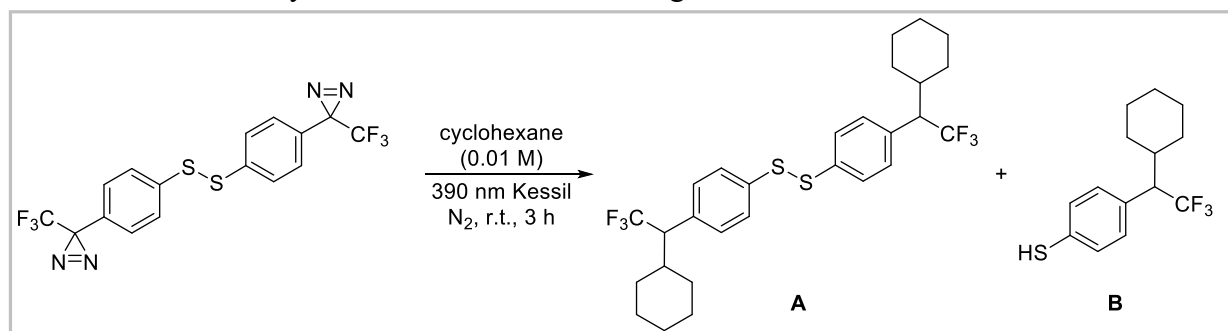


Figure S82. Additional cross-section SEM images of the LDPE-*i*PP-PLLA ternary blend compatibilised with UDC3.

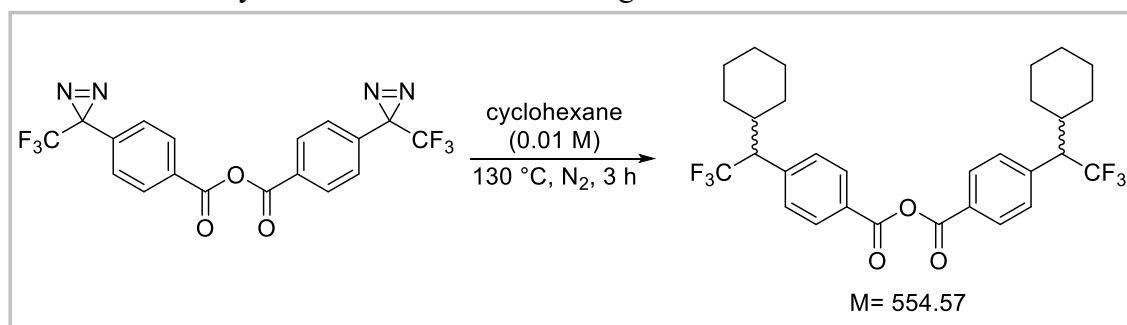
Supplementary Tables

Table S1. Tabulated cyclohexane insertion screening under varied conditions for UDC2.



Entry	Deviation from standard conditions	Yield A ^a	Yield B ^a
1	none	15%	3%
2	370 nm Kessil lamp	12%	2%
3	air	11%	traces
4	H ₂ O (2.0 equiv)	15%	4%
5	O ₂ atmosphere	traces	n.d.
6	130 °C in the dark	39%	traces
7	130 °C in the dark + air	33%	n.d.
8	130 °C in the dark + H ₂ O (15.0 equiv)	38%	n.d.
9	130 °C in the dark, O ₂ atmosphere	14%	n.d.

Reactions run on 0.04 mmol scale. n.d. = not detected. (a) Yields were determined by ¹H-NMR spectroscopy of crude reaction mixtures using 1,4-dinitrobenzene as an internal standard.

Table S2. Tabulated cyclohexane insertion screening under varied conditions for UDC3.

Entry	Deviation from standard conditions	Yield ^a
1	none	53%
2	air	51%
3	H ₂ O (5.0 equiv)	49%
4	390 nm Kessil lamp	29%

Reactions run on 0.02 mmol scale. (a) Yields were determined by ¹H-NMR spectroscopy of crude reaction mixtures using 1,4-dinitrobenzene as an internal standard.

Table S3. Evolution of thermal transitions in LMWPE with varied UDC loading.

Polymer	<i>T_m</i> (°C)	ΔH_f (J/g)
LMWPE 0%	105	103
LMWPE 5% UDC1	104	88.9
LMWPE 10% UDC1	98.6	62.6
LMWPE 5% UDC2	104	85.8
LMWPE 10% UDC2	91.5	74.4
LMWPE 5% UDC3	105	92.1
LMWPE 10% UDC3	104	84.1

Table S4. Evolution of thermal transitions in LDPE with varied UDC loading.

Polymer	T_m (°C)	ΔH_f (J/g)
LDPE 0%	110	127
LDPE-UDC1 5%	103	97.6
LDPE-UDC1 10%	99.0	88.3
LDPE-UDC3 5%	107	98.2
LDPE-UDC3 10%	101	95.8

Table S5. Evolution of thermal transitions in HDPE with varied UDC loading.

Polymer	T_m (°C)	ΔH_f (J/g)
HDPE 0%	132	127
HDPE-UDC1 5%	132	194
HDPE-UDC1 10%	122	138
HDPE-UDC3 5%	129	187
HDPE-UDC3 10%	123	147

Table S6. Evolution of thermal transitions in UHMWPE with varied UDC loading.

Polymer	T_m (°C)	ΔH_f (J/g)
HMWPE 0%	133	150
HMWPE-UDC1 5%	114	118
HMWPE-UDC1 10%	114	114
HMWPE-UDC3 5%	130	141
HMWPE-UDC3 10%	123	118

Table S7. Evolution of thermal transitions in *it*-PP with varied UDC loading.

Polymer	T_m (°C)	ΔH_f (J/g)
<i>it</i> -PP 0%	162	88.0
<i>it</i> -PPUDC1 5%	156	76.7
<i>it</i> -PPUDC1 10%	149	60.4
<i>it</i> -PPUDC3 5%	156	79.6
<i>it</i> -PPUDC3 10%	156	71.8

Table S8. Evolution of thermal transitions in PLA with varied UDC loading.

Polymer	T_m (°C)	ΔH_f (J/g)	T_g (°C)
PLA 0%	173	47.2	56.1
PLA-UDC1 5%	166	37.1	55.2
PLA-UDC1 10%	156	28.3	58.1
PLA-UDC3 5%	163	23.3	61.8
PLA-UDC3 10%	160	4.3	63.5

Table S9. Evolution of thermal transitions in P3HB with varied UDC loading.

Polymer	T_m (°C)	ΔH_f (J/g)	T_g (°C)
P3HB 0%	171	89.0	5.9
P3HB-UDC1 5%	166	87.2	0.4
P3HB-UDC1 10%	161	72.6	1.1
P3HB-UDC3 5%	165	79.8	4.3
P3HB-UDC3 10%	159	72.4	4.2

Table S10. Temperature-ramp frequency sweep results for virgin and UDC-treated LDPE/HDPE samples (0.3 % strain, 1 Hz, -50 to 200 °C, 5 °C/min).

Polymer	E'_{RT} (MPa)	E'_{max} (MPa)
LDPE 0 %	784 ± 149	2531 ± 208
LDPE 5 % UDC1	730 ± 92	3055 ± 157
LDPE 5 % UDC3	977 ± 110	3198 ± 12
HDPE 0 %	2990 ± 74	3818 ± 138
HDPE 5 % UDC1	2840 ± 105	3941 ± 72
HDPE 5 % UDC3	3127 ± 158	4224 ± 188

Table S11. Tensile stress/strain data for each reported LDPE-UDC and LDPE-USC sample, along with reprocessing trial data.

Polymer	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
LDPE	10.5 ± 0.1	113 ± 5.8	345 ± 14	12.4 ± 0.7
LDPE 5 % UDC3	13 ± 0.4	116 ± 4.0	245 ± 3.0	12.7 ± 0.6
LDPE 5 % UDC3 R1	12 ± 0.4	91 ± 6.6	166 ± 16	8.9 ± 0.5
LDPE 5 % USC	8.9 ± 1.0	38 ± 12	166 ± 10	2.8 ± 1.1
LDPE 5 % USC R1	7.5 ± 0.5	16 ± 3.7	160 ± 6.4	1.0 ± 0.3

Table S12. Creep-recovery data for virgin and UDC-treated LDPE and HDPE by DMA, in tension film mode, below the melt thermal transition (40 – 110 °C, 2 MPa, 5 °C/min 600 s or 4 h as specified creep duration, 300 s or 0.5 h as specified recovery time).

Sample	Temperature (°C)	Creep/Recovery (min)	Creep (%)	Recovered (%)
LDPE (MFI 21)	80	10/5	26.5	19.1
HDPE (MFI 7.6)	110	10/5	7.4	4.7
HDPE (MFI 7.6)	40	240/30	2.8	0.4
LDPE UDC1 5%	80	10/5	12.4	11.7
LDPE UDC3 5%	80	10/5	9.0	8.1
HDPE UDC1 5%	110	10/5	4.8	4.2
HDPE UDC3 5%	110	10/5	5.7	5.1
HDPE UDC1 5%	40	240/30	1.8	1.3
HDPE UDC3 5%	40	240/30	1.5	1.3

Table S13. Creep-recovery data for virgin, USC-, and UDC-treated LDPE and HDPE by bulk shear rheology in the flow-state (130 – 160 °C, 10 min creep, 5 min recovery, 2.5 kPa).

Sample	Temperature (°C)	Creep (%)	Recovered (%)
LDPE (MFI 21)	130	90877	112
HDPE (MFI 7.6)	150	77681	28
LDPE UDC1 5%	130	53 ± 8.0	22 ± 1.1
LDPE UDC1 5%	140	103 ± 7.5	66 ± 0.6
LDPE UDC3 5%	130	89 ± 34	41 ± 1.2
LDPE UDC3 5%	140	190 ± 33	40 ± 1.6
HDPE UDC1 5%	150	411 ± 16	25 ± 0.3
HDPE UDC1 5%	160	610 ± 20	31 ± 1.4
HDPE UDC3 5%	150	521 ± 25	73 ± 14
HDPE UDC3 5%	160	808 ± 19	207 ± 7.5
LDPE USC 5%	130	24 ± 1.6	21 ± 1.1

Table S14. Rheological high-temperature frequency sweeps: rubbery plateau storage moduli (G') and crosslinking density (C_x) (130-160 °C, 0.1 % shear strain, 0.5 to 5 rad/s).

Sample	Temperature (°C)	G' (Pa)
LDPE UDC1 5%	130	23185 ± 646
LDPE UDC1 5%	140	23377 ± 208
LDPE UDC1 5%	150	23226 ± 307
LDPE UDC1 5%	160	23381 ± 32
LDPE UDC3 5%	130	11027 ± 61
LDPE UDC3 5%	140	10433 ± 144
LDPE UDC3 5%	150	9173 ± 42
LDPE UDC3 5%	160	8293 ± 61

Table S15. Baseline thermal transition and crystallinity data for homopolymers advanced to dynamic blending (-50 to 200 °C, 10 °C/min heat/cool ramp).

Polymer	T_m °C	ΔH_f (J/g)	T_g (°C)	% X_c
LMWPE	105	55.4	-	18.9
LDPE	110	127	-	43.2
P3HB	171	89.0	5.9	61.4
PLA	173	47.2	58.0	50.6

Table S16. LMWPE-PLA blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

Sample	T_m LMWPE (°C)	ΔH_f LMWPE (J/g)	X_c (%)	T_m PLA (°C)	ΔH_f PLA (J/g)	X_c (%)	T_g PLA (°C)
LMWPE-PLA 0%	108	20.2	6.6	171	28.8	29.3	59.0
LMWPE-PLA 5% UDC1	99.9	18.5	6.0	167	20.8	21.1	58.0
LMWPE-PLA 5% UDC2	91.4	8.8	2.9	169	27.1	27.5	59.2
LMWPE-PLA 5% UDC3	105	25.8	8.4	164	15.3	15.5	56.3
LMWPE-PLA 5% USC	100	31.0	10.1	168	17.9	18.2	58.0

Table S17. LMWPE-P3HB blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

Sample	T_m LMWPE (°C)	ΔH_f LMWPE (J/g)	X_c (%)	T_m P3HB (°C)	ΔH_f P3HB (J/g)	X_c (%)	T_g P3HB (°C)
LMWPE-P3HB 0%	105	25.2	8.2	175	35.9	23.6	-
LMWPE-P3HB 5% UDC1	101	15.8	5.1	161	32.2	21.1	1.6
LMWPE-P3HB 5% UDC2	104	16.3	5.3	168	31.9	20.9	3.4
LMWPE-P3HB 5% UDC3	103	19.1	6.2	161	36.7	24.0	3.0
LMWPE-P3HB 5% USC	100	12.2	4.0	139	19.9	13.1	-

Table S18. LDPE-PLA blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

Sample	T_m LDPE (°C)	ΔH_f LDPE (J/g)	X_c (%)	T_m PLA (°C)	ΔH_f PLA (J/g)	X_c (%)	T_g PLA (°C)
LDPE-PLA 0%	108	15.3	4.9	170	27.3	27.7	59.3
LDPE-PLA 5% UDC1	102	16.8	5.4	168	13.9	14.2	58.7
LDPE-PLA 5% UDC2	107	13.5	4.4	169	22.4	22.7	60.9
LDPE-PLA 5% UDC3	105	14.0	4.6	165	12.8	13.0	59.3
LDPE-PLA 5% USC	105	19.3	6.3	165	18.6	18.9	60.0

Table S19. LDPE-P3HB blend thermal transition and crystallinity profiles at virgin and UDC or USC incorporation stage (-50 to 200 °C, 10 °C/min heat/cool ramp).

Sample	T_m LDPE (°C)	ΔH_f LDPE (J/g)	X_c (%)	T_m P3HB (°C)	ΔH_f P3HB (J/g)	X_c (%)
LDPE-P3HB 0%	110	24.0	7.8	170	33.7	22.1
LDPE-P3HB 5% UDC1	103	17.0	5.4	166	26.5	17.4
LDPE-P3HB 5% UDC2	103	30.0	9.7	157	15.5	10.2
LDPE-P3HB 5% UDC3	105	24.8	8.1	163	30.1	19.8
LDPE-P3HB 5% USC	103	31.6	10.3	137	20.7	13.6

Table S20. Tabulated maximum storage modulus values (-50 °C) for LDPE-PLA/P3HB blends at virgin and with UDC or USC incorporation (0.3 % strain, 1 Hz, -50 – 200 °C, 5 °C/min).

LDPE-P3HB Blend	$E'_{\max}$ (-50 °C, MPa)
0%	1635 ± 14
5% UDC1	3535 ± 45
5% UDC3	2883.9 ± 11.2
5% USC	2179 ± 856
LDPE-PLA Blend	$E'_{\max}$ (-50 °C, MPa)
0%	2795 ± 91
5% UDC1	3714 ± 148
5% UDC3	3008 ± 79
5% USC	3634 ± 187
Extruded LDPE-PLA Blend	$E'_{\max}$ (-50 °C, MPa)
1 st Cycle	2458 ± 229
Reprocessed 2 nd Cycle	2312 ± 68

Table S21. Tabulated maximum storage modulus values (-50 °C) for blends of LDPE-PLA/P3HB at virgin and with UDC/USC incorporation by extrusion (0.3 %, 1 Hz, -50 – 200 °C, 5 °C/min).

Polymer	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJ m ⁻³)
LDPE-PLA	5.6 ± 0.7	1.9 ± 0.8	1100 ± 87	0.04 ± 0.2
LDPE-PLA 5 % UDC3	17 ± 2.6	3.0 ± 1.0	978 ± 18	0.34 ± 0.2
LDPE-PLA 5 % UDC3 R1	19.4 ± 0.6	5.1 ± 0.5	1003 ± 34	0.74 ± 0.1

Table S22. Average diameter (micrometers) and median diameter (micrometers) for droplets imaged within the cross-sections of LMWPE-PLA/P3HB binary blends both of virgin quality and once crosslinked with UDCs 1-3, USC, or functionalized with MDC as described (10 micrometers gold, 3 kV).

Blend Sample	Average Diameter (μm)	Median Diameter (μm)	Notes
Virgin PE-PLA	29 ± 11	29	Minority smaller droplets also found
PE-PLA UDC2	-	-	No droplets found
PE-PLA USC	2.1 ± 0.9	2.0	Minority larger droplets also found
PE-PLA MDC	45 ± 23	43	Minority smaller droplets also found
Virgin PE-P3HB	32 ± 13	25	Minority smaller droplets also found
PE-P3HB UDC1	2.8 ± 1.4	2.7	Low droplet population
PE-P3HB UDC2	-	-	No droplets found
PE-P3HB UDC3	-	-	No droplets found
PE-P3HB USC	1.6 ± 0.7	1.8	Minority smaller droplets also found
PE-P3HB MDC	48 ± 17	47	Minority larger droplets also found

Table S23. Average diameter (micrometers) for droplets imaged within the cross-sections of blends both of virgin quality and once crosslinked with UDCs 1-3 as described (10 micrometers gold, 3 kV).

Blend	Average Diameter (μm)
LDPE-PLLA	6.6 ± 4.8
PE-PLLA UDC1	-
PE-PLLA UDC2	-
PE-PLLA UDC3	-
Post-Consumer LDPE-PLLA	17.5 ± 26.5
Post-Consumer LDPE-PLLA UDC3	-
LDPE-P3HB	5.1 ± 2.6
PE-P3HB UDC1	-
PE-P3HB UDC2	-
PE-P3HB UDC3	-
LDPE- <i>i</i> PP	3.5 ± 5.4
PE- <i>i</i> PP UDC3	-
PS-PLLA	18.3 ± 20.4
PS-PLLA UDC3	-
LDPE- <i>i</i> PP-PLLA	10.3 ± 8.3
LDPE- <i>i</i> PP-PLLA UDC3	-

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