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Supplementary Information

Janus faced fluorocyclohexanes for supramolecular assembly: Synthesis and solid state structures of equatorial mono-, di- and tri alkylated cyclohexanes and with tri-axial C-F bonds to impart polarity

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1 Analytical Instrumentation supporting synthesis

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. Dry hexane was obtained from SPS in house (4Å), and dry methanol from Sigma-Aldrich.

Hydrogenation reactions at elevated pressure were carried out in stainless steel autoclaves using hydrogen gas. Commercially available chemicals were obtained from Acros, Alfa Aeser, Fluorochem, Sigma Aldrich, TCI (UK) and used as received unless otherwise stated. Degassing methodology achieved by bubbling nitrogen through the reagents via syringe for 20-40 min.

Analytical thin layer chromatography was performed on pre-coated aluminium plates (Kieselgel 60 F254 silica) and visualisation was achieved using ultraviolet light (254 nm) and/or staining with aqueous $KMnO_4$ solution followed by heating. Flash column chromatography was performed in glass columns fitted with porosity 3 sintered discs over Kieselgel 60 silica using the solvent system stated. Automated chromatography was performed on a Biotage Selekt 2 system with a UV/Vis detector using the method stated and cartridges filled with Kieselgel 60 silica.

Melting points were recorded on an Electrothermal 9100 melting point apparatus and (dec) refers to decomposition.

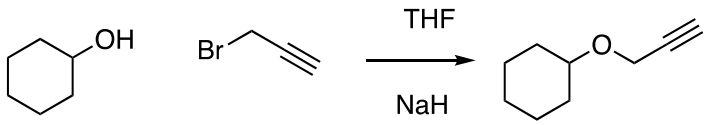
Ir were recorded on a Shimadzu IRAffinity-1 Fourier transform IR spectrophotometer fitted with a Specac Quest ATR accessory (diamond puck). Spectra were recorded of either thin films or solids, with characteristic absorption wavenumbers (ν_{max}) reported in cm^{-1}.

^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were acquired on either a Bruker AVII 400 with a BBFO probe (^{1}H 400 MHz; $^{13}C\{^{1}H\}$ 101 MHz; $^{19}F\{^{1}H\}$ 376 MHz), a Bruker AVIII-HD 500 with a SmartProbe BBFO+ probe (^{1}H 500 MHz, $^{13}C\{^{1}H\}$ 126 MHz, $^{19}F\{^{1}H\}$ 470 MHz) or a Bruker AVIII 500 with a CryoProbe Prodigy BBO probe (^{1}H 500 MHz, $^{13}C\{^{1}H\}$ 126 MHz, $^{19}F\{^{1}H\}$ 470 MHz) in the deuterated solvent stated. All chemical shifts are quoted in parts per million (ppm) relative to the residual solvent peak. All coupling constants, J, are quoted in Hz. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and multiples thereof. The abbreviation Ar denotes aromatic and app denotes apparent. NMR peak assignments were confirmed using 2D ^{1}H correlated spectroscopy (COSY), 2D ^{1}H nuclear Overhauser effect spectroscopy (NOESY), 2D ^{1}H–^{13}C heteronuclear multiple-bond correlation spectroscopy (HMBC), and 2D ^{1}H–^{13}C heteronuclear single quantum coherence (HSQC) where necessary.

Mass spectrometry (m/z) data were acquired by either electrospray ionisation (ESI), chemical ionisation (CI), electron impact (EI), atmospheric solids analysis probe (ASAP), atmospheric pressure chemical ionization (APCI) or nanospray ionisation (NSI).

2. Synthesis methods and product characterization

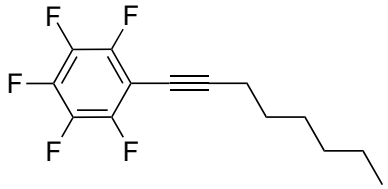
(Prop-2-yn-1-yloxy)cyclohexane



NaH (2.4 g, 60.0 mmol, 60 wt% in mineral oil) was slowly added into a solution of cyclohexanol (5 ml, 48 mmol) in 100 ml THF at 0 °C. After stirring for 5 minutes at 0 °C, propargyl bromide (80 wt% in toluene, 4.5 mL, 48 mmol) was added to the mixture and the solution was left to warm to room temperature. After 3 hours the reaction was quenched with saturated aqueous NH_4Cl (30 mL), followed by extraction with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (25 mL) then the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The resulting yellow liquid was purified by flash chromatography (0—5% diethyl ether in hexane) yielding title compound as a yellow oil with spectroscopic data in accordance with the literature,[1] (33%, 2.195 g, 15.88 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.17 (d, J = 2.4 Hz, 2H, C≡CC<u>H</u>$_2$), 3.46 (dp, J = 8.8, 3.7 Hz, 1H, cyclo-C<u>H</u>), 2.38 (t, J = 2.4 Hz, 1H, <u>H</u>C≡C), 1.93-1.88 (m, 2H), 1.74-1.73 (m, 2H), 1.55-1.53 (m, 1H), 1.33-1.19 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 80.7 (HC≡<u>C</u>CH$_2$), 76.7 (H<u>C</u>≡CCH$_2$), 73.7 (cyclo-<u>C</u>H), 55.0 (HC≡C<u>C</u>H$_2$), 32.0 (2xortho-<u>C</u>H$_2$), 25.8 (para-<u>C</u>H$_2$), 24.2 (2xmeta-<u>C</u>H$_2$).

1,2,3,4,5-Pentafluoro-6-(octynyl)benzene 6

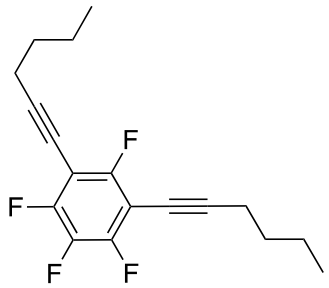


1,2,3,4,5-Pentafluoro-6-iodobenzene (0.33 ml, 2.5 mmol), 1-octyne (0.44 ml, 3 mmol), palladium catalyst (0.2632 g, 0.375 mmol), and copper (I) iodide (0.0714 g, 0.375 mmol) were all added to a 100 ml RBF. Diisopropylamine (25 ml) was then added, and the reaction mixture was heated to 80 ˚C under argon and stirred for 22 hours. The reaction mixture was then cooled to room temperature and slowly passed through a pad of silica gel with an elusion of ethyl acetate. The solvent was removed via concentration *in vacuo*, and then purified via flash chromatography (pentane) to afford **6** as a colourless oil (65%, 0.23 g, 0.82 mmol).

IR ν_{max} (film): 2930 (sp^2 C-H stretch), 2860 (sp^3 C-H stretch), 2247 (C≡C stretch), 1518 (aromatic C=C stretch), 1468 (sp^3 C-H bend) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.49 (t, J = 7.1 Hz, 2H,

C≡CC$\underline{H_2}$), 1.63 (app. quint., J = 7.2 Hz, 2H, C≡CCH$_2$C$\underline{H_2}$), 1.39-1.24 (m, 6H, C≡CCH$_2$CH$_2$C$\underline{H_2}$C$\underline{H_2}$C$\underline{H_2}$), 0.90 (m, 3H, C$\underline{H_3}$); ^{19}F{^{1}H} 470 MHz, CDCl3) δ : -137.3 (m, 2F), -154.5 (t, J = 20.8 Hz, 1F), -162.5 (td, J = 21.9 and 6.7 Hz, 2F); ^{13}C NMR (126 MHz, CDCl3) δ : 147.6 (d, J = 266.2 Hz, Ar-$\underline{C}$F), 141.1 (d, J = 256.0 Hz, Ar-$\underline{C}$F), 137.8 (d, J = 274.6 Hz, Ar-CF), 104.3 (Ar-$\underline{C}$C≡C), 65.4 (C≡$\underline{C}$CH$_2$), 64.8 ($\underline{C}$≡CH$_2$), 31.4 ($\underline{C}$H$_2$CH$_2$CH$_3$), 28.5 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 22.7 (C≡CCH$_2$$\underline{C}H_2$), 19.9 ($\underline{C}H_2CH_3$), 19.4 (C≡C$\underline{C}H_2$), 14.2 ($\underline{C}H_3$); HRMS (EI) $C_{14}H_{13}F_5$ [M] found 276.0932, requires 276.0937.

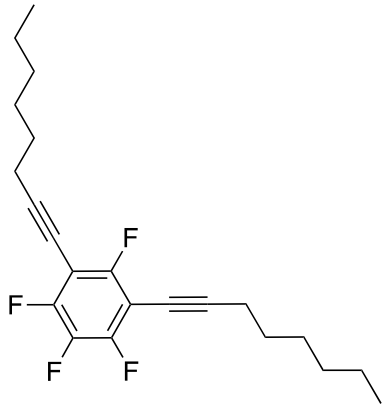
1,2,3,5-Tetrafluoro-4,6-di(1-hexynyl)benzene 10a



1,2,3,5-Tetrafluoro-4,6-diiodobenzene (1.01 g, 2.5 mmol), 1-hexyne (0.69 mL, 6 mmol), palladium catalyst (0.263 g, 0.375 mmol), and copper (I) iodide (0.071 g, 0.375 mmol) were all added to a 100 mL RBF. Diisopropylamine (25 mL) was then added, and the reaction mixture was heated to 80 °C under argon and stirred for 22 hours. The reaction mixture was then cooled to room temperature and slowly passed through a 3 cm pad of silica gel, eluting with ethyl acetate. The solvent was removed via concentration *in vacuo*, and then purified via flash chromatography (pentane), care was taken to separate hexyne from final product to afford **10a** as an oil (89%, 0.66 g, 2.12 mmol).

IR ν_{max} (film): 2958 (sp^2 C-H stretch), 2933 (sp^3 C-H stretch), 2243 (C≡C stretch), 1627 (aromatic C=C stretch), 1500 (sp^3 C-H bend) cm^{-1}; ^{1}H ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.48 (t, J = 7.0 Hz, 4H, C≡CC$\underline{H_2}$), 1.61 (p, J = 7.1 Hz, 4H, C≡CCH$_2$C$\underline{H_2}$), 1.41 (m, 4H, C$\underline{H_2}$CH$_3$), 0.95 (t, J = 7.3 Hz, 6H, C$\underline{H_3}$); ^{19}F NMR (470 MHz, $CDCl_3$) δ : -110.5 (d, J = 10.1 Hz, 1F), -130.4 (d, J = 21.6 Hz, 2F), -164.5 (td, J = 21.6, 10.1 Hz, 1F); ^{13}C NMR (126 MHz, $CDCl_3$) δ : 158.6 (d, J = 253.0 Hz, Ar-$\underline{C}$F), 150.9 (d, J = 252.5 Hz, Ar-$\underline{C}$F, 2C), 137.3 (d, J = 244.1 Hz, Ar-$\underline{C}$F), 102.7 (Ar-$\underline{C}$C), 100.4 (C≡$\underline{C}$CH$_2$), 65.5 ($\underline{C}$≡CCH$_2$), 30.5 ($\underline{C}$H$_2$CH$_2$CH$_3$), 22.0 ($\underline{C}$H$_2$CH$_3$), 19.3 (C≡C$\underline{C}$H$_2$), 13.7 ($\underline{C}$H$_3$); HRMS (EI) calculated for $C_{18}H_{18}F_4$ [M]$^+$ 309.1261, requires 309.1265.

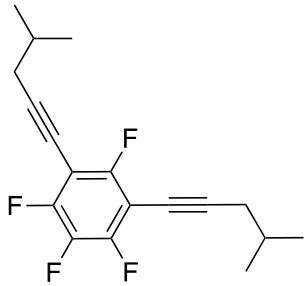
1,2,3,5-Tetrafluoro-4,6-(dioctynyl)benzene 10b



1,2,3,5-Tetrafluoro-4,6-diiodobenzene (1.01 g, 2.5 mmol), 1-octyne (0.89 ml, 6 mmol), palladium catalyst (0.263 g, 0.375 mmol), and copper (I) iodide (0.071 g, 0.375 mmol) were all added to a 100 ml RBF. Diisopropylamine (25 mL) was then added, and the reaction mixture was heated to 80 ˚C under argon and stirred for 22 hours. The reaction mixture was then cooled to room temperature and slowly passed through a 3 cm pad of silica gel, with an elusion of ethyl acetate. The solvent was removed via concentration *in vacuo*, and then purified via flash chromatography (pentane), care was taken to separate octyne from final product to afford **10b** as an oil (>99%, 0.95 g, 2.6 mmol).

IR ν_{max} (film): 2953 (sp^2 C-H stretch), 2929 (sp^3 C-H stretch), 2245 (C≡C stretch), 1647 (aromatic C=C stretch), 1616 (aromatic C=C stretch), 1489 (sp^3 C-H bend), 1480 (sp^3 C-H bend) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.47 (t, J = 7.1 Hz, 4H, C≡CC$\underline{H}_2$), 1.62 (dt, J = 14.8, 7.2 Hz, 4H, C≡CCH$_2$C$\underline{H}_2$), 1.32 (m, 12H, C≡CCH$_2$CH$_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$), 0.90 (m, 6 H, C$\underline{H}_3$); ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ : -110.5 (d, J = 10.0 Hz, 1F), -130.4 (d, J = 21.6 Hz, 2F), -164.5 (td, J = 21.6, 10.1 Hz, 1F); ^{13}C NMR (126 MHz, CDCl3) δ : 157.6 (m, Ar-$\underline{C}$F), 151.9 (m, Ar-$\underline{C}$F (2C)), 149.9 (m, Ar-$\underline{C}$F), 102.7 (Ar-$\underline{C}$C≡C), 65.6 (C≡$\underline{C}$CH$_2$), 65.4 (C≡$\underline{C}$CH$_2$), 31.4 ($\underline{C}$H$_2$CH$_2$CH$_3$), 28.6 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 28.4 ($\underline{C}$H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 22.7 ($\underline{C}$H$_2$CH$_3$), 19.6 (C≡C$\underline{C}$H$_2$), 14.2 ($\underline{C}$H$_3$); HRMS (ESI) $C_{22}H_{26}F_4$ [M] found 366.1968, requires 366.1971.

1,2,3,5-Tetrafluoro-4,6-bis(4-methylpentynyl)benzene 10c



1,2,3,5-Tetrafluoro-4,6-diiodobenzene (1.01 g, 2.5 mmol), 4-methyl-1-pentyne (0.70 mL, 6 mmol), palladium catalyst (0.267 g, 0.375 mmol), and copper (I) iodide (0.078 g, 0.375 mmol)

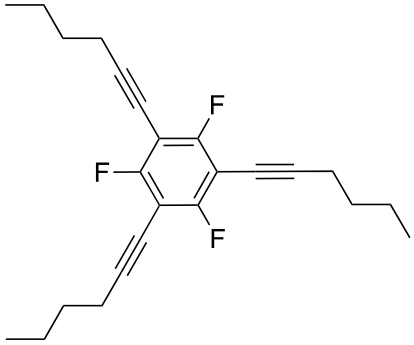
were all added to a 100 ml RBF. Diisopropylamine (25 mL) was then added, and the reaction mixture was heated to 80 ˚C under argon and stirred for 22 hours. The reaction mixture was then cooled to room temperature and slowly passed through a 3 cm pad of silica gel, with an elusion of ethyl acetate. The solvent was removed via concentration *in vacuo*, and then purified via flash chromatography (pentane), care was taken to separate starting alkyne from final product to afford **10b** as an oil (94%, 0.73 g, 2.36 mmol).

IR ν_{max} (film): 2958 (sp^2 C-H stretch), 2927 (sp^3 C-H stretch), 2243 (C≡C stretch), 1629 (aromatic C=C stretch), 1480 (sp^3 C-H bend) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 2.37 (d, J = 6.5 Hz, 4H, C≡CC$\underline{H}_2$), 1.94 (dp, J = 13.2, 6.6 Hz, 2H, C$\underline{H}$), 1.05 (d, J = 6.7 Hz, 12H, C$\underline{H}_3$); ^{19}F NMR (470 MHz, $CDCl_3$) δ : -110.4 (d, J = 10.1 Hz, 1F), -130.4 (d, J = 21.6 Hz, 2F), -164.5 (td, J = 21.7, 10.2 Hz, 1F); ^{13}C NMR (126 MHz, CDCl3) δ : 158.6 (d, J = 253.0 Hz, Ar-$\underline{C}$F), 150.6 (d, J = 252.5 Hz, Ar-$\underline{C}$F, 2C), 137.3 (d, J = 244.1 Hz, Ar-$\underline{C}$F), 101.7 (Ar-$\underline{C}$C), 66.4 ($\underline{C}$≡CCH$_2$), 66.2 (C≡$\underline{C}$CH$_2$), 28.7 ($\underline{C}$H), 28.1 ($\underline{C}$H$_2$CH), 22.1 ($\underline{C}$H$_3$); HRMS (ESI$^-$) $C_{18}H_{18}F_4$ [M] found 310.1292, requires 310.1345.

General Procedure 1

1,3,5-Trifluoro-2,4,6-triiodobenzene (1 eq), appropriate acetylene (3.6 eq), palladium catalyst (0.15 eq), and copper (I) iodide (0.15 eq) were added to a RBF. Diisopropylamine (20—34 mL) was then added and the reaction was heated to 80 °C for 24 hours. The reaction mixture was then cooled to r.t. and slowly passed through a pad of silica gel with elusion of ethyl acetate. The solvent was removed *in vacuo* to give the crude product, which was purified by flash chromatography.

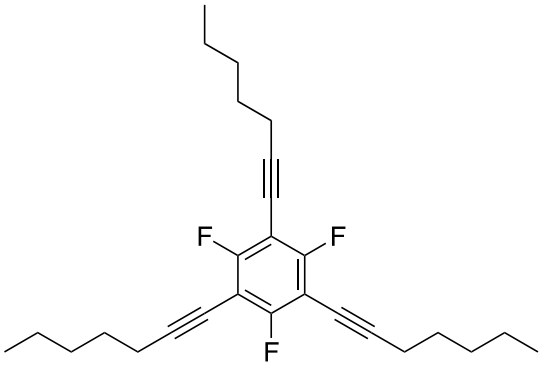
1,3,5-Trifluoro-2,4,6-tri-1-hexynylbenzene 14a



Following General Procedure 1, 1,3,5-trifluoro-2,4,6-triiodobenzene (1.27 g, 2.5 mmol), 1-hexyne (1.03 mL, 9 mmol), bis(triphenylphosphine)palladium(II) chloride (263 mg, 0.375 mmol), copper (I) iodide (71.4 mg, 0.375 mmol), and DIPA (21 mL) for 24 h gave, after purification by flash chromatography (hexane), **14a** (99%, 1.18 g, 2.5 mmol); isolated as a yellow oil.

IR ν_{max} (film): 2958 (sp^2 C-H stretch), 2933 (sp^3 C-H stretch), 2872 (sp^3 C-H stretch), 2243 (C≡C stretch), 1604 (aromatic C=C stretch), 1323 (C-F bond), 760 (C-F) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.47 (t, J = 7.1 Hz, 6H, C≡CC$\underline{H}_2$), 1.60 (p, J = 7.0 Hz, 6H, C≡CCH$_2$C$\underline{H}_2$), 1.49 (m, 6H, C≡CCH$_2$CH$_2$C$\underline{H}_2$), 0.94 (t, J = 7.3 Hz, 9H, C$\underline{H}_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -103.9 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 163.1 (t, J = 7.6 Hz, Ar-$\underline{C}$F), 161.0 (t, J = 7.7 Hz, Ar-$\underline{C}$C), 101.3 (m, C≡$\underline{C}$CH$_2$), 65.9 ($\underline{C}$≡CCH$_2$), 30.4 ($\underline{C}$H$_2$CH$_2$CH$_3$), 21.9 ($\underline{C}$H$_2$CH$_3$), 19.2 (C≡C$\underline{C}$H$_2$), 13.6 ($\underline{C}$H$_3$).

1,3,5-trifluoro-2,4,6-tri(heptynyl)benzene 14b

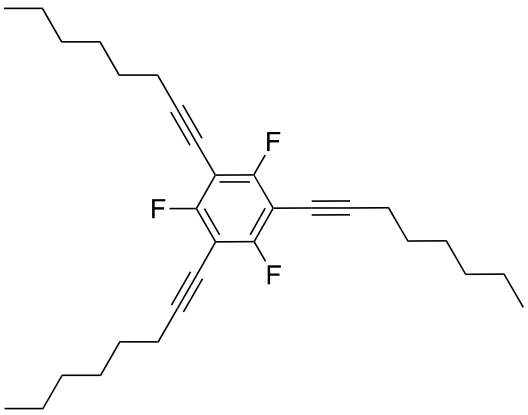


Following General Procedure 1, 1,3,5-trifluoro-2,4,6-triiodobenzene (1.27 g, 2.5 mmol), 1-heptyne (1.18 mL, 9 mmol), bis(triphenylphosphine)palladium(II) chloride (263 mg, 0.375 mmol), copper (I) iodide (71.4 mg, 0.375 mmol), and DIPA (34 mL) for 24 h gave, after purification by flash chromatography (hexane), **14b** (71%, 74 mg, 1.78 mmol); isolated as a yellow oil.

IR ν_{max} (film): 2956 (sp^2 C-H stretch), 2931 (sp^3 C-H stretch), 2860 (sp^3 C-H stretch), 2243 (C≡C stretch), 1710 (aromatic C=C stretch), 1606 (aromatic C=C stretch), 1460 (sp^3 C-H bend), 1039

(alkene sp^2 C-H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ : 2.46 (t, J = 7.0 Hz, 6H, C≡CC<u>H</u>$_2$), 1.62 (p, J = 7.1 Hz, 6H, C≡CCH$_2$C<u>H</u>$_2$), 1.41 (m, 12H, C<u>H</u>$_2$C<u>H</u>$_2$CH$_3$), 0.92 (t, J = 7.2 Hz, 9H, C<u>H</u>$_3$); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ : -103.9 (s, 3F); ^{13}C NMR (101 MHz, CDCl3) δ : 162.2 (dt, J = 257.7, 7.8 Hz, Ar-<u>C</u>F), 101.5 (Ar-<u>C</u>C≡C), 66.0 (Ar-CC≡<u>C</u>), 65.4 (Ar-C<u>C</u>≡C), 31.1 (<u>C</u>H$_2$CH$_2$CH$_3$), 28.1 (<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 22.3 (<u>C</u>H$_2$CH$_3$), 19.8 (Ar-CC≡C<u>C</u>H$_2$), 14.1 (<u>C</u>H$_3$); HRMS (ESI^+) $C_{27}H_{33}F_3$ $[M^-]$ found 413.2449, requires 413.2454.

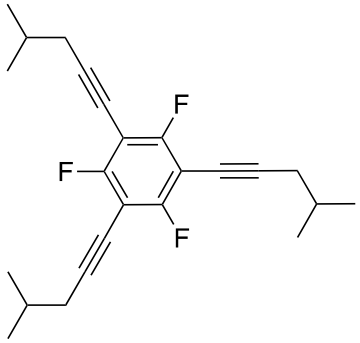
1,3,5-Trifluoro-2,4,6-(trioctynyl)benzene 14c



Following General Procedure 1, 1,3,5-trifluoro-2,4,6-triiodobenzene (1.27 g, 2.5 mmol), 1-octyne (1.33 mL, 9 mmol), bis(triphenylphosphine)palladium(II) chloride (263 mg, 0.375 mmol), copper (I) iodide (71.4 mg, 0.375 mmol), and DIPA (21 mL) for 24 h gave, after purification by flash chromatography (hexane), **14c** (99%, 1.18 g, 2.5 mmol); isolated as a yellow oil.

IR ν_{max} (film): 2927 (sp^2 C-H stretch), 2858 (sp^3 C-H stretch), 2243(C≡C stretch), 1710 (aromatic C=C stretch), 1606 (aromatic C=C stretch), 1450 (sp^3 C-H bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.46 (t, J = 7.0 Hz, 6H, C≡CC<u>H</u>$_2$), 1.61 (dt, J = 14.8, 7.2 Hz, 6H, C≡CCH$_2$C<u>H</u>$_2$), 1.29 (m, 18H, long chain hydrogens), 0.90 (t, J = 7.2 Hz, 9H C<u>H</u>$_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -103.9 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ : 162.2 (dt, J = 258.0, 7.8 Hz, Ar-<u>C</u>F), 101.5 (Ar-<u>C</u>C), 66.0 (C≡<u>C</u>CH$_2$), 65.4 (<u>C</u>≡CCH$_2$), 31.4 (<u>C</u>H$_2$CH$_2$CH$_3$), 28.6 (<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 28.4 (C≡CCH$_2$<u>C</u>H$_2$), 22.7 (<u>C</u>H$_2$CH$_3$), 19.6 (C≡C<u>C</u>H$_2$), 14.2 (CH$_3$); HRMS (ESI) $C_{30}H_{39}F_3$ $[M\text{-}Cl]^+$ found 455.2923, requires 455.2924.

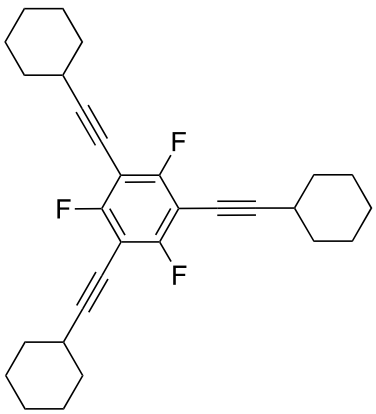
1,3,5-Trifluoro-2,4,6-tris(4-methylpent-1-yn-1-yl)benzene 14d



Following General Procedure 1, 1,3,5-trifluoro-2,4,6-triiodobenzene (1.27 g, 2.5 mmol), 4-methyl-1-pentyne (1.06 mL, 9 mmol), bis(triphenylphosphine)palladium(II) chloride (263 mg, 0.375 mmol), copper (I) iodide (71.4 mg, 0.375 mmol), and DIPA (21 mL) for 24 h gave, after purification by flash chromatography (hexane), **14d** (81%, 76 mg, 2.0 mmol); isolated as a yellow oil.

IR ν_{max} (film): 2960 (sp^2 C-H stretch), 2929 (sp^3 C-H stretch), 2872 (sp^3 C-H stretch), 2243 (C≡C stretch), 1606 (aromatic C=C stretch), 1460 (sp^3 C-H bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.36 (d, *J* = 6.4 Hz, 6H, C≡CC$\underline{H}_2$), 1.93 (hept, *J* = 6.6 Hz, 3H, C$\underline{H}$), 1.04 (d, *J* = 6.7 Hz, 18H, C$\underline{H}_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -103.8 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 142.1 (apparent d, J = 71.8 Hz, Ar-$\underline{C}$F), 100.4 (Ar-$\underline{C}$C), 66.9 ($\underline{C}$≡CCH_2), 29.0 (C≡$\underline{C}CH_2$), 28.5 ($\underline{C}$H), 28.1 (d, J = 12.6 Hz, $\underline{C}H_2CH$), 22.1 (d, J = 14.1 Hz, $\underline{C}H_3$); HRMS (ESI^-) $C_{24}H_{27}F_3$ [M] found 372.2037, requires 372.2065.

(2,4,6-Trifluorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl)tricyclohexane 14e

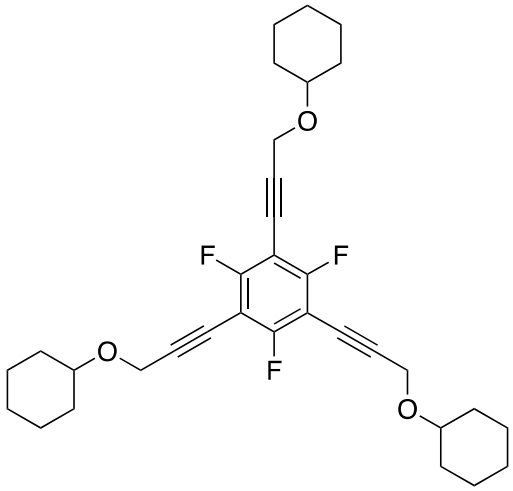


Following General Procedure 1, 1,3,5-trifluoro-2,4,6-triiodobenzene (1.27 g, 2.5 mmol), ethynylcyclohexane (1.20 mL, 9 mmol), bis(triphenylphosphine)palladium(II) chloride (263 mg, 0.375 mmol), copper (I) iodide (71.4 mg, 0.375 mmol), and DIPA (24 mL) for 24 h gave, after

purification by flash chromatography (hexane), **14e** (98%, 1.11 g, 2.46 mmol); isolated as a yellow oil.

IR ν_{max} (film): 2927 (sp^2 C-H stretch), 2235 (C≡C stretch), 1600 (aromatic C=C stretch), 1442 (aromatic C=C stretch), 1410 (aromatic C=C stretch) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ : 2.70 (apparent tt, J = 8.2, 3.7 Hz, 3H, Ar-CC≡CC$\underline{H}_2$), 1.81-1.67 (m, 12H, aryl-ortho-C$\underline{H}_2$), 1.46-1.29 (m, 18H, aryl-meta, para-C$\underline{H}_2$); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ : -103.7 (s, 3F); ^{13}C NMR (101 MHz, CDCl3) δ : 162.0 (dt, J = 257.3, 7.3 Hz, Ar-$\underline{C}$F), 117.6 (Ar-$\underline{C}$C≡C), 105.2 (Ar-CC≡$\underline{C}$), 66.2 (Ar-C$\underline{C}$≡C), 32.3 (aryl-$\underline{C}$H), 29.9 (aryl-meta-$\underline{C}H_2$), 26.0 (aryl-para-$\underline{C}H_2$), 24.7 (aryl-ortho-$\underline{C}H_2$); HRMS (ESI^+) $C_{30}H_{33}F_3$ [M] found 450.2491, requires 450.2534.

(((2,4,6-trifluorobenzene-1,3,5-triyl)tris(prop-2-yne-3,1-diyl))tris(oxy))tricyclohexane 14f



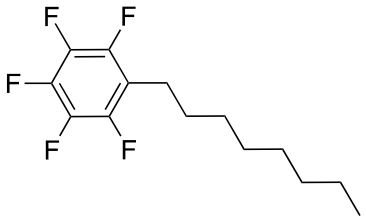
Following General Procedure 1, 1,3,5-trifluoro-2,4,6-triiodobenzene (1.65 g, 3.24 mmol), (prop-2-yn-1-yloxy)cyclohexane (1.6133 g, 11.67 mmol), bis(triphenylphosphine)palladium(II) chloride (341 mg, 0.486 mmol), copper (I) iodide (92.6 mg, 0.486 mmol), and DIPA (30 mL) for 24 h gave, after purification by flash chromatography (0-20% Et_2O in hexane), **14f** (59%, 1.04 g, 1.93 mmol); isolated as a yellow oil.

IR ν_{max} (film): 2929 (sp^2 C-H stretch), 2160 (C≡C stretch), 1606 (aromatic C-H stretch), 1456 (aromatic C-H stetch), 1082 (C-O stretch) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.44 (s, 6H, C≡CC$\underline{H}_2$), 3.55 (tt, J = 8.9, 4.0 Hz, 3H, cyclo-C$\underline{H}$), 1.97—1.95 (m, 6H, ortho), 1.77—1.75 (m, 6H, meta), 1.56—1.53 (m, 3H, para), 1.37—1.21 (m, 15H, cyclo-H); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -100.2 (3x C$\underline{F}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 162.9 (dt, J = 261.5, 7.5 Hz, 3x Ar-$\underline{C}$F), 97.4 (3xAr-$\underline{C}$C), 77.1 (3x cyclo-$\underline{C}$H), 70.6 (C≡$\underline{C}CH_2$), 55.8 ($\underline{C}$≡CCH$_2$), 31.9 (3x C≡C$\underline{C}H_2$), 25.9 (6x cyclo-ortho-$\underline{C}H_2$), 24.2 (3x cyclo-para-$\underline{C}H_2$), 22.8 (6x cyclo-meta-$\underline{C}H_2$); HRMS (ESI^+) $C_{33}H_{39}F_3O_3$ [M-Na] found 563.2744, requires 563.2749.

General Procedure 2

A solution of alkyne (1 eq) was dissolved in either hexane, methanol, or ethyl acetate (10—100 mL), and 10% palladium on carbon catalyst (10% wt eq) was added to the solution. The hydrogenation was then carried out using either atmospheric pressure of H_2 gas from a balloon or using a stainless steal autoclave with H_2 pressure of 15 bar. The reaction was carried out for 1—4 days. The reaction mixture was then slowly passed through a pad of celite with elusion of ethyl acetate. The solvent was removed under reduced pressure to give the crude product, which was purified by flash chromatography.

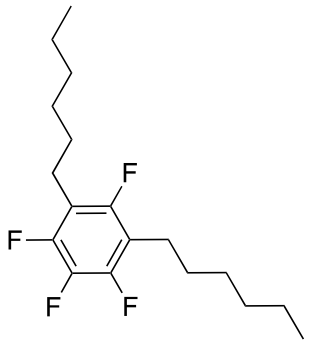
1,2,3,4,5-Pentafluoro-6-octylbenzene 7



Following General Procedure 2, 1,2,3,4,5-pentafluoro-6-(oct-1-yn-yl)benzene (100 mg, 0.366 mmol), 10% palladium on carbon catalyst (10 mg, 10% wt eq), and hexane (10 mL), under atmospheric pressure H_2 for 24 h gave, after purification by flash chromatography (hexane), **7** (72%, 70 mg, 0.26 mmol) as a colourless oil.

IR ν_{max} (film): 2956 (alkane C-H stretch), 2924 (alkane C-H stretch), 2854 (alkane C-H stretch), 1654 (aromatic C=C stretch), 1485 (aromatic C=C stretch) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.68 (t, J = 7.63 Hz, 2H, C$\underline{H_2}$), 1.56 (q, J = 7.8, 7.4 Hz, 2H, $CH_2C\underline{H_2}$), 1.31—1.25 (m, 17H, $CH_2CH_2C\underline{H_2}C\underline{H_2}C\underline{H_2}C\underline{H_2}C\underline{H_2}CH_3$), 0.88 (t, J = 6.9 Hz, 3H, C$\underline{H_3}$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -144.5 (m, 2F), -158.5 (t, J = 20.8 Hz, 1F), -163.2 (td, J = 22.1, 8.0 Hz, 2F); ^{13}C NMR (126 MHz, $CDCl_3$) δ : 146.0 (m, Ar-$\underline{C}$F), 144.1 (m, Ar-$\underline{C}$F), 140.4 (m, Ar-$\underline{C}$F), 138.4 (Ar-$\underline{C}CH_2$), 124.2 ($\underline{C}H_2CH_2CH_3$), 115.6 ($\underline{C}H_2CH_2CH_2CH_2CH_2CH_2CH_3$), 31.9 (d, J = 16.2 Hz, $\underline{C}H_2CH_2CH_2CH_2CH_2CH_3$), 29.7 (d, J = 9.2 Hz, $\underline{C}H_2CH_2CH_2CH_3$), 29.3 ($\underline{C}H_2CH_2CH_2CH_2CH_3$), 22.7 (d, J = 9.2 Hz, Ar-$\underline{C}H_2$), 22.3 ($\underline{C}H_2CH_3$), 14.1 (d, J = 6.4 Hz, $\underline{C}H_3$); HRMS (EI) $C_{14}H_{17}F_5$ [M] found 280.1252, requires 280.1250.

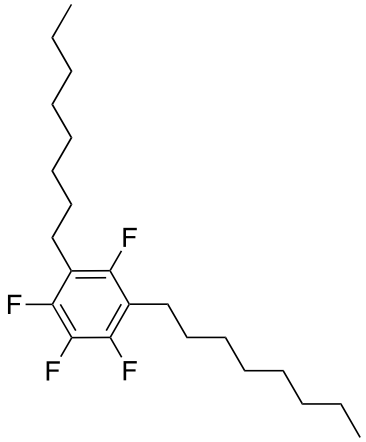
1,2,3,5-Tetrafluoro-4,6-dihexylbenzene 11a



Following General Procedure 2, 1,2,3,5-tetrafluoro-4,6-di(hex-1-yn-1-yl)benzene (118 mg, 0.38 mmol), 10% palladium on carbon catalyst (13 mg, 10% wt eq), and hexane (10 mL), under atmospheric pressure H_2 for 24 h gave, after purification by flash chromatography (hexane), **11a** (99%, 120 mg, 0.38 mmol) as a colourless oil.

IR ν_{max} (film): 2956 (sp^2 C-H stretch), 2927 (sp^3 C-H stretch), 2858 (sp^3 C-H stretch), 1647 (aromatic C-H stretch), 1490 (aromatic C-H stretch), 1467 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.62 (t, J = 7.6 Hz, 4H, Ar-C$\underline{H}_2$), 1.55 (q, J = 7.7 Hz, 4H, Ar-$CH_2C\underline{H}_2$), 1.29 (m, 12H, remaining chain-C$\underline{H}_2$), 0.88 (m, 6H, C$\underline{H}_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -126.1 (d, J = 11.4 Hz, 1F), -142.2 (d, J = 21.7 Hz, 2F), -166.8 (td, J = 21.8, 11.5 Hz, 1F); ^{13}C NMR (126 MHz, CDCl3) δ : 153.8 (dtd, J = 241.5, 9.7, 3.4 Hz, Ar-$\underline{C}$F), 147.5 (dtd, J = 244.5, 11.3, 5.6 Hz, Ar-$\underline{C}$F), 136.9 (dtd, J = 246.2, 16.3, 4.8 Hz, Ar-$\underline{C}$F), 114.6 (ddd, J = 22.2, 16.3, 4.2 Hz, Ar-$\underline{C}CH_2$), 31.5 ($\underline{C}H_2CH_2CH_3$), 29.5 ($\underline{C}H_2CH_2CH_2CH_2CH_3$), 28.9 ($\underline{C}H_2CH_2CH_2CH_3$), 22.6 (Ar-C$\underline{C}H_2$), 22.4 ($\underline{C}H_2CH_3$), 14.0 ($\underline{C}H_3$).

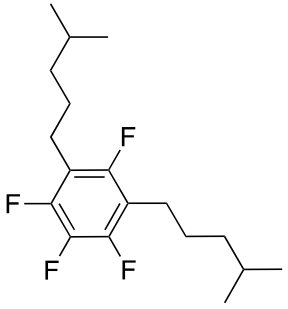
1,2,3,5-Tetrafluoro-4,6-(dioctyl)benzene 11b



Following General Procedure 2, 1,2,3,5-tetrafluoro-4,6-di(oct-1-yn-1-yl)benzene (100 mg, 0.273 mmol), 10% palladium on carbon catalyst (10 mg, 10% wt eq), and hexane (10 mL), under atmospheric pressure H_2 for 24 h gave, after purification by flash chromatography (hexane), **11b** (81%, 83 mg, 0.22 mmol) as a colourless oil.

IR ν_{max} (film): 2956 (sp^2 C-H stretch), 2924 (sp^3 C-H stretch), 2854 (sp^3 C-H stretch), 1645 (aromatic C-H stretch), 1517 (aromatic C-H stretch), 1465 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.62 (t, J = 7.6 Hz, 4H, Ar-CC$\underline{H}_2$), 1.53 (m, 4H, Ar-CCH$_2$C$\underline{H}_2$), 1.28 (m, 20H, Ar-CCH$_2$CH$_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$), 0.88 (t, J = 7.0 Hz, 6H, C$\underline{H}_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -126.0 (d, J = 11.4 Hz, 1F), -142.2 (d, J = 22.2 Hz, 2F), -166.8 (td, J = 21.7, 11.5 Hz, 1F); ^{13}C NMR (126 MHz, CDCl3) δ : 154.0 (apparent d, J = 235.7 Hz, Ar-$\underline{C}$F), 147.6 (apparent d, J = 244.5 Hz, Ar-$\underline{C}$F), 137.0 (apparent d, J = 251.1 Hz, Ar-$\underline{C}$F), 114.8 (Ar-$\underline{C}$CH$_2$), 32.0 ($\underline{C}$H$_2$CH$_2$CH$_3$), 29.6 (remaining C), 22.8 (Ar-$\underline{C}$H$_2$), 22.5 ($\underline{C}$H$_2$CH$_3$), 14.3 ($\underline{C}$H$_3$); HRMS (ESI) $C_{22}H_{34}F_4$ [M] found 374.2598, requires 374.2597.

1,2,3,5-Tetrafluoro-4,6-bis(4-methylpentyl)benzene 11c

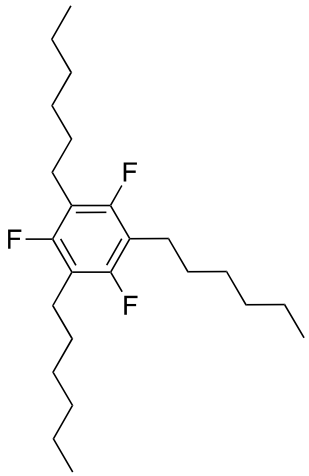


Following General Procedure 2, 1,2,3,5-tetrafluoro-4,6-bis(4-methylpent-1-yn-1-yl)benzene (675 mg, 2.175 mmol), 10% palladium on carbon catalyst (68 mg, 10% wt eq), and hexane (30 mL),

under 15 bar H_2 for 24 h gave, after purification by flash chromatography (hexane), **11c** (83%, 580 mg, 1.82 mmol) as a colourless oil.

IR ν_{max} (film): 2954 (sp^2 C-H stretch), 2926 (sp^3 C-H stretch), 2854 (sp^3 C-H stretch), 1645 (aromatic C-H stretch), 1490 (aromatic C-H stretch), 1467 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.61 (t, J = 7.6 Hz, 4H, Ar-C$\underline{H_2}$), 1.55 (ttd, J = 16.6, 8.6, 7.6, 5.1 Hz, 6H, C$\underline{H_2}CH_2C\underline{H}$), 0.87 (m, 16H, C$\underline{H_3}$ and CHC$\underline{H_2}$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -126.0 (d, J = 11.4 Hz, 1F), -142.1 (d, J = 21.7 Hz, 2F), -166.2 (td, J = 21.8, 11.5 Hz, 1F); ^{13}C NMR (126 MHz, CDCl3) δ : 158.7 (apparent d, J = 256.1 Hz, Ar-$\underline{C}$F), 150.9 (apparent d, J = 262.0 Hz, Ar-$\underline{C}$F, 2C), 137.4 (apparent d, J = 248.4 Hz, Ar-$\underline{C}$F), 129.6 (Ar-$\underline{C}CH_2$), 101.7 ($\underline{C}H_2CH$), 32.1 ($\underline{C}H$), 28.7 ($\underline{C}H_2CH_2CH$), 28.1 (Ar-C$\underline{C}H_2$), 22.1 ($\underline{C}H_3$).

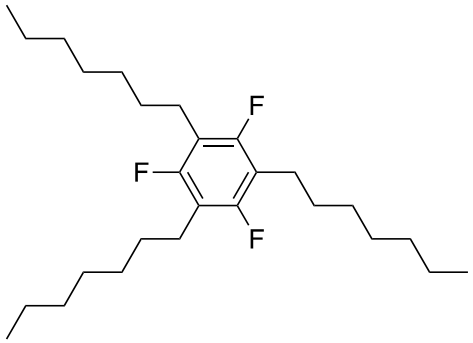
1,3,5-Trifluoro-2,4,6-trihexylbenzene 15a



Following General Procedure 2, 1,3,5-trifluoro-2,4,6-tri(hex-1-yn-1-yl)benzene (391.4 mg, 1.05 mmol), 10% palladium on carbon catalyst (39 mg, 10% wt eq), and hexane (20 mL), under atmospheric pressure H_2 for 24 h gave, after purification by flash chromatography (hexane), **15a** (77%, 310 mg, 0.81 mmol) as a colourless oil.

IR ν_{max} (film): 2956 (sp^2 C-H stretch), 2890 (sp^3 C-H stretch), 2856 (sp^3 C-H stretch), 1622 (aromatic C-H stretch), 1450 aromatic C-H stretch cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.60 (t, *J* = 7.6 Hz, 6H, Ar-C$\underline{H_2}$),1.54 (tt, *J* = 7.5, 5.8 Hz, 6H, Ar-$CH_2C\underline{H_2}$), 1.39 – 1.26 (m, 22H, $\underline{CH_2}\underline{CH_2}\underline{CH_2}CH_3$), 0.90 (td, *J* = 6.9, 1.8 Hz, 9H, C$\underline{H_3}$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -124.1 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 157.8 (dt, J = 241.9, 12.2 Hz, Ar-$\underline{C}$F), 113.1 (Ar-$\underline{C}$C), 32.1 ($\underline{C}H_2CH_2CH_3$), 29.9 ($\underline{C}H_2CH_2CH_2CH_2CH_3$), 29.5 ($\underline{C}H_2CH_2CH_2CH_3$), 22.9 (Ar-C$\underline{C}H_2$), 22.7 ($\underline{C}H_2CH_3$), 14.2 ($\underline{C}H_3$).

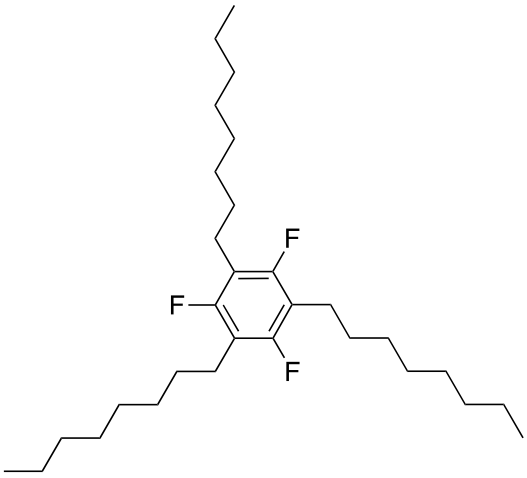
1,3,5-Trifluoro-2,4,6-triheptylbenzene 15b



Following General Procedure 2, 1,3,5-trifluoro-2,4,6-tri(hept-1-yn-1-yl)benzene (720 mg, 1.74 mmol), 10% palladium on carbon catalyst (108 mg, 15% wt eq), and methanol (100 mL), under atmospheric pressure H_2 for 3 d gave, after purification by flash chromatography (hexane), **15b** (85%, 631 mg, 1.48 mmol) as a colourless oil.

IR ν_{max} (film): 2956 (alkane C-H stretch), 2920 (alkane C-H stretch), 2854 (alkane C-H stretch), 1622 (aromatic C=C stretch), 1458 (aromatic C=C stretch) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.57 (t, J = 7.6 Hz, 6H, Ar-C$\underline{H}_2$), 1.55-1.49 (m, 6H, Ar-CH$_2$C$\underline{H}_2$), 1.32-1.25 (m, 24H, C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 0.87 (t, J = 7.0 Hz, 9H, C$\underline{H}_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -124.1 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ : 157.5 (dt, J = 241.8, 12.1 Hz, Ar-$\underline{C}$F), 113.1 (Ar-$\underline{C}$CH$_2$), 32.0 ($\underline{C}$H$_2$CH$_2$CH$_3$), 29.8 (Ar-CH$_2\underline{C}$H$_2$), 29.3 (Ar-CH$_2$CH$_2\underline{C}$H$_2\underline{C}$H$_2$), 22.8 (Ar-C$\underline{C}$H$_2$), 22.4 ($\underline{C}$H$_2$CH$_3$), 14.3 ($\underline{C}$H$_3$); HRMS (ESI^-) $C_{27}H_{45}F_3$ [M]+1 found 465.3028, requires 465.311.

1,3,5-Trifluoro-2,4,6-trioctylbenzene 15c

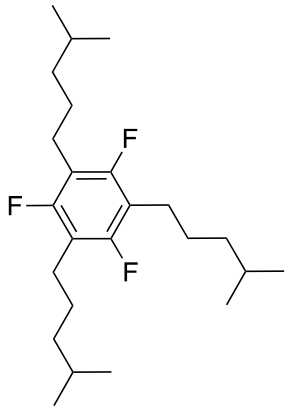


Following General Procedure 2, 1,3,5-trifluoro-2,4,6-tri(oct-1-yn-1-yl)benzene (871 mg, 1.9 mmol), 10% palladium on carbon catalyst (89 mg, 10% wt eq), and hexane (100 mL), under

atmospheric pressure H_2 for 24 h gave, after purification by flash chromatography (hexane), **15c** (99%, 936 mg, 1.9 mmol) as a colourless oil.

IR ν_{max} (film): 2956 (sp^2 C-H stretch), 2875 (alkane C-H stretch), 2852 (alkane C-H stretch), 1622 (aromatic C-H stretch), 1458 (aromatic C-H stretch) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.57 (t, J = 7.6 Hz, 6H, Ar-C$\underline{H_2}$), 1.52 (m, 6H, Ar-$CH_2C\underline{H_2}$), 1.27 (m, 35H, long chain hydrogens), 0.87 (m, 9H, C$\underline{H_3}$); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ : -124.07 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 157.5 (dt, J = 241.9, 12.2 Hz, Ar-$\underline{C}$F), 113.1 (m, Ar-$\underline{C}$C), 32.1 (d, J = 8.2 Hz, $\underline{C}H_2CH_2CH_3$), 29.9 (Ar-$CCH_2\underline{C}H_2$), 29.6 (Ar-$CH_2CH_2\underline{C}H_2CH_2$), 29.5 (Ar-$CH_2CH_2CH_2\underline{C}H_2$), 29.4 (Ar-$CH_2CH_2CH_2CH_2\underline{C}H_2$), 22.70 (d, J = 5.3 Hz, Ar-C$\underline{C}H_2$), 22.33 ($\underline{C}H_2CH_3$), 14.14 (d, J = 3.0 Hz, $\underline{C}H_3$); HRMS (ESI^-) $C_{30}H_{51}F_3Na$ [M^+] found 491.3.

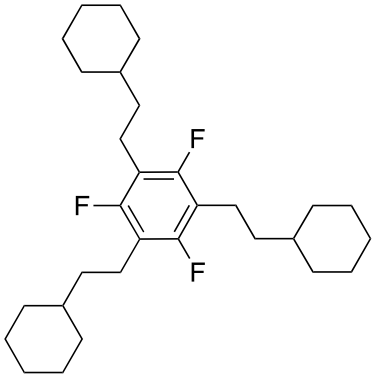
1,3,5-trifluoro-2,4,6-tris(4-methylpentyl)benzene 15d



Following General Procedure 2, 1,3,5-trifluoro-2,4,6-tris(4-methylpent-1-yn-1-yl)benzene (724 mg, 1.94 mmol), 10% palladium on carbon catalyst (109 mg, 15% wt eq), and hexane (40 mL), under atmospheric pressure H_2 for 24 h gave, after purification by flash chromatography (hexane), **15d** (89%, 660 mg, 1.72 mmol) as a colourless oil.

IR ν_{max} (film): 2954 (sp^2 C-H stretch), 2927 (alkane C-H stretch), 2870 (alkane C-H stretch), 1622 (aromatic C-H stretch), 1462 (aromatic C-H stretch), 1384 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 2.57 (t, J = 7.6 Hz, 6H, Ar-C$\underline{H_2}$), 1.54 (tq, J = 14.1, 6.7 Hz, 6H, Ar-$CH_2C\underline{H_2}$), 1.23 (m, 6H, Ar-$CH_2CH_2C\underline{H_2}$), 1.15 (q, J = 6.5 Hz, 3H, C$\underline{H}$), 0.87 (dd, J = 6.6, 2.9 Hz, 18H, C$\underline{H_3}$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -124.0 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 157.5 (dt, J = 242.0, 12.2 Hz, Ar-$\underline{C}$F), 113.1 (Ar-$\underline{C}$C), 39.2 ($\underline{C}H_2CH$), 38.6 ($\underline{C}H$), 30.1 ($\underline{C}H_2CH_2CH$), 27.9 (Ar-C$\underline{C}H_2$), 22.7 ($\underline{C}H_3$); HRMS (ESI^+) $C_{24}H_{40}F_3$ [$M+H^+$] found 385.2.

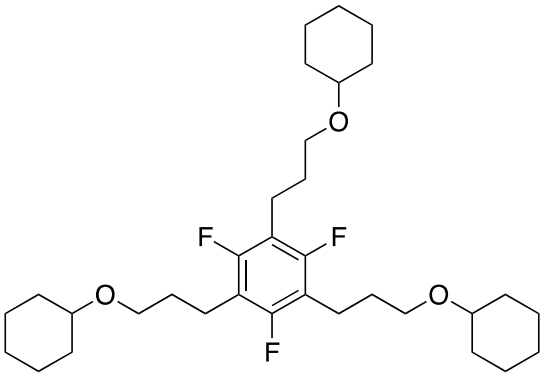
((2,4,6-Trifluorobenzene-1,3,5-triyl)tris(ethane-2,1-diyl))tricyclohexane 15e



Following General Procedure 2, ((2,4,6-trifluorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tricyclohexane (1.09 g, 2.42 mmol), 10% palladium on carbon catalyst (162 mg, 15% wt eq), and ethyl acetate (100 mL), under atmospheric pressure H_2 for 2 d gave, after purification by flash chromatography (hexane), **15e** (91%, 1.018 g, 2.2 mmol) as a colourless oil.

IR ν_{max} (film): 2990 (sp^2 C-H stretch), 1622 (aromatic C-H stretch), 1450 (aromatic C-H stretch), 1446 (aromatic C-H stretch) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ : 2.58 (t, J = 8.1 Hz, 6H, Ar-CC$\underline{H_2}$), 1.40 (dt, J = 10.4, 6.7 Hz, 6H, Ar-CCH$_2$C$\underline{H_2}$), 1.29-0.82 (m, 33H, cyclic-$\underline{H}$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ: -124.7 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 157.5 (dd, J = 243.1, 14.0 Hz, Ar-$\underline{C}$F), 113.6 (d, J = 21.6 Hz, Ar-$\underline{C}CH_2$), 37.8 (cyclo-$\underline{C}$H), 33.5 (cyclo-ortho-$\underline{C}H_2$), 27.4 (Ar-C$\underline{C}H_2$), 26.9 (Ar-CCH$_2\underline{C}H_2$), 26.6 (cyclo-meta,$\underline{C}H_2$), 20.0 (cyclo-para-$\underline{C}H_2$); HRMS (ESI^+) $C_{30}H_{44}F_3$ $[M-H]^+$ found 461.4.

(((2,4,6-Trifluorobenzene-1,3,5-triyl)tris(propane-3,1-diyl))tris(oxy))tricyclohexane 15f



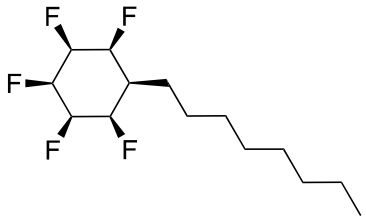
Following General Procedure 2, (((2,4,6-trifluorobenzene-1,3,5-triyl)tris(prop-2-yne-3,1-diyl))tris(oxy))tricyclohexane (1.04 g, 1.9 mmol), 10% palladium on carbon catalyst (124 mg, 15% wt eq), and methanol (40 mL), under 15 bar H_2 for 3 d gave, after purification by flash chromatography (0—70% Et_2O in hexane), **15f** (49%, 410 mg, 0.74 mmol) as a colourless oil.

IR ν_{max} (film): 2989 (sp^2 C-H stretch), 1558 (aromatic C-H stretch), 1506 (aromatic C-H stretch), 1072 (C-O stretch) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 3.44 (t, J = 6.5 Hz, 6H, OCH_2), 3.19 (tt, J = 8.8, 3.9 Hz, 3H, OCH), 2.67 (t, J = 7.3 Hz, 6H, Ar-CH_2), 1.90—1.85 (m, 6H, $CH_2C\underline{H}_2CH_2$), 1.80 (apparent p, J = 6.6 Hz, 6H, ortho-C<u>H</u>H), 1.73—1.71 (m, 6H, ortho CH<u>H</u>), 1.30—0.87 (m, 18H, remaining cyclo-H); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -122.8 (3xCF); ^{13}C NMR (126 MHz, $CDCl_3$) δ : 160.8 (apparent d, J = 267.0 Hz, 3xCF), 122.0 (3xAr-<u>C</u>HCH_2), 77.7 (3xOCH), 67.2 (OCH_2), 32.5 (6x ortho-CH_2), 30.2 (3xAr-$CH_2\underline{C}H_2$), 26.0 (3xAr-CH_2), 24.4 (3x para-CH_2), 19.3 (6x meta-CH_2); HRMS (ESI^+) $C_{33}H_{51}F_3O_3$ $[M]^+$ found 553.3865, requires 553.3869.

General Procedure 3

Rhodium-CAAC-COD-Cl catalyst (1.6—2 mol%) was added to an oven- dried 9 mL screw-cap vial or a 50 mL glass cylinder equipped with a stirring bar and activated 4 Å molecular sieves (0.2—3.2 g) and/or silica (0.2—1.6 g). Hexane (2—40 mL) and the aromatic substrate (1 eq) were added under argon atmosphere. The glass vial/cylinder was placed in a 150 mL stainless steel autoclave under argon atmosphere. The autoclave was pressurized and depressurized with hydrogen gas three times before the indicated pressure was set (50—70 bar). The reaction mixture was stirred at 25—50 °C for 1—10 d. After the autoclave was carefully depressurized, the mixture was filtered through cotton wool inside a long glass pipette and washed with 10% methanol in DCM. The solvent was removed under reduced pressure to give the crude product, which was purified by flash chromatography.

All-cis 1,2,3,4,5-pentafluoro-6-octylcyclohexane 8

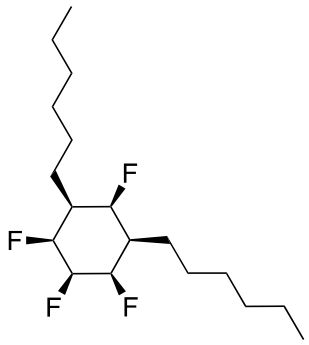


Following General Procedure 3, 1,2,3,4,5-pentafluoro-6-octylbenzene (46.7 mg, 0.17 mmol), Rh-CAAC-COD-Cl (1.6 mg, 0.0028 mmol), 4Å molecular sieves (200 mg), and hexane (2 mL) for 24 h, r.t., at 50 bar H_2 gave, after purification by flash chromatography (60:40 diethyl ether:pentane), **8** (>99%, 72 mg, 0.25 mmol) as a white crystalline solid.

m.p. 138—140 °C. IR ν_{max} (solid): 2920 (alkane C-H stretch), 1506 (methyl C-H bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 5.37—5.24 (m, 1H, para-<u>H</u>F), 4.92 (apparent d, J = 48.7 Hz, 2H, meta-<u>H</u>F), 4.4 (apparent dt, J = 41.1, 26.7 Hz, 2H, ortho-<u>H</u>F), 1.86—1.77 (m, 1H, ring-<u>H</u>C), 1.29—1.18 (m, 14H, chain-C<u>H</u>$_2$), 0.86 (t, J = 7.1 Hz, 3H, C<u>H</u>$_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -203.3 (ddd, J = 11.6, 7.8, 4.9 Hz, 2F), -212.1 (ddd, J = 26.7, 7.3, 4.5 Hz, 2F), -216.7 (tt, 26.6, 11.3 Hz, 1F-para); ^{13}C NMR (126 MHz, $CDCl_3$) δ : 87.1 (m, 5x <u>C</u>F), 38.6 (ring-<u>C</u>H), 34.3 (<u>C</u>$H_2CH_2CH_3$), 32.0 ($CHCH_2CH_2\underline{C}H_2$), 29.8

($CHCH_2CH_2\underline{C}H_2\underline{C}H_2$), 29.5 ($\underline{C}H_2CH_2CH_2CH_3$), 26.3 ($CH\underline{C}H_2$), 22.5 ($CHCH_2\underline{C}H_2$), 15.4 ($\underline{C}H_2CH_3$), 14.2 ($\underline{C}H_3$); HRMS ($ESI^+$) $C_{14}H_{23}F_5$ [M-Na] found 309.1607, requires 309.1618.

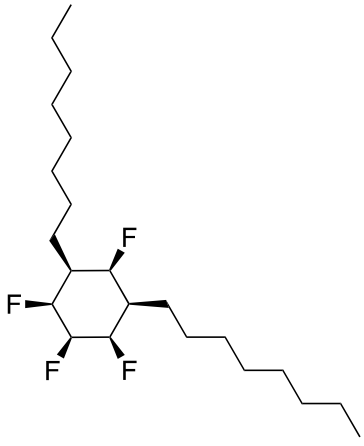
All-*cis* 1,2,3,5-tetrafluoro-4,6-dihexylcyclohexane 12a



Following General Procedure 3, 1,2,3,5-tetrafluoro-4,6-dihexylbenzene (56.2 mg, 0.18 mmol), Rh-CAAC-COD-Cl (2.0 mg, 0.0035 mmol), silica gel (200 mg), and hexane (2 mL) for 24 h, r.t., at 50 bar H_2 gave, after purification by flash chromatography (25—42% diethyl ether in hexane), **12a** (50%, 32 mg, 0.09 mmol) as a white crystalline solid.

m.p. 100—103 °C. IR ν_{max} (solid): 3600 (alkane C-H stretch), 1508 (methyl C-H bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 4.96 (apparent d, J = 43.9 Hz, 2H, ring 1,3C-$\underline{H}$F), 4.59 (apparent d, J = 47.7 Hz, 1H, ring 2C-$\underline{H}$F), 4.48—4.29 (m, 1H, ring 5C-$\underline{H}$F), 1.81 (apparent q, J = 7.7 Hz, 2H, ring 4,6C-$\underline{H}$C), 1.36—1.25 (m, 20H, chain-C$\underline{H}_2$), 0.89 (t, J = 6.6 Hz, 6H, C$\underline{H}_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ : -198.1 (t, J = 13.0 Hz, 1F), -205.1 (t, J = 19.7 Hz, 2F), -212.1 (dd, J = 19.7, 13.0 Hz, 1F); ^{13}C NMR (126 MHz, CDCl3) δ : 88.9 (apparent d, J = 274.5 Hz, 1,2,3,5-$\underline{C}$HF), 37.5 (4,6-$\underline{C}$HC), 32.1 ($\underline{C}H_2CH_2CH_3$), 29.8 ($\underline{C}H_2CH_2CH_2CH_3$), 26.7 (ring-$\underline{C}H_2$), 22.9 (ring-$CH_2\underline{C}H_2$), 19.4 ($\underline{C}H_2CH_3$), 14.4 ($\underline{C}H_3$); HRMS ($ESI^+$) $C_{18}H_{32}F_4$ [M-Na] found 347.2329, requires 347.2338.

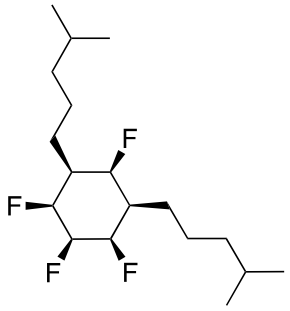
All-*cis* 1,2,3,5-tetrafluoro-4,6-dioctylcyclohexane 12b



Following General Procedure 3, 1,2,3,5-tetrafluoro-4,6-dioctylbenzene (75.8 mg, 0.21 mmol), Rh-CAAC-COD-Cl (2.0 mg, 0.0035 mmol), 4Å molecular sieves (400 mg), and hexane (2 mL) for 10 d, r.t., at 50 bar H_2 gave, after purification by flash chromatography (25—42% diethyl ether in hexane), **12b** (49%, 42 mg, 0.11 mmol) as a white crystalline solid.

m.p. 117—120 °C. IR ν_{max} (solid): 2920 (alkane C-H stretch), 1506 (methyl C-H bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 4.96 (apparent dd, J = 49.8, 6.9 Hz, 2H, ring 1,3C-HF), 4.59 (apparent d, J = 47.3 Hz, 1H, ring 2C-HF), 4.39 (apparent dt, J = 42.0, 28.5 Hz, 1H, ring 5C-HF), 1.80 (q, J = 7.7 Hz, 2H, ring 4,6C-HC), 1.32—1.25 (m, 28H, long chain hydrogens), 0.88 (t, J = 6.9 Hz, 6H, CH_3); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -198.1 (t, J = 13.0 Hz, 1F), -205.1 (t, J = 19.7 Hz, 2F), -212.1 (dd, J = 19.7, 13.0 Hz, 1F); ^{13}C NMR (126 MHz, CDCl3) δ : 89.2 (apparent d, J = 17.0 Hz, 3,5-CHF), 88.5 (apparent d, J = 6.8 Hz, 1-CHF), 87.0 (apparent d, J = 17.0 Hz, 4-CHF), 42.4 (2,6-$CHCH_2$), 32.0 ($CH_2CH_2CH_3$), 30.0 ($CH_2CH_2CH_2CH_3$), 29.6 ($CHCH_2CH_2CH_2$), 29.4 ($CH_2CH_2CH_2CH_2CH_3$), 26.9 ($CHCH_2$), 26.8 ($CHCH_2CH_2$), 22.8 (CH_2CH_3), 14.3 (CH_3); HRMS (ESI^+) $C_{22}H_{40}F_4$[M-Na]$^+$ found 403.2958, requires 403.2963.

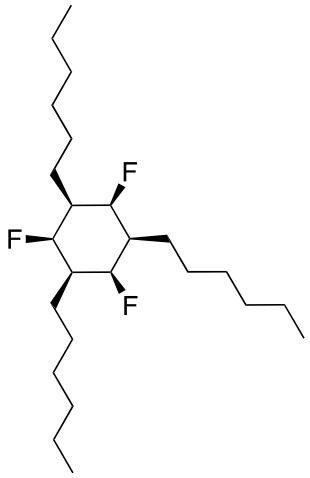
All-*cis* 1,2,3,5-tetrafluoro-4,6-bis(4-methylpentyl)cyclohexane 12c



Following General Procedure 3, 1,2,3,5-tetrafluoro-4,6-bis(4-methylpentyl)benzene (80 mg, 0.25 mmol), Rh-CAAC-COD-Cl (2.0 mg, 0.0035 mmol), 4Å molecular sieves (400 mg), and hexane (2 mL) for 3 d, 50 °C, at 70 bar H_2 gave, after purification by flash chromatography (25—42% diethyl ether in hexane), **12c** (42%, 34.3 mg, 0.11 mmol) as a white crystalline solid.

m.p. 111—119 °C. IR ν_{max} (solid): 3184 (sp^3 C-H stretch), 2848 (sp^3 C-H stretch), 1521 ((sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 4.97 (apparent dd, J = 49.8, 7.0 Hz, 2H, ring1,3C-HF), 4.59 (apparent d, J = 49.4 Hz, 1H, ring 2C-HF), 4.40 (apparent dtt, J = 41.8, 28.5, 2.9 Hz, 1H, ring 5C-HF), 2.17 (m, 1H, ring 4,6C-CHC), 1.79 (q, J = 7.6 Hz, 2H, CH), 1.58 (m, 6H, ring-$CHHCH_2$), 1.43 (dq, J = 15.1, 7.5 Hz, 2H, ring-CHH), 1.23 (q, J = 7.6 Hz, 4H, CH_2CH), 0.89 (d, J = 6.6 Hz, 12H, CH_3); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -198.1 (t, J = 13.1 Hz, 1F), -205.0 (t, J = 19.7 Hz, 1F), -212.1 (dd, J = 19.6, 13.0 Hz, 2F); ^{13}C NMR (126 MHz, CDCl3) δ : 88.5 (m, 1,2,3,5-CHF), 55.1 (4,6-$CHCH_2$), 38.9 (CH_2CH), 28.0 ($CH_2CH_2CH_2CH$), 27.0 (CH), 24.5 (CH_2CH_2CH), 22.7 (CH_3); HRMS (ESI^+) $C_{18}H_{32}F_4$ [M-Na] found 347.2327, requires 347.2338

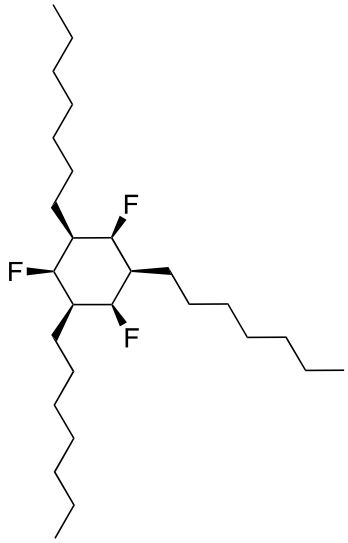
All-*cis* 1,3,5-trifluoro-2,4,6-trihexylcyclohexane 16a



Following General Procedure 3, 1,3,5-trifluoro-2,4,6-trihexylbenzene (87.3 mg, 0.23 mmol), Rh-CAAC-COD-Cl (2.0 mg, 0.0035 mmol), 4Å molecular sieves (400 mg), and hexane (2 mL) for 7 d, 50 °C, at 70 bar H_2 gave, after purification by flash chromatography (25—42% diethyl ether in hexane), **16a** (41%, 36.5 mg, 0.09 mmol) as a white crystalline solid.

m.p. 121—127 °C. IR ν_{max} (solid): 2900 (alkane C-H stretch), 1506 (methyl C-H bend) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 4.60 (m, 3H, ring-$\underline{H}F$), 1.75 (q, J = 7.6 Hz, 3H, ring-$\underline{H}CH_2$) 1.41 (q, J = 7.4 Hz, 6H, ring-$C\underline{H_2}$), 1.30 (m, 18H, long chain hydrogens), 0.89 (m, 9H, $C\underline{H_3}$); $^{19}F\{^{1}H\}$ NMR (470 MHz, $CDCl_3$) δ : -205.3 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 90.4 (apparent d, J = 191.6 Hz, $\underline{C}HF$), 66.2 ($\underline{C}HCH_2$), 31.8 ($\underline{C}H_2CH_2CH_3$), 29.4 ($\underline{C}H_2CH_2CH_2CH_3$), 27.6 ($\underline{C}H_2CH_2CH_2CH_2CH_2CH_3$), 26.7 ($\underline{C}H_2CH_2CH_2CH_2CH_3$), 22.6 ($\underline{C}H_2CH_3$), 14.1 ($\underline{C}H_3$); HRMS ($ESI^+$) $C_{24}H_{45}F_3$[M-Na] found 413.3357, requires 414.3371.

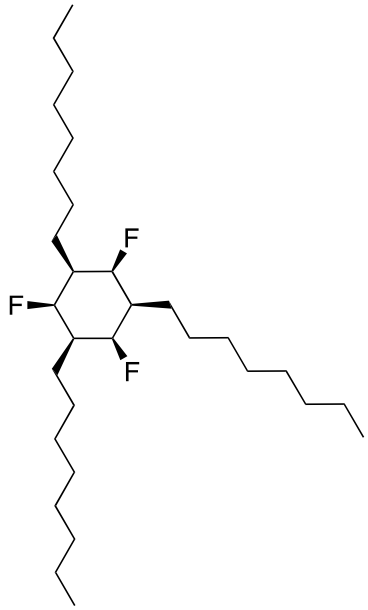
All-*cis* 1,3,5-trifluoro-2,4,6-triheptylcyclohexane 16b



Following General Procedure 3, 1,3,5-trifluoro-2,4,6-triheptylbenzene (90.7 mg, 0.21 mmol), Rh-CAAC-COD-Cl (2.0 mg, 0.0035 mmol), 4Å molecular sieves (400 mg), and hexane (2 mL) for 7 d, 50 °C, at 70 bar H_2 gave, after purification by flash chromatography (25—42% diethyl ether in hexane), **16b** (22%, 19.7 mg, 0.05 mmol) as a white crystalline solid.

m.p. 125—130 °C.IR ν_{max} (solid): 2920 (sp^3 C-H stretch), 1440 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 4.70-4.59 (m, 3H, aryl-HF), 1.75 (apparent q, J = 7.1 Hz, 3H, aryl-HCH_2), 1.43-1.25 (m, 36H, alkyl-H), 0.89 (t, J = 6.9 Hz, 9H, CH_3); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -205.3 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 101.5 (apprarent d, J = 196.8 Hz, aryl-CF), 40.1 (aryl-CCH_2), 29.8 ($CH_2CH_2CH_3$), 29.4 ($CH_2CH_2CH_2CH_2CH_3$), 26.9 ($CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 22.8 ($CH_2CH_3$), 14.3 ($CH_3$); HRMS ($ESI^+$) $C_{27}H_{51}F_3$ [M-Na] found 455.3831, requires 455.3841.

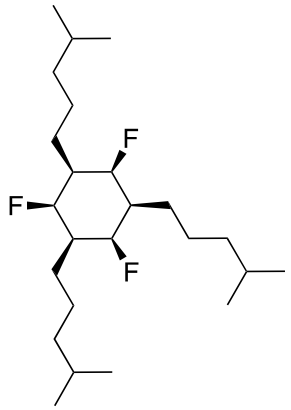
All-cis 1,3,5-trifluoro-2,4,6-trioctylcyclohexane 16c



Following General Procedure 3, 1,3,5-trifluoro-2,4,6-trioctylbenzene (33.6 mg, 0.0717 mmol), Rh-CAAC-COD-Cl (1.6 mg, 0.0028 mmol), 4Å molecular sieves (400 mg), and hexane (2 mL) for 10 d, 50 °C, at 70 bar H_2 gave, after purification by flash chromatography (25—42% diethyl ether in hexane), **16c** (40%, 13.7 mg, 0.029 mmol) as a white crystalline solid.

m.p. 119-122 °C. IR ν_{max} (solid): 2954 (sp^3 C-H stretch), 2875 (sp^3 C-H stretch), 2852 (sp^3 C-H stretch), 1460 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 4.64 (apparent d, J = 46.9 Hz, 3H, ring-C<u>H</u>F), 1.75 (apparent q, J = 7.4 Hz, 3H, ring-C<u>H</u>C), 1.44—1.39 (m, 6H, long chain-C<u>H</u>$_2$), 1.31—1.26 (m, 36H, long chain-C<u>H</u>$_2$), 0.88 (t, J = 6.8 Hz, 9H, C<u>H</u>$_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -205.3 (s, 3F); ^{13}C NMR (126 MHz, CDCl3) δ : 92.3 (apparent d, J = 179.0 Hz, <u>C</u>HF), 42.8 (<u>C</u>HCH$_2$), 32.1 (<u>C</u>H$_2$CH$_2$CH$_3$), 29.9 (<u>C</u>H$_2$CH$_2$CH$_2$CH$_3$), 29.7 (<u>C</u>H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 29.4 (<u>C</u>H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 27.8 (CH<u>C</u>H$_2$), 27.1 (CHCH$_2$<u>C</u>H$_2$), 22.8 (<u>C</u>H$_2$CH$_3$), 14.3 (<u>C</u>H$_3$); HRMS (ESI^+) $C_{30}H_{57}F_3$ [M-Na] found 497.4305, requires 497.4310.

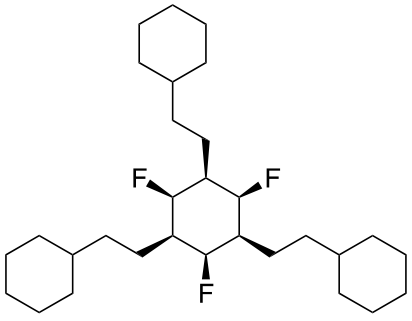
All-*cis* 1,3,5-trifluoro-2,4,6-tris(4-methylpentyl)cyclohexane 16d



Following General Procedure 3, 1,3,5-trifluoro-2,4,6-tris(4-methylpentyl)benzene (292.5 mg, 0.76 mmol), Rh-CAAC-COD-Cl (6.5 mg, 0.0114 mmol), 4Å molecular sieves (1.5 g), silica gel (700 mg), and hexane (15 mL) for 7 d, 50 °C, at 50 bar H_2 gave, after purification by flash chromatography (25—42% diethyl ether in hexane), **16d** (68%, 201.2 mg, 0.515 mmol) as a white crystalline solid.

m.p. 123—130 °C. IR ν_{max} (solid): 2899 (sp^3 C-H stretch), 1462 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ : 4.65 (dt, *J* = 48.0, 2.4 Hz, 3H, ring-C<u>H</u>F), 1.74 (q, *J* = 7.6 Hz, 3H, ring-C<u>H</u>), 1.62 – 1.49 (m, 12H, ring-CHC<u>H</u>$_2$C<u>H</u>$_2$CH$_2$CH$_2$CH isoCH$_3$), 1.48 – 1.36 (m, 3H, C<u>H</u> isoCH$_3$), 0.89 (d, *J* = 6.6 Hz, 18H, isoC<u>H</u>$_3$), 0.87 – 0.78 (m, 4H, C<u>H</u>$_2$CH isoCH$_3$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ : -205.24 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ : 99.2 (apparent d, J = 165.3 Hz, <u>C</u>HF), 39.5 (<u>C</u>HCH$_2$), 39.1 (<u>C</u>H$_2$CH), 28.0 (<u>C</u>H$_2$CH$_2$CH$_2$CH), 27.9 (<u>C</u>H), 24.6 (<u>C</u>H$_2$CH$_2$CH), 22.8 (<u>C</u>H$_3$); HRMS (ESI^+) $C_{24}H_{45}F_3$ [M-K] found 429.3095, requires 429.3110.

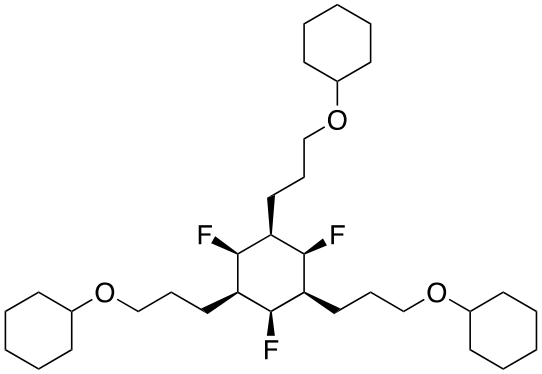
All-cis 2,4,6-trifluorocyclohexane-1,3,5-triyl)tris(ethane-2,1-diyl))tricyclohexane 16e



Following General Procedure 3, ((2,4,6-trifluorobenzene-1,3,5-triyl)tris(ethane-2,1-diyl))tricyclohexane (361 mg, 0.78 mmol), Rh-CAAC-COD-Cl (6.4 mg, 0.013 mmol), 4Å molecular sieves (1.5 g), silica gel (700 mg), and hexane (15 mL) for 7 d, 50 °C, at 50 bar H_2 gave, after purification by flash chromatography (0—5% Et_2O in hexane), **16e** (31%, 112.7 mg, 0.24 mmol) as a white crystalline solid.

m.p. 225—227 °C. IR ν_{max} (solid): 3116 (sp^3 C-H stretch), 1456 (sp^3 bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.64 (apparent dt, J = 48.0, 2.2 Hz, 3H, C<u>H</u>F), 1.42—1.38 (m, 3H, C<u>H</u>CH_2), 1.32—1.11 (m, 33H, side ring-<u>H</u>), 0.94—0.79 (m, 12H, $C\underline{H}_2C\underline{H}_2$); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ: -205.3 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 90.4 (apparent d, J = 204.1 Hz, 3C, aryl-<u>C</u>F), 38.0 (s, 3C, aryl-<u>C</u>H), 34.7 (s, 3C, trirings-<u>C</u>HCH_2), 33.5 (s, 6C, trirings-ortho-<u>C</u>H_2), 26.8 (s, 6C, aryl-CH<u>C</u>H_2<u>C</u>H_2), 26.5 (s, 6C, trirings-meta-<u>C</u>H_2), 25.0 (s, 3C, trirings-para-<u>C</u>H_2); HRMS (ESI^+) $C_{30}H_{51}F_3$ [M+Na] found 491.3829, requires 491.3840.

(All-*cis*-2,4,6-trifluorocyclohexane-1,3,5-triyl) tris(propane-3,1-diyl))tris(oxy))tricyclohexane 16f

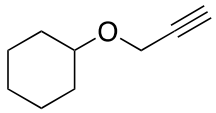


Following General Procedure 3, (((2,4,6-trifluorobenzene-1,3,5-triyl)tris(propane-3,1-diyl))tris(oxy))tricyclohexane (410.3 mg, 0.74 mmol), Rh-CAAC-COD-Cl (12.7 mg, 0.022 mmol), 4Å molecular sieves (3.2 g), silica gel (1.6 mg), and hexane (40 mL) for 8 d, 50 °C, at 50 bar H_2 gave, after purification by flash chromatography (5—10% acetone in DCM), **16f** (30%, 112.6 mg, 0.22 mmol) as a white crystalline solid.

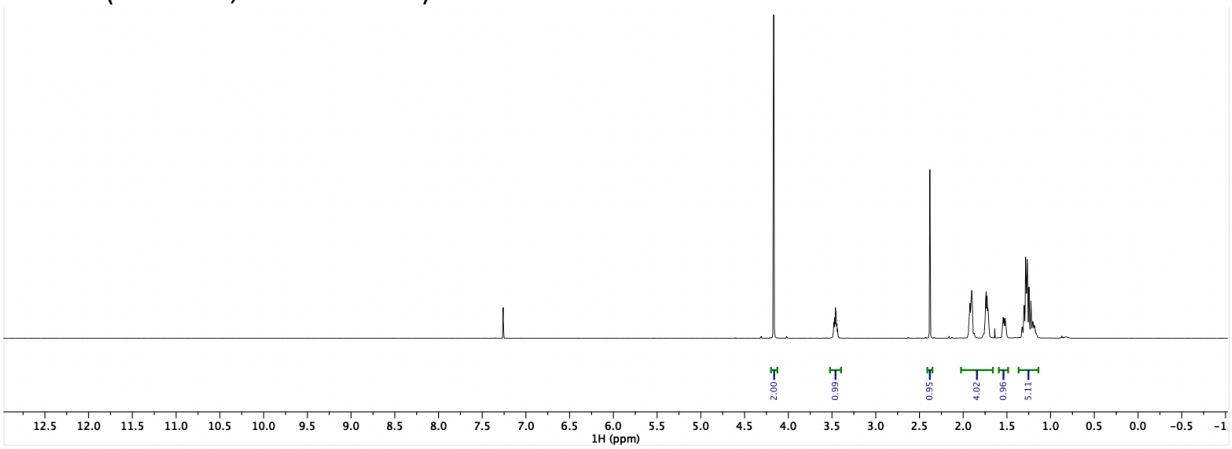
m.p. 91-92 °C. IR ν_{max} (solid): 2926 (sp^3 C-H stretch), 2852 (C-H stretch), 1446 (sp^3 bend), 1076 (C-O stretch) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.69 (apparent d, J = 47.7 Hz, 3H, CFH), 3.49 (t, J = 6.4 Hz, 6H, CH_2O), 3.21 (m, 3H, OCH), 1.89 (apparent q, J = 7.0, 5.1 Hz, 6H, ortho-$C\underline{H}_2$ top or bottom), 1.82 (apparent dd, J = 10.1, 5.6 Hz, 6H, para-$C\underline{H}_2$), 1.70 (apparent dt, J = 10.5, 6.7 Hz, 12H, $C\underline{H}_2CH_2O$ & meta-$C\underline{H}_2$ top or bottom), 1.55—1.52 (m, 6H, $CHC\underline{H}_2$), 1.24 (apparent h, J = 10.0, 8.9 Hz, 15H, remaining H); $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ: -205.6 (C<u>F</u>H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 90.4 (apparent d, J = 181.6 Hz, 3x<u>C</u>FH), 77.7 (3x<u>C</u>HO), 68.0 (<u>C</u>H_2O), 43.7 (<u>C</u>HCH_2), 33.5 (6x ortho-<u>C</u>H_2), 27.4 (3x<u>C</u>H_2CH_2O), 26.0 (3xCH<u>C</u>H_2), 24.7 (3x para-<u>C</u>H_2), 24.3 (6x meta-<u>C</u>H_2); HRMS (ESI^+) $C_{33}H_{57}F_3O_3$ [M-Na] found 581.4141, requires 581.4158.

3 Images of NMR spectra for synthesized compounds

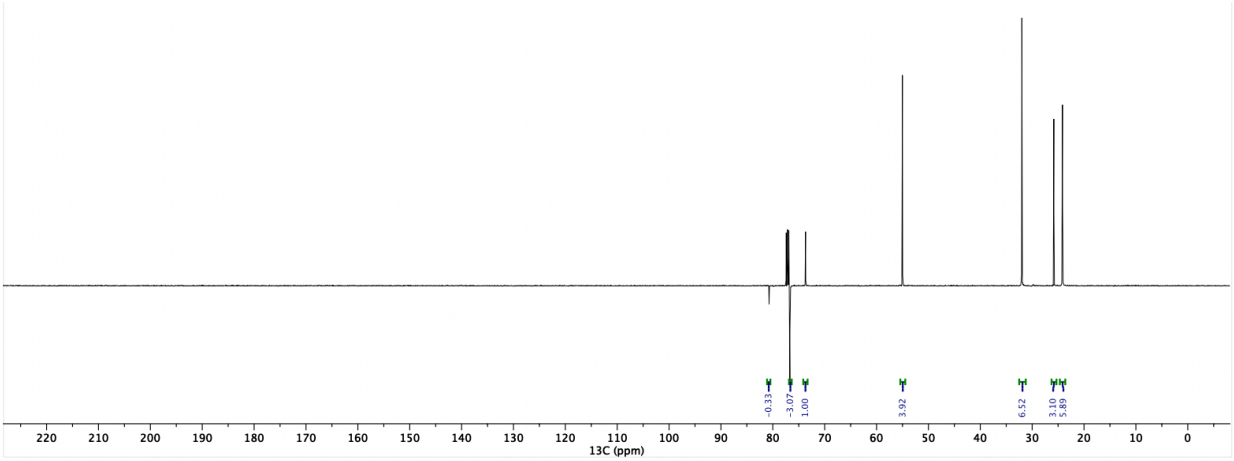
(Prop-2-yn-1-yloxy)cyclohexane



^{1}H NMR (500 MHz, Chloroform-*d*)

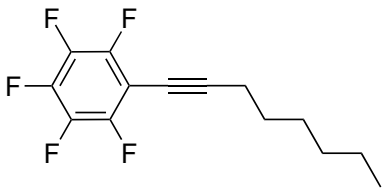


^{13}C NMR (126 MHz, Chloroform-*d*)

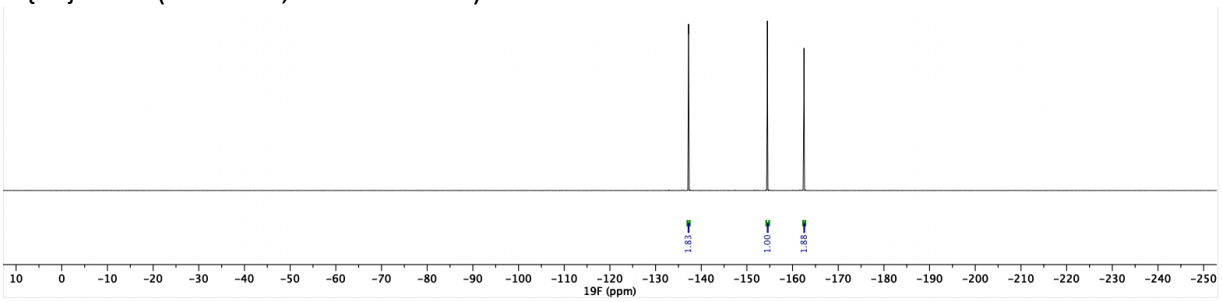


Data is in agreement with that reported in the literature.[1]

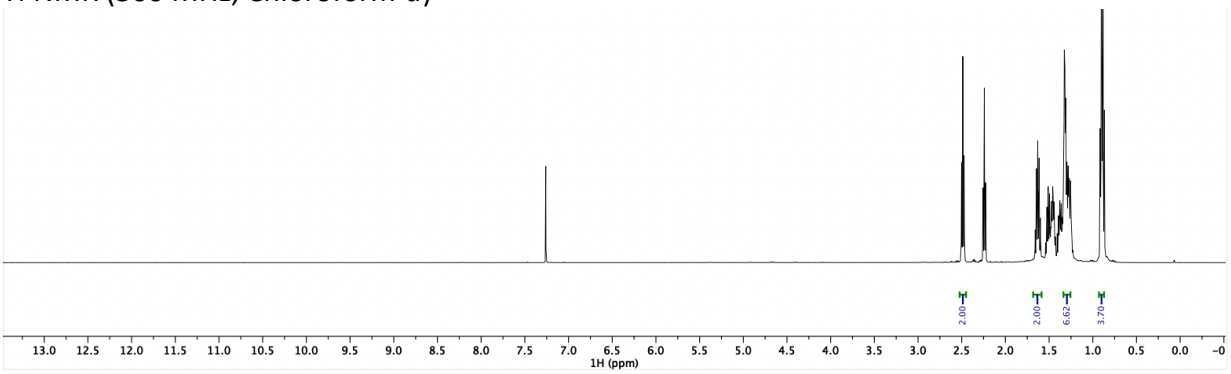
1,2,3,4,5-Pentafluoro-6-(octynyl)benzene (6)



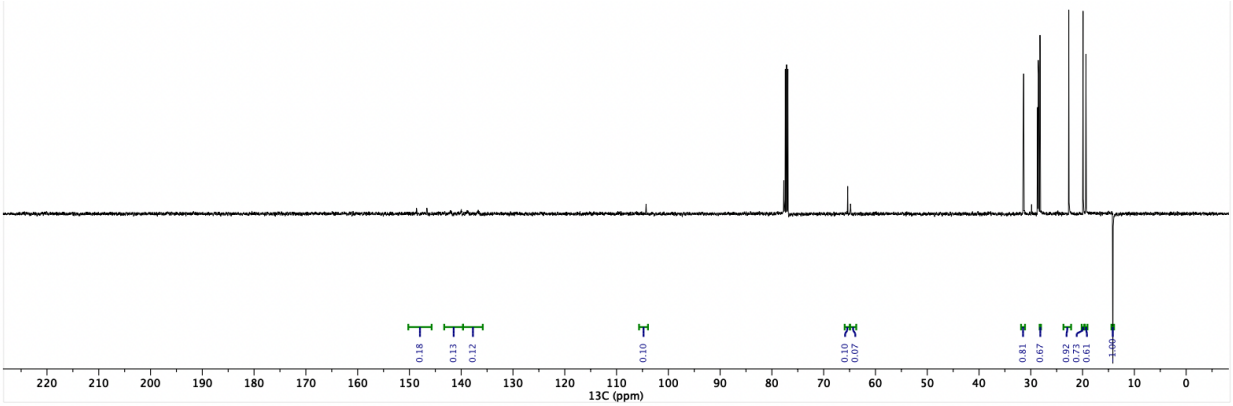
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



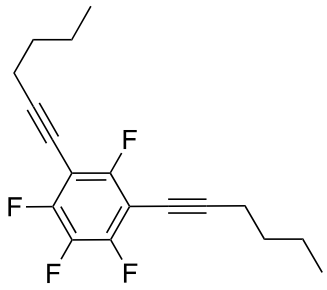
^{1}H NMR (500 MHz, Chloroform-*d*)



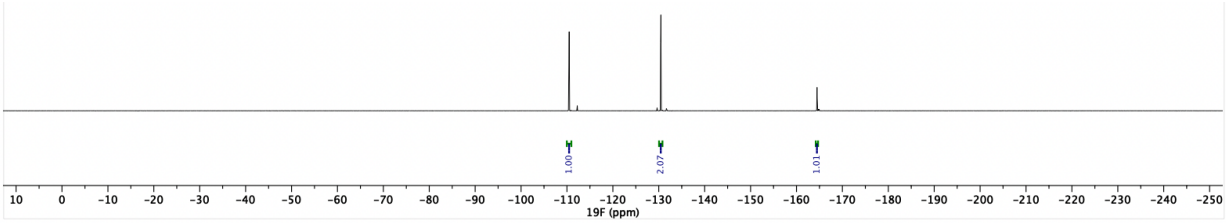
^{13}C NMR (126 MHz, Chloroform-*d*)



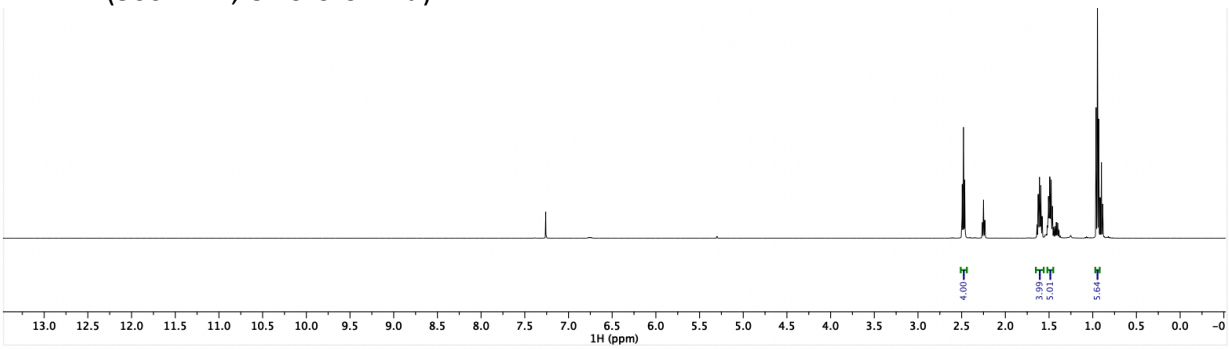
1,2,3,5-Tetrafluoro-4,6-di(1-hexynyl)benzene (10a)



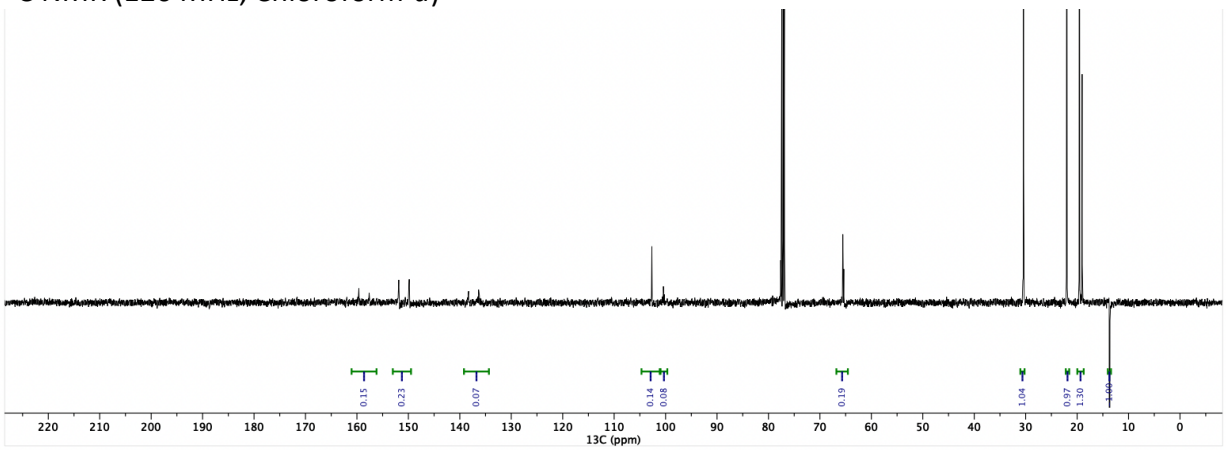
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



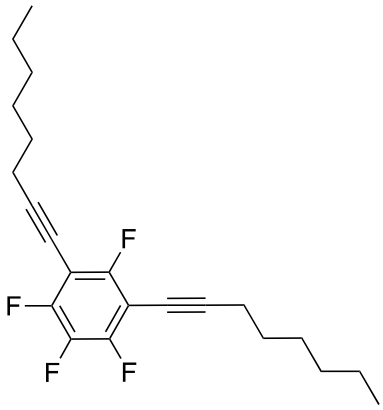
^{1}H NMR (500 MHz, Chloroform-*d*)



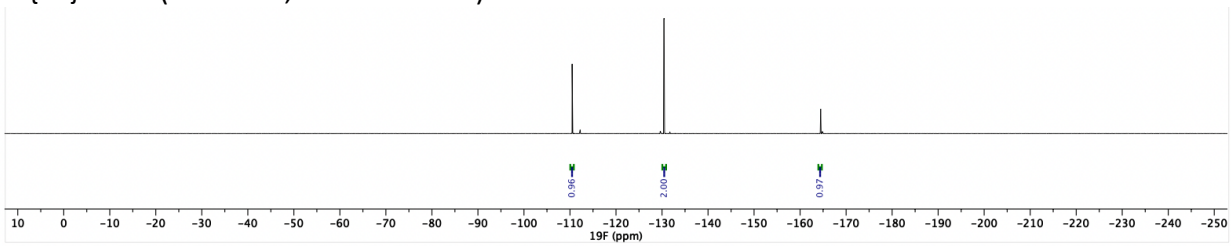
^{13}C NMR (126 MHz, Chloroform-*d*)



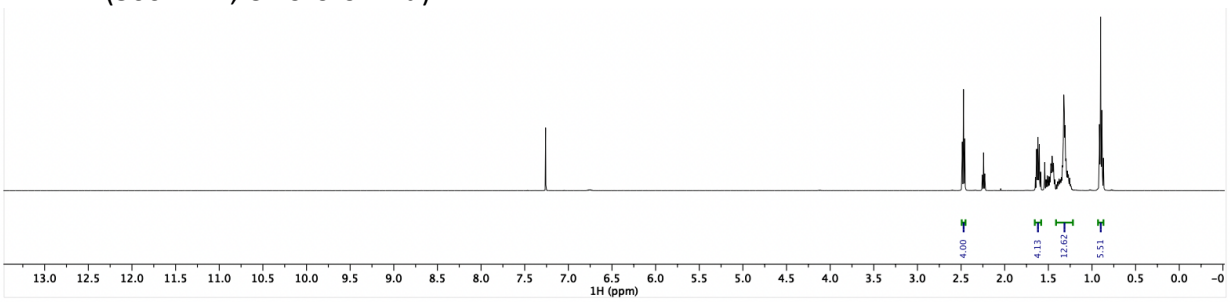
1,2,3,5-Tetrafluoro-4,6-(dioctynyl)benzene (10b)



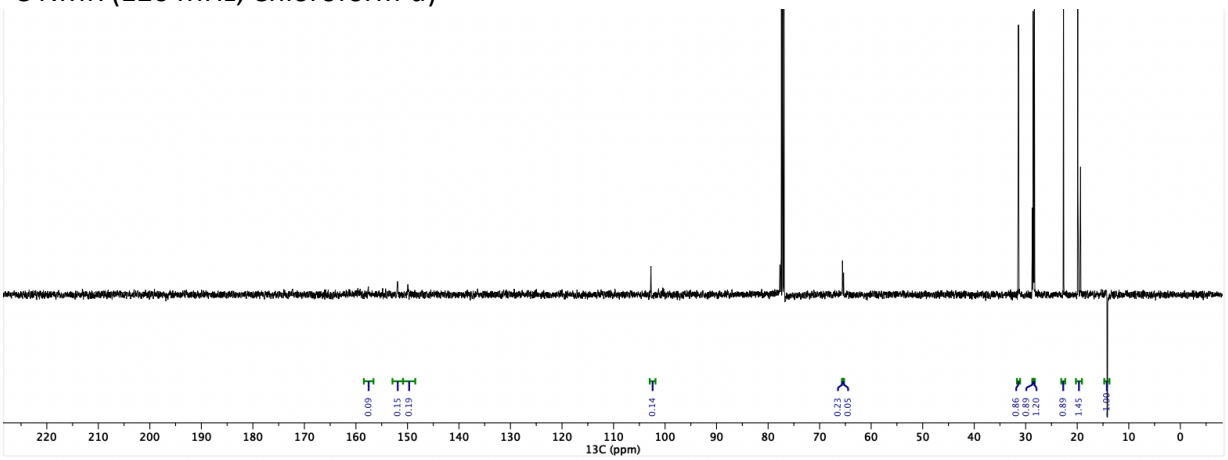
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



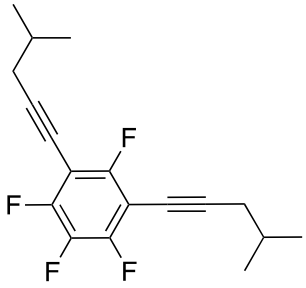
^{1}H NMR (500 MHz, Chloroform-*d*)



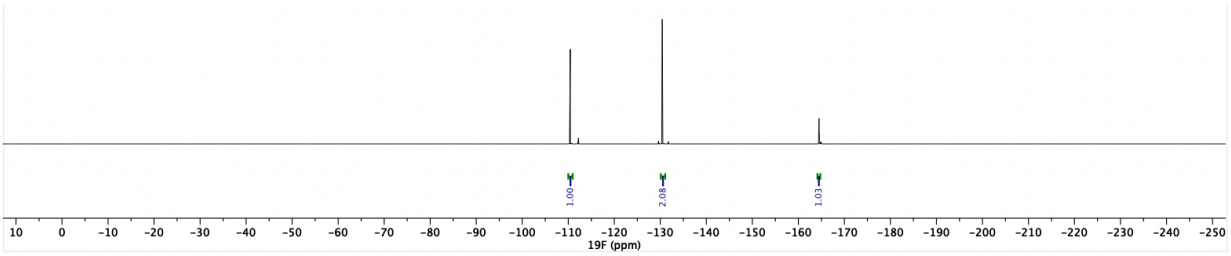
^{13}C NMR (126 MHz, Chloroform-*d*)



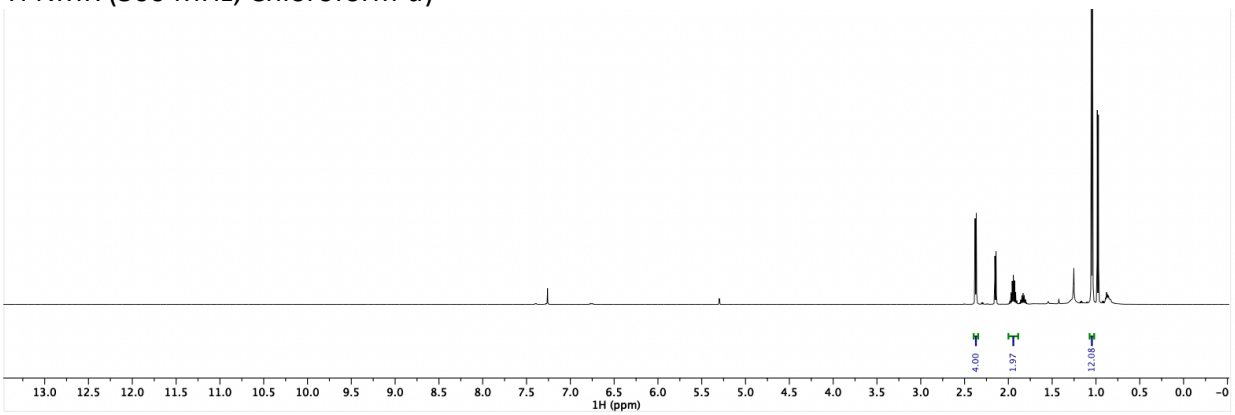
1,2,3,5-Tetrafluoro-4,6-bis(4-methylpentynyl)benzene (10c)



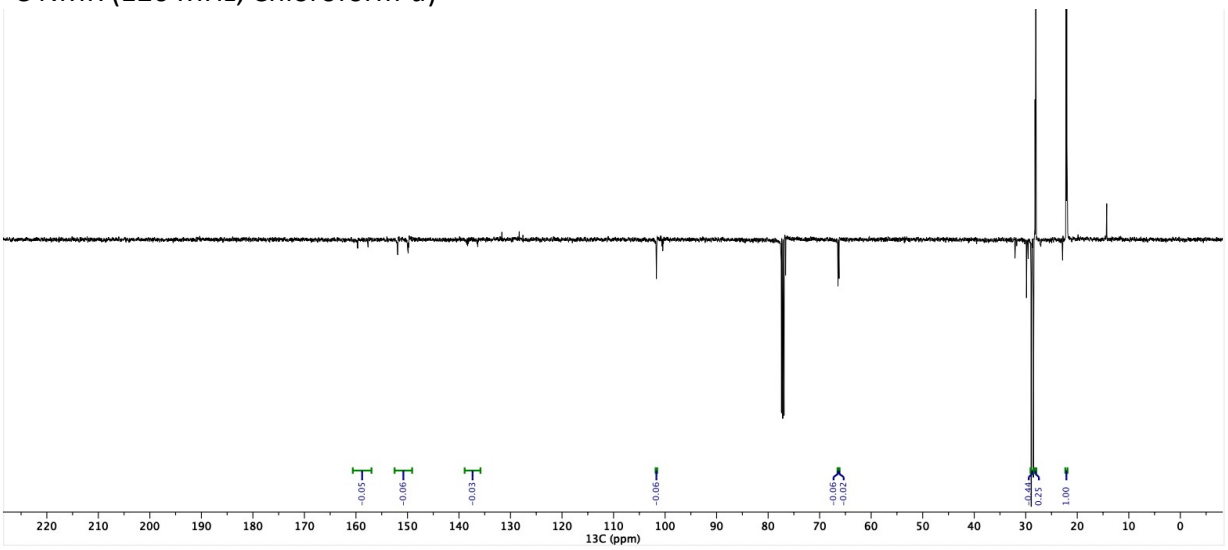
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



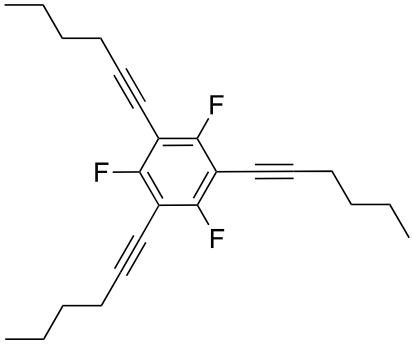
^{1}H NMR (500 MHz, Chloroform-*d*)



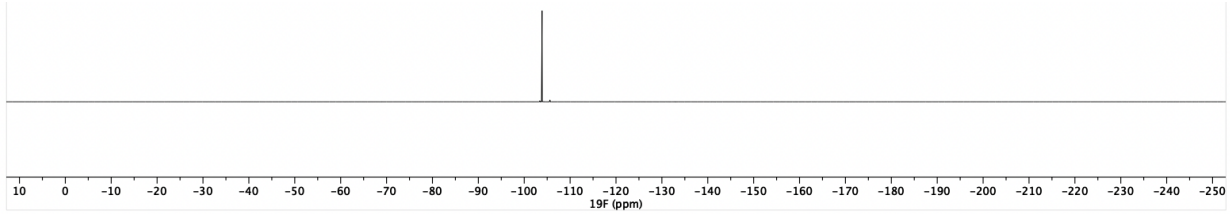
^{13}C NMR (126 MHz, Chloroform-*d*)



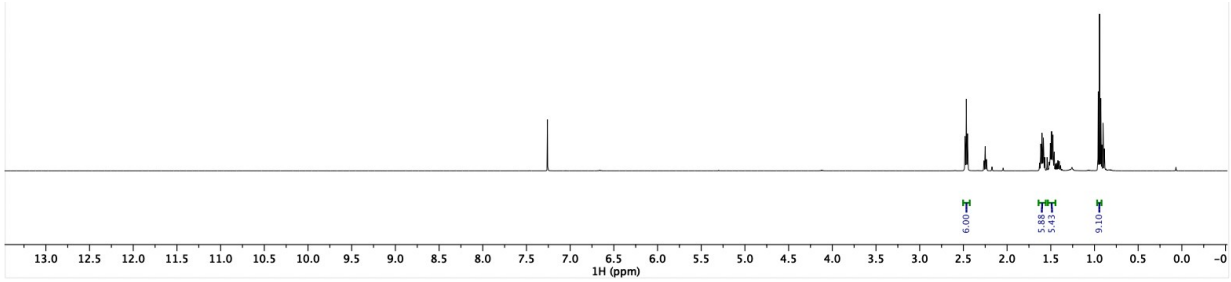
1,3,5-Trifluoro-2,4,6-tri-1-hexynylbenzene (14a)



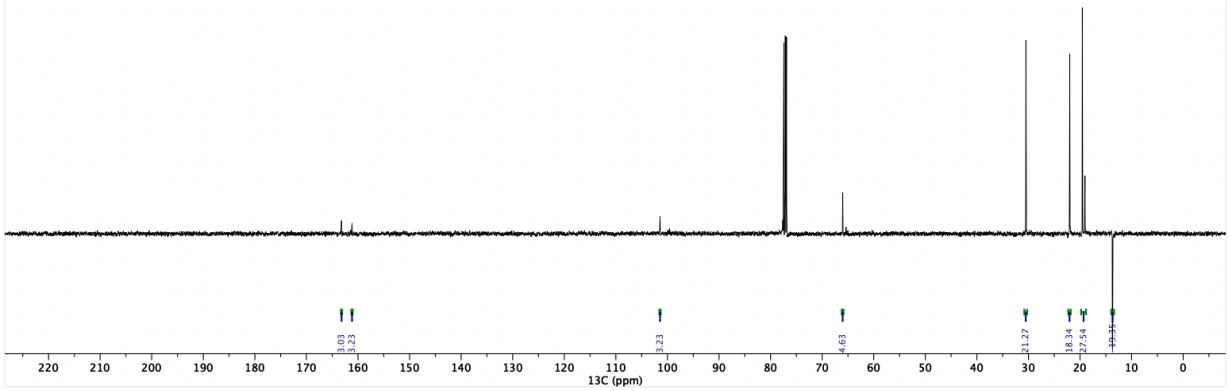
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



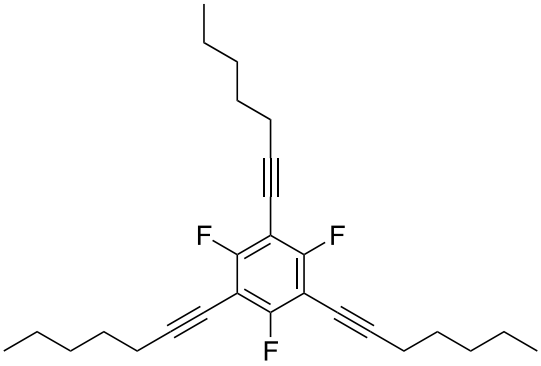
^{1}H NMR (500 MHz, Chloroform-*d*)



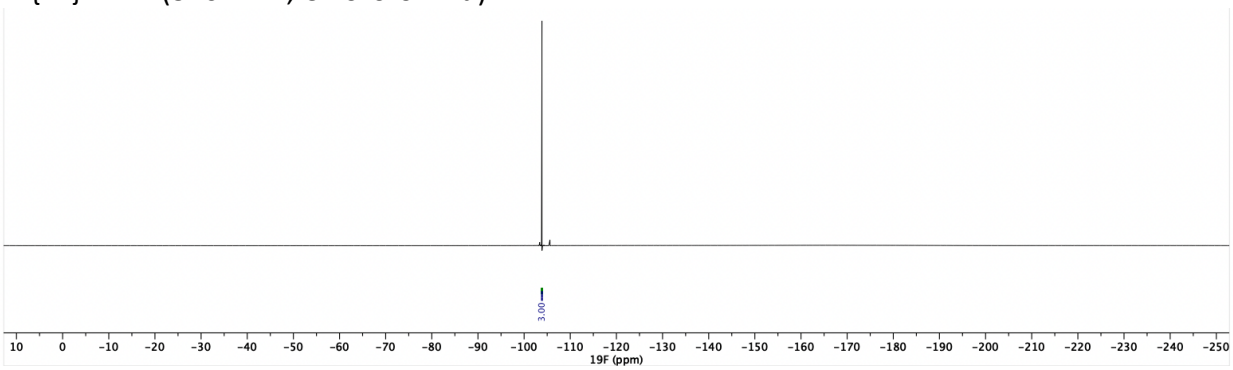
^{13}C NMR (126 MHz, Chloroform-*d*)



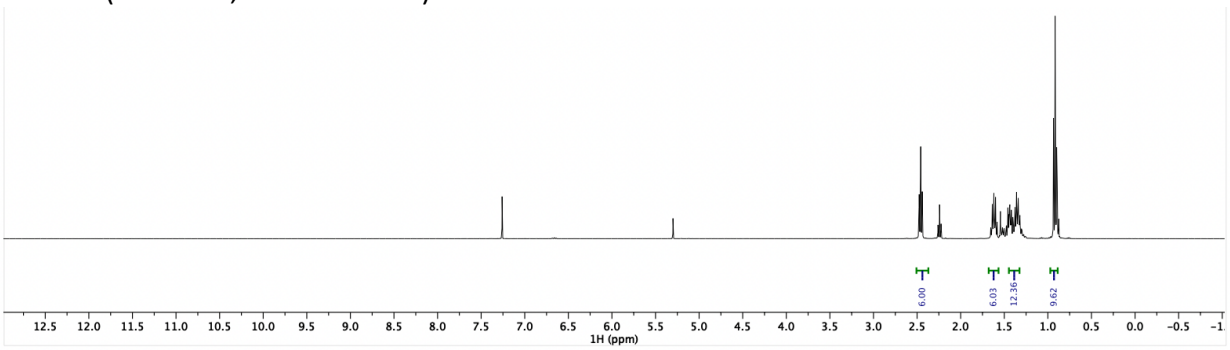
1,3,5-trifluoro-2,4,6-tri(heptynyl)benzene (14b)



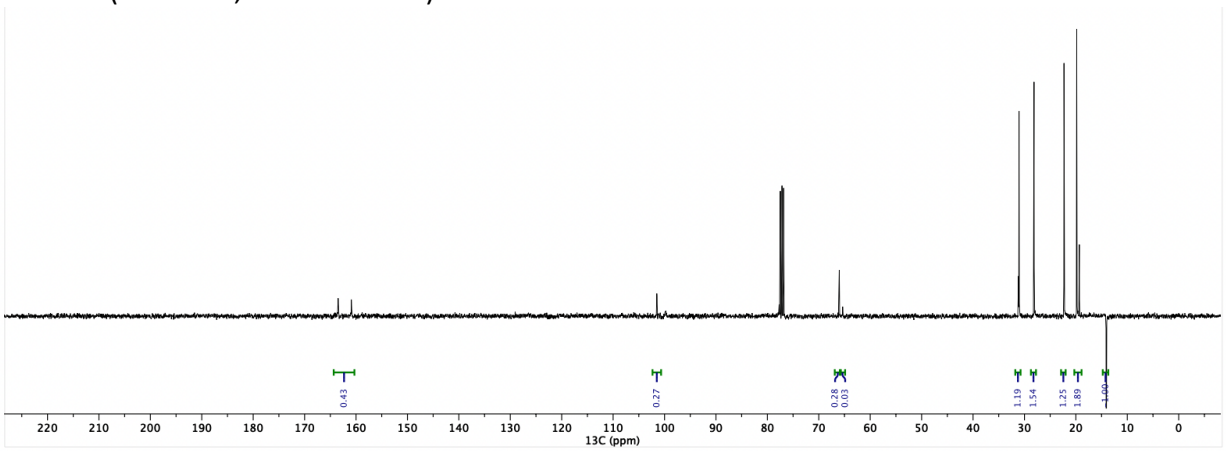
$^{19}F\{^{1}H\}$ NMR (376 MHz, Chloroform-*d*)



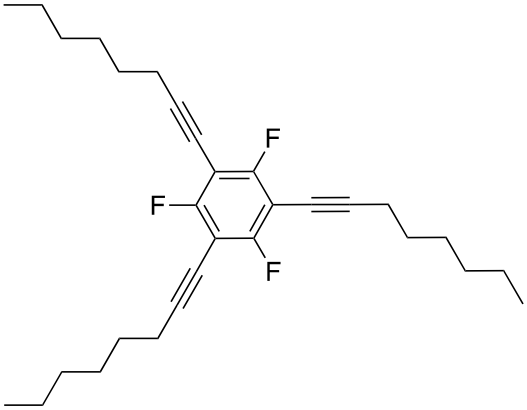
^{1}H NMR (400 MHz, Chloroform-*d*)



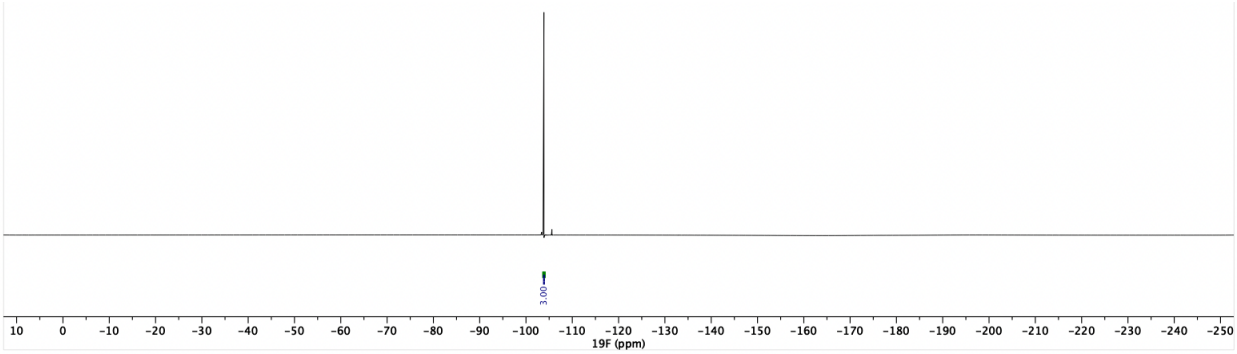
^{13}C NMR (101 MHz, Chloroform-*d*)



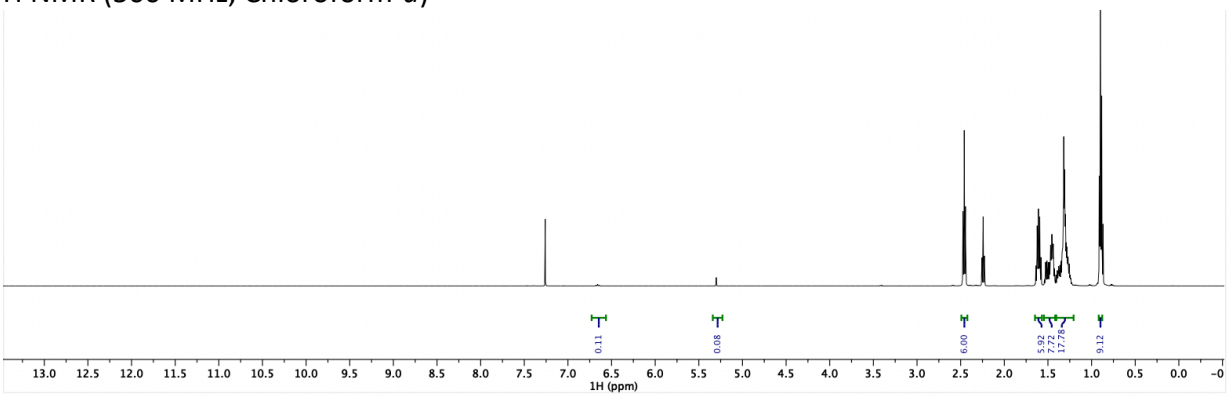
1,3,5-Trifluoro-2,4,6-(trioctynyl)benzene (14c)



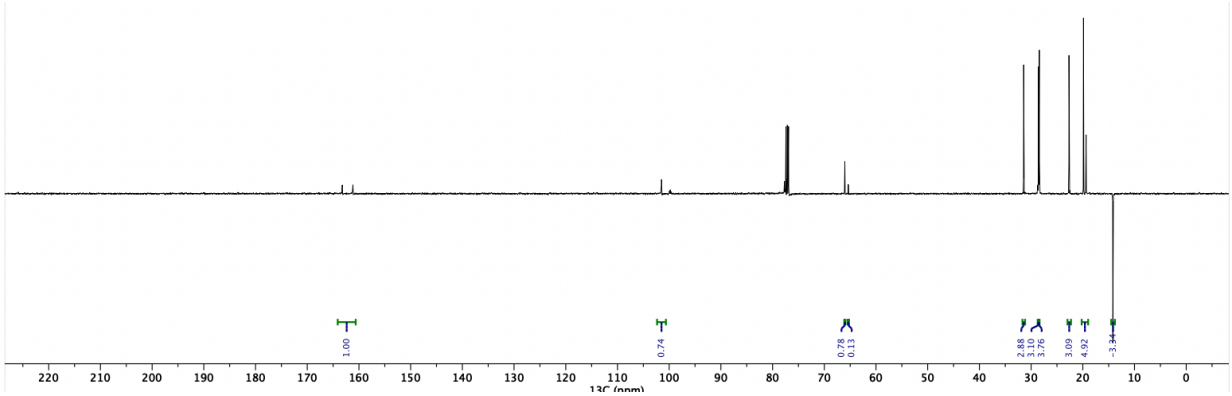
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



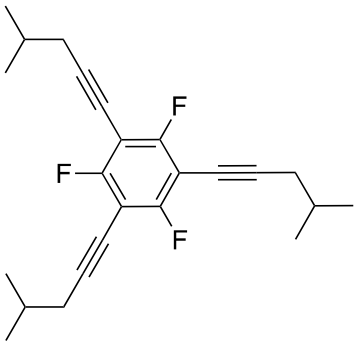
^{1}H NMR (500 MHz, Chloroform-*d*)



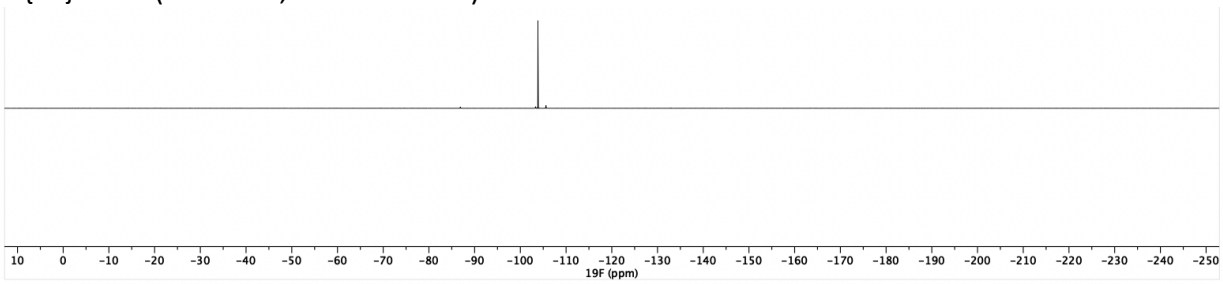
^{13}C NMR (126 MHz, Chloroform-*d*)



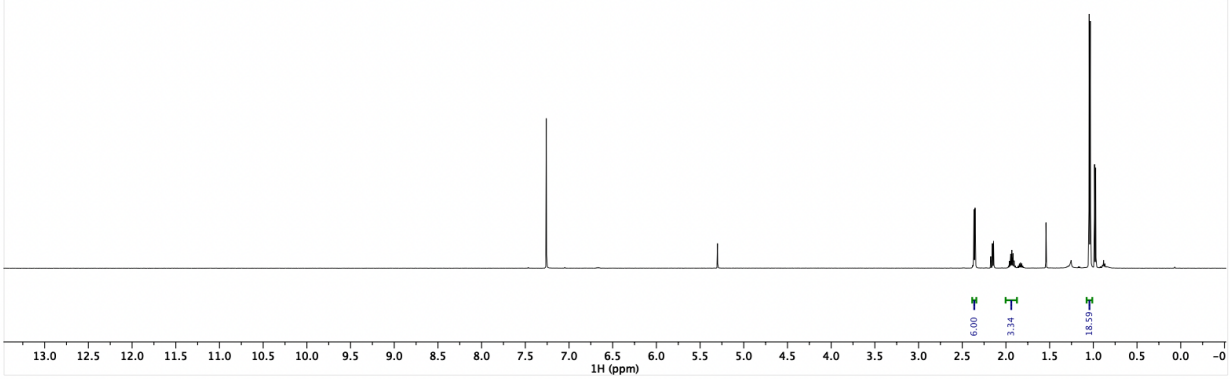
1,3,5-Trifluoro-2,4,6-tris(4-methylpent-1-yn-1-yl)benzene (14d)



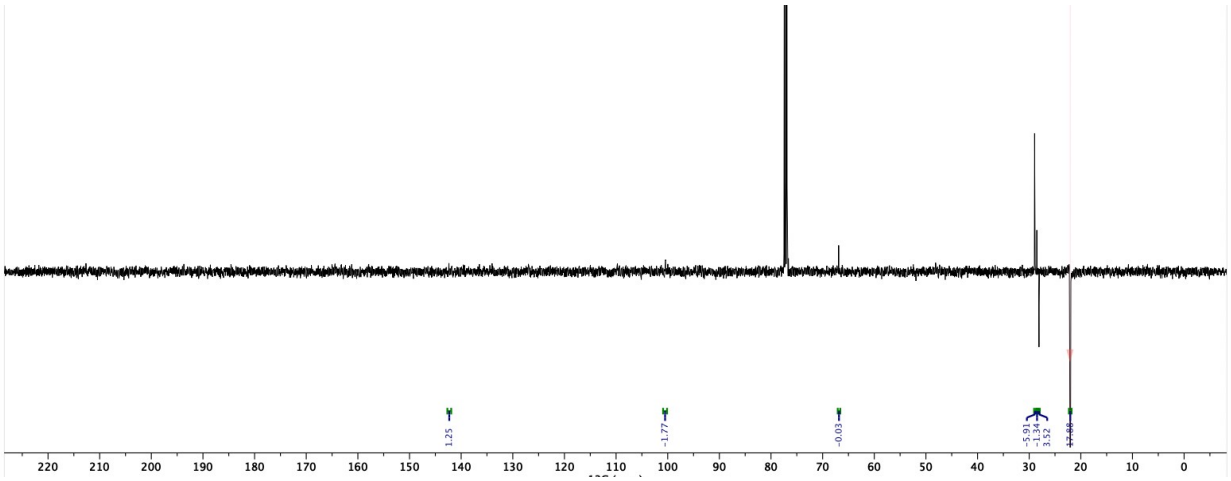
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



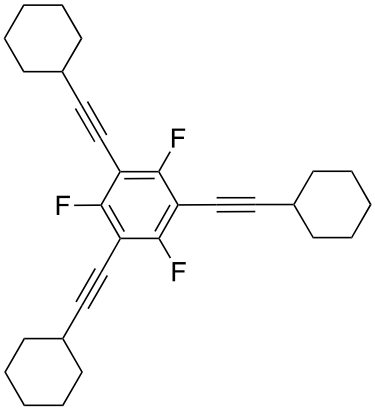
^{1}H NMR (500 MHz, Chloroform-*d*)



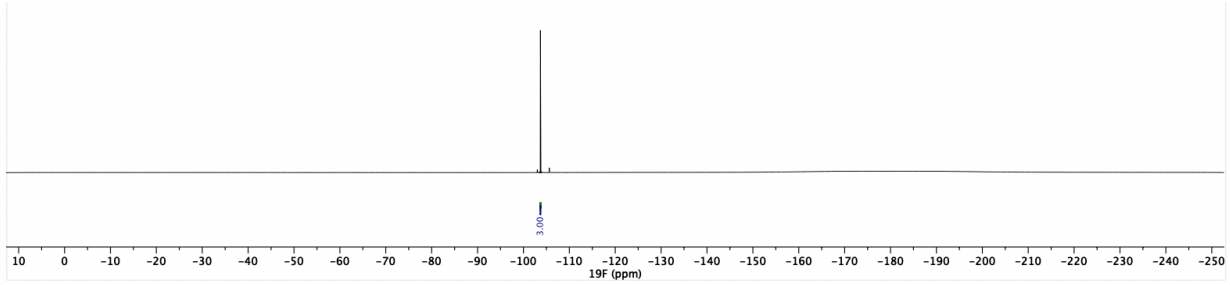
^{13}C NMR (126 MHz, Chloroform-*d*)



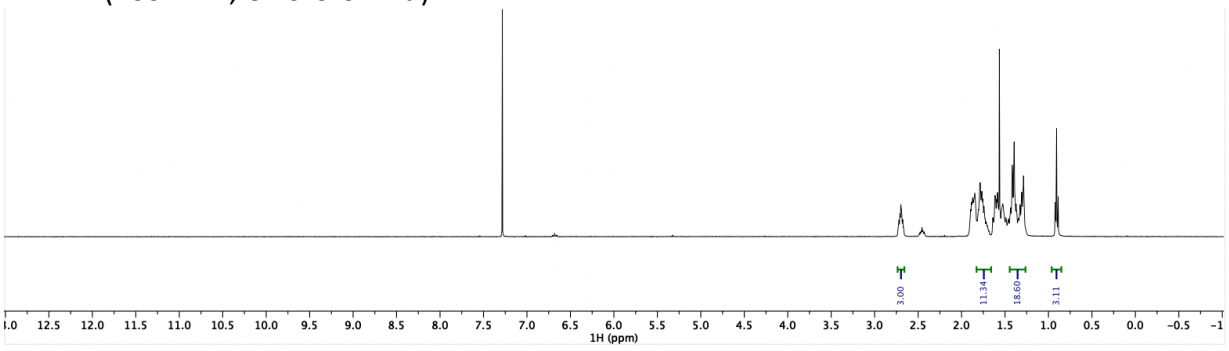
((2,4,6-Trifluorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl)tricyclohexane (14e)



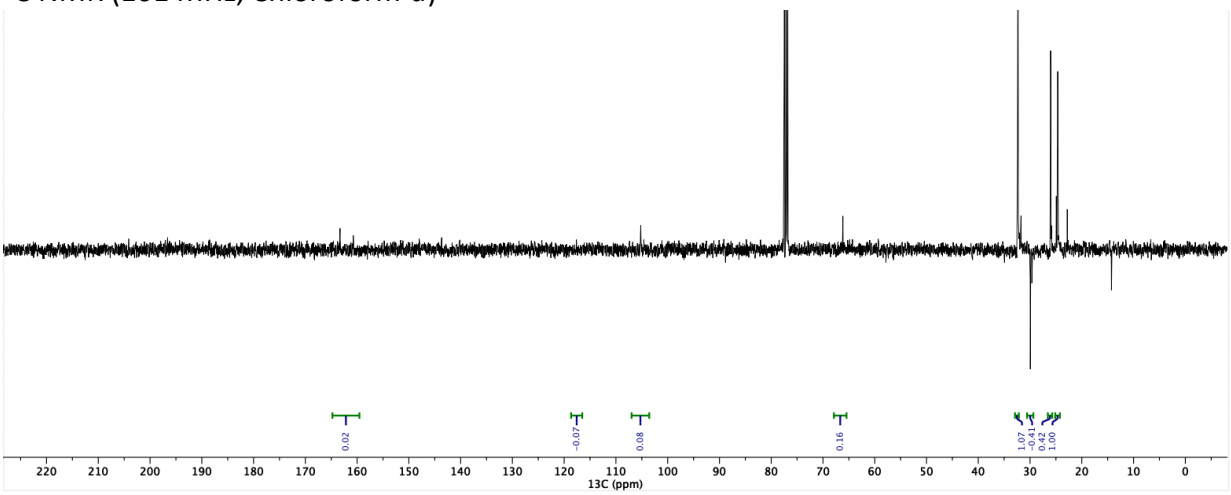
$^{19}F\{^{1}H\}$ NMR (376 MHz, Chloroform-*d*)



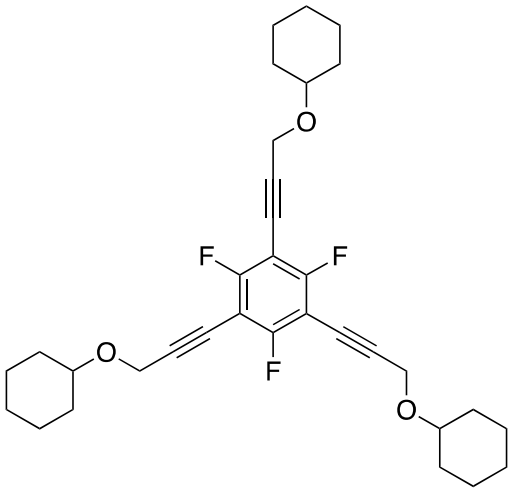
^{1}H NMR (400 MHz, Chloroform-*d*)



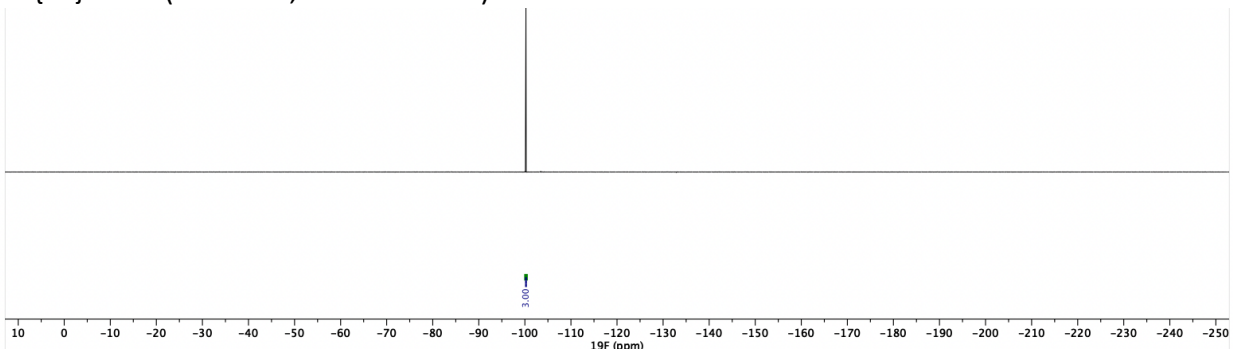
^{13}C NMR (101 MHz, Chloroform-*d*)



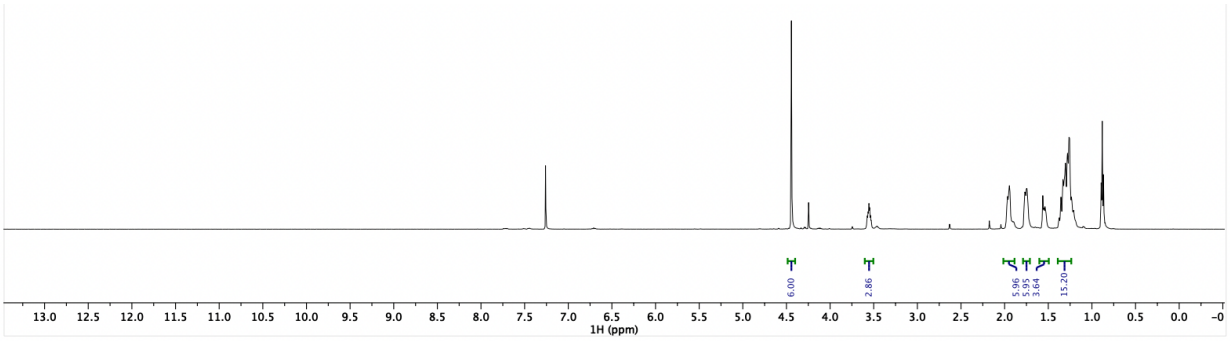
(((2,4,6-trifluorobenzene-1,3,5-triyl)tris(prop-2-yne-3,1-diyl))tris(oxy))tricyclohexane (14f)



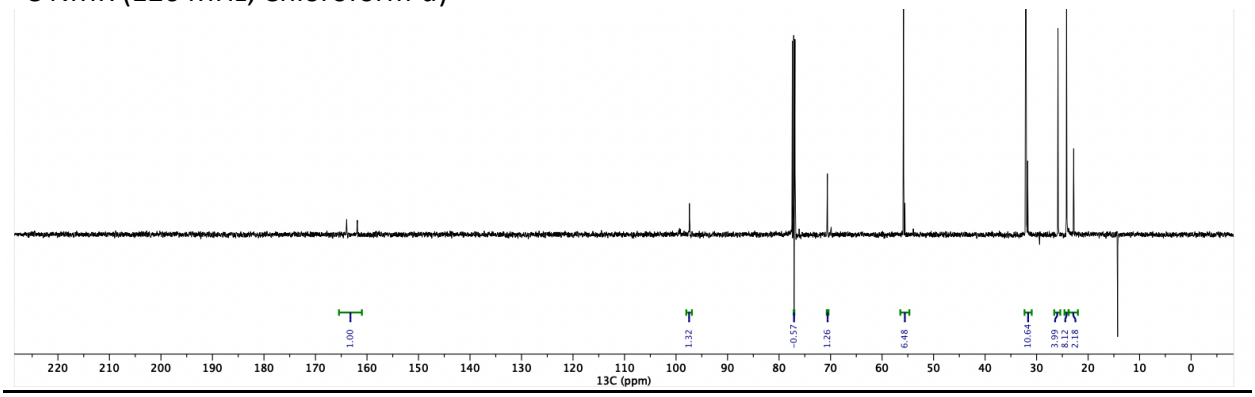
^{19}F{^{1}H} NMR (470 MHz, Chloroform-*d*)



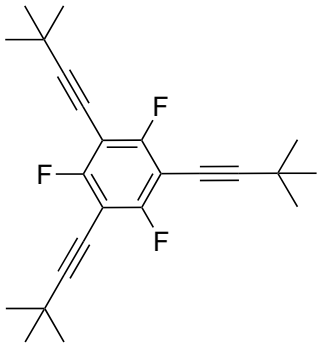
^{1}H NMR (500 MHz, Chloroform-*d*)



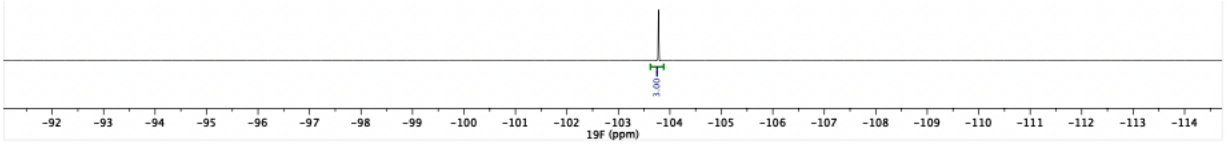
^{13}C NMR (126 MHz, Chloroform-*d*)



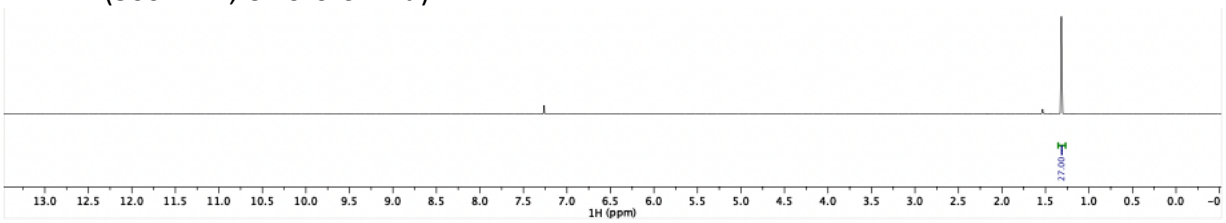
1,3,5-tris(3,3-dimethylbut-1-yn-1-yl)-2,4,6-trifluorobenzene (14g)



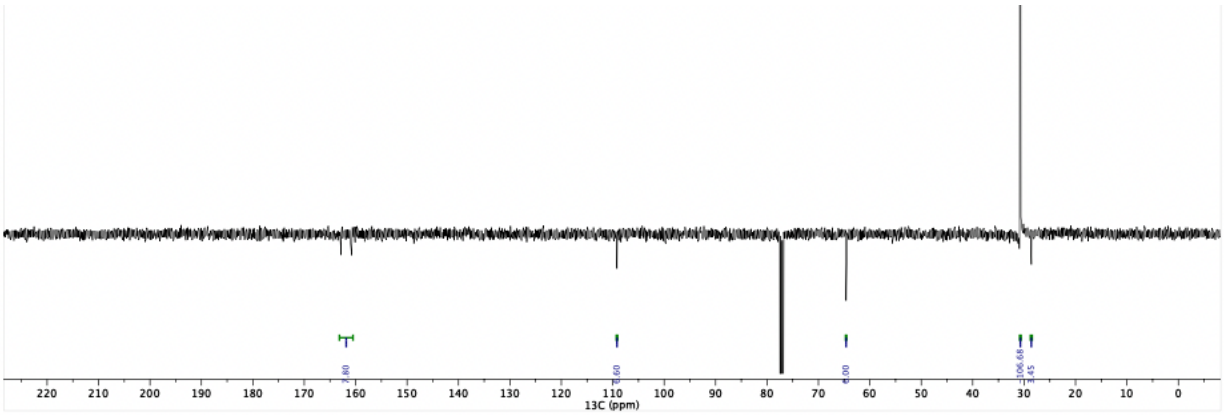
^{19}F{^{1}H} NMR (470 MHz, Chloroform-*d*)



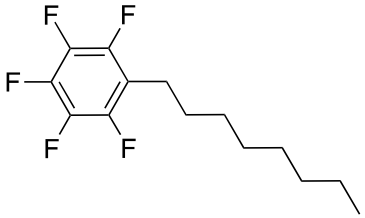
^{1}H NMR (500 MHz, Chloroform-*d*)



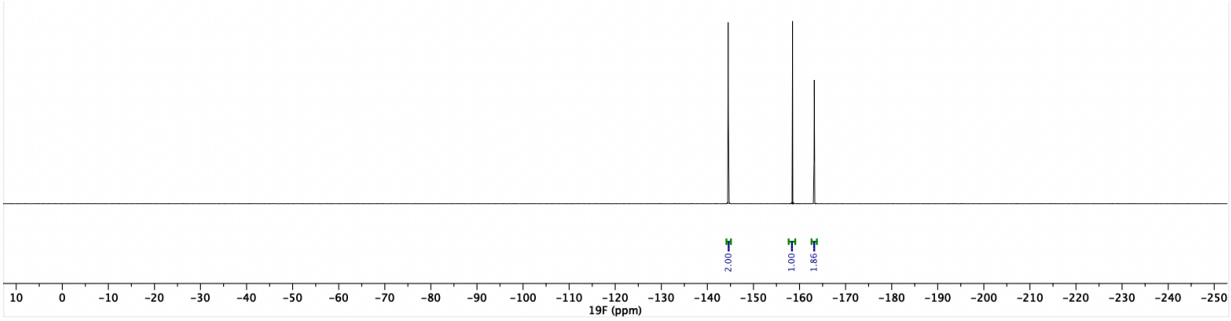
^{13}C NMR (126 MHz, Chloroform-*d*)



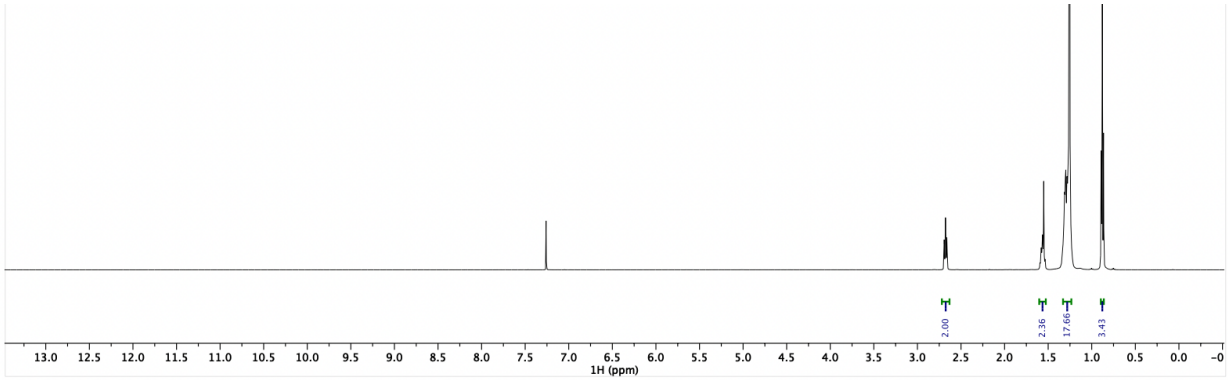
1,2,3,4,5-Pentafluoro-6-octylbenzene (7)



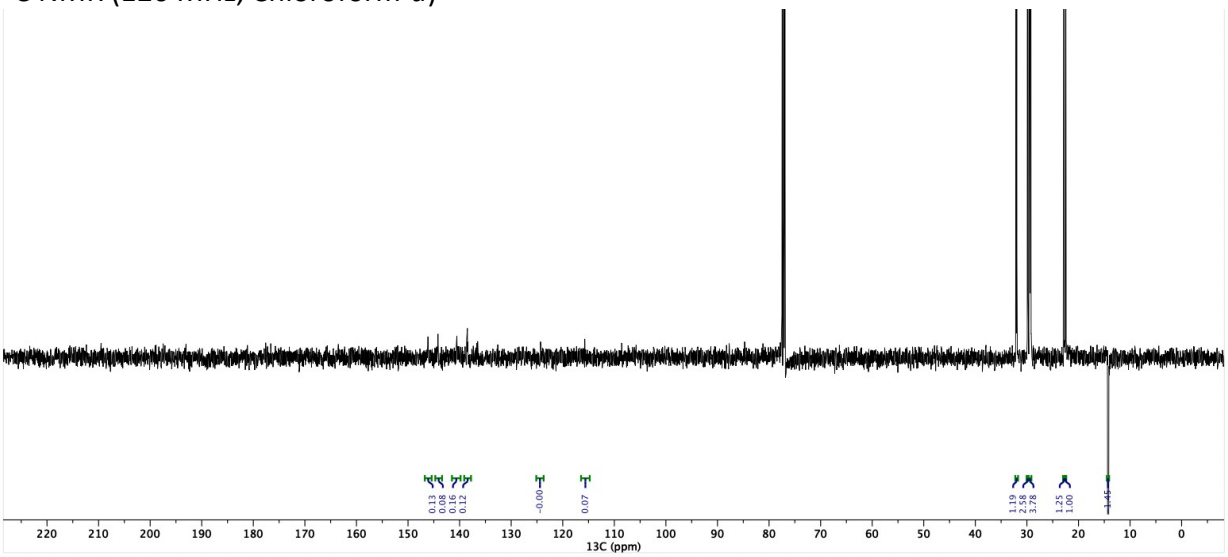
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



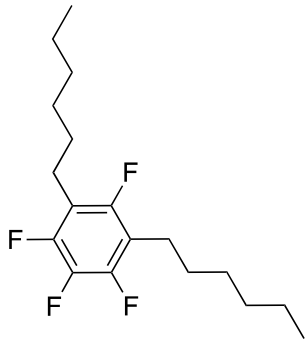
^{1}H NMR (500 MHz, Chloroform-*d*)



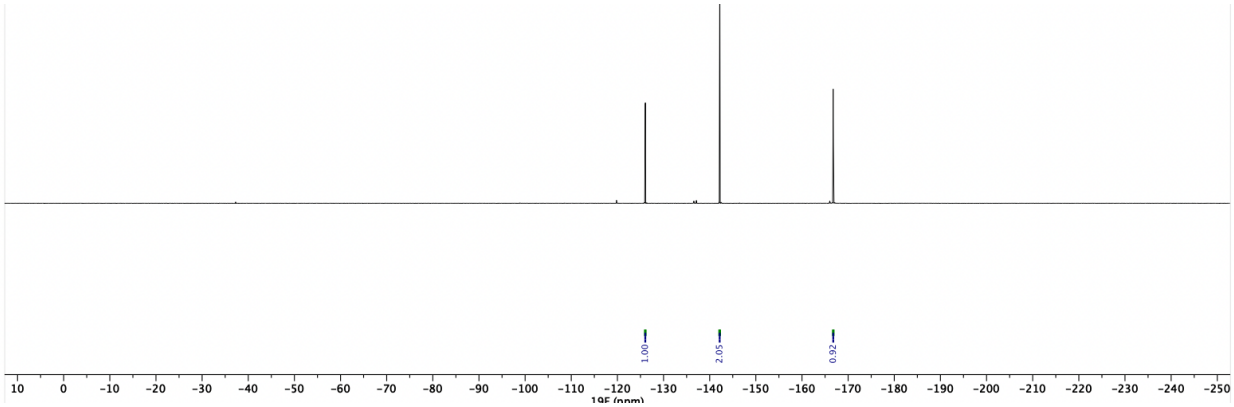
^{13}C NMR (126 MHz, Chloroform-*d*)



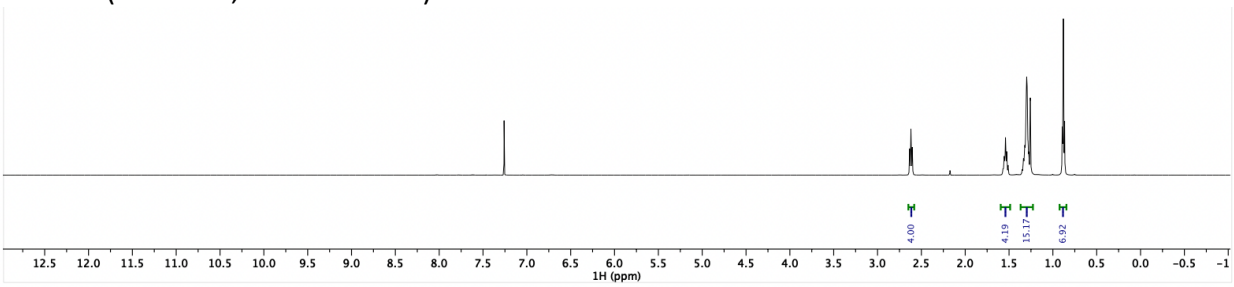
1,2,3,5-Tetrafluoro-4,6-dihexylbenzene (11a)



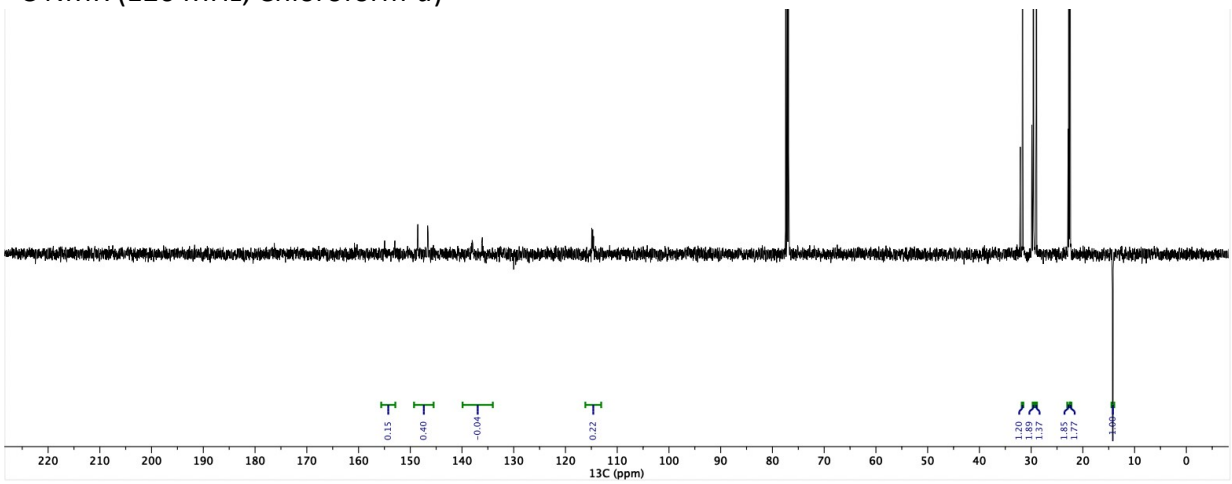
^{19}F{^{1}H} NMR (470 MHz, Chloroform-*d*)



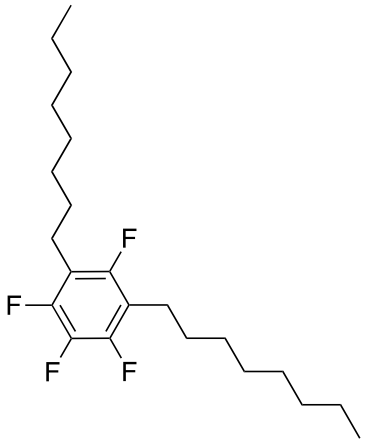
^{1}H NMR (500 MHz, Chloroform-*d*)



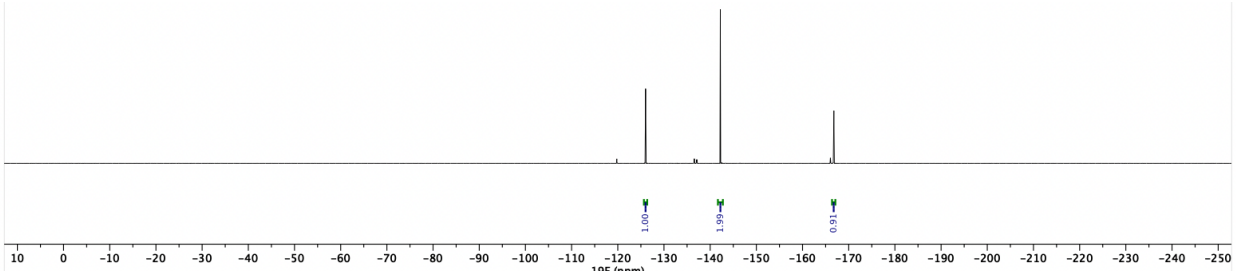
^{13}C NMR (126 MHz, Chloroform-*d*)



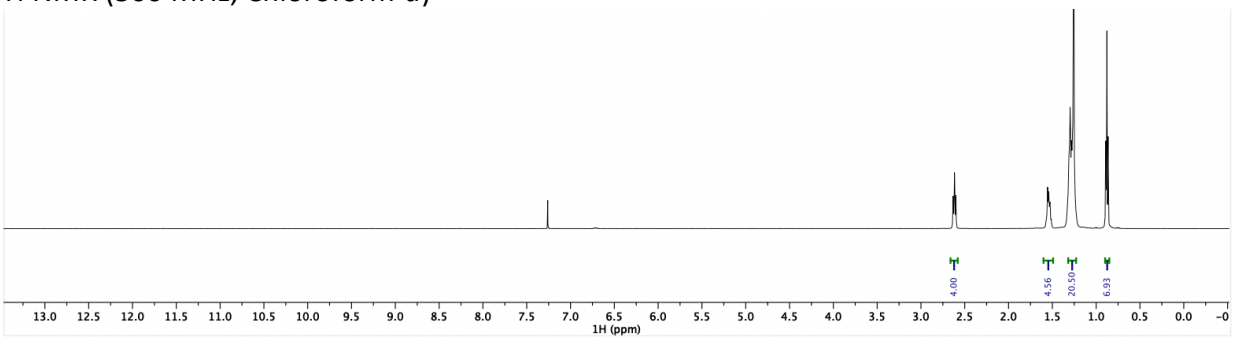
1,2,3,5-Tetrafluoro-4,6-(dioctyl)benzene (11b)



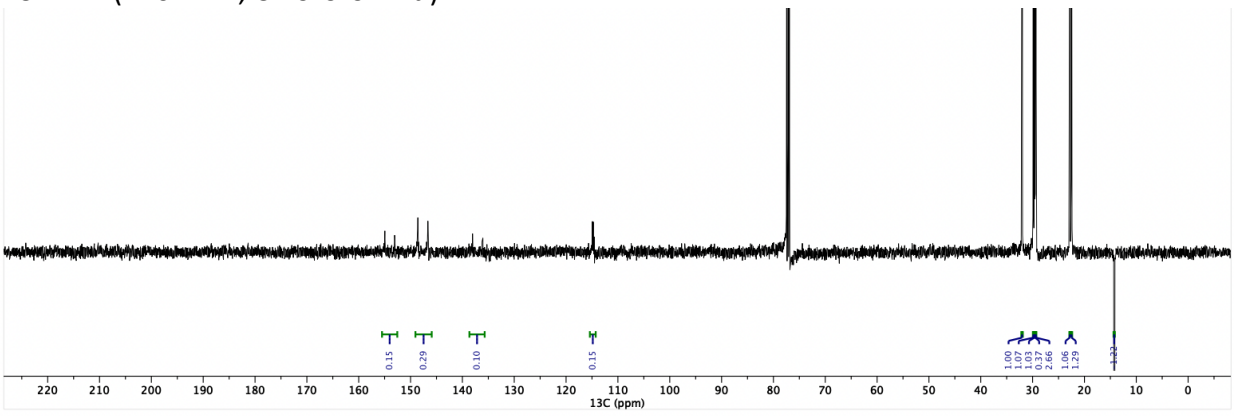
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



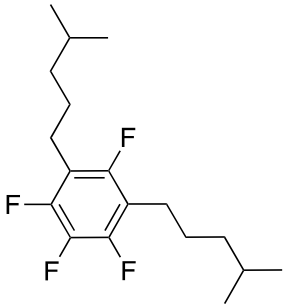
^{1}H NMR (500 MHz, Chloroform-*d*)



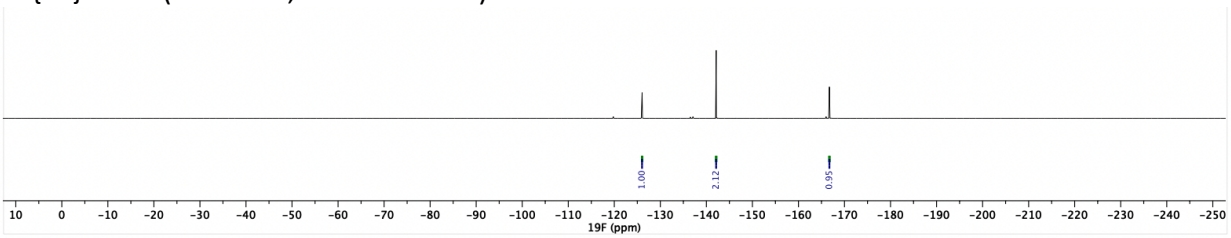
^{13}C NMR (126 MHz, Chloroform-*d*)



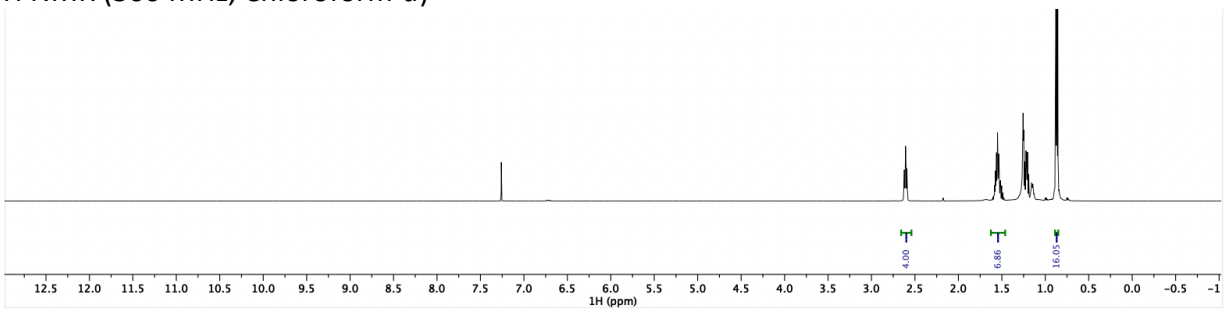
1,2,3,5-Tetrafluoro-4,6-bis(4-methylpentyl)benzene (11c)



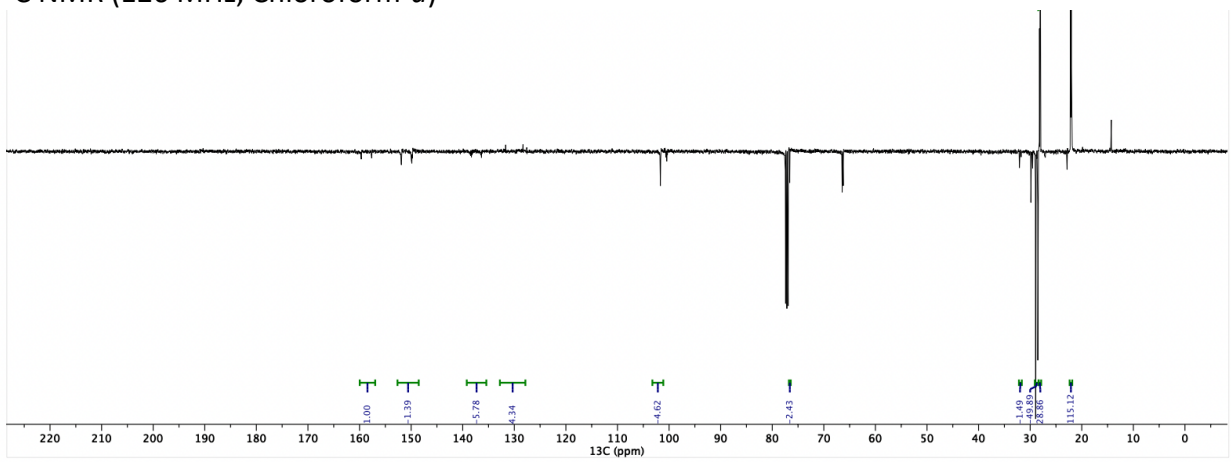
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



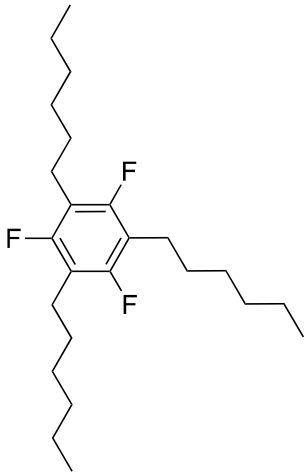
^{1}H NMR (500 MHz, Chloroform-*d*)



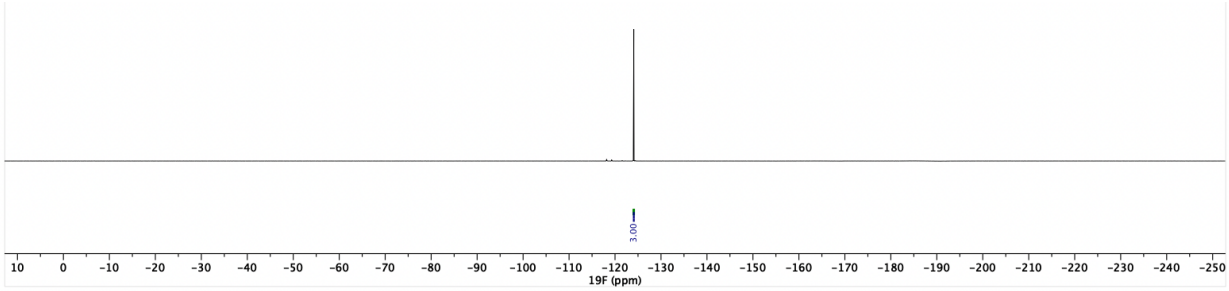
^{13}C NMR (126 MHz, Chloroform-*d*)



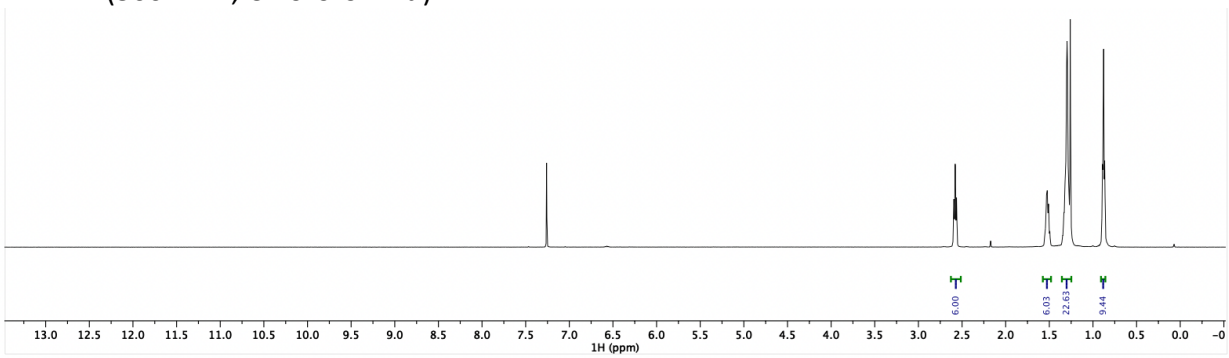
1,3,5-Trifluoro-2,4,6-trihexylbenzene (15a)



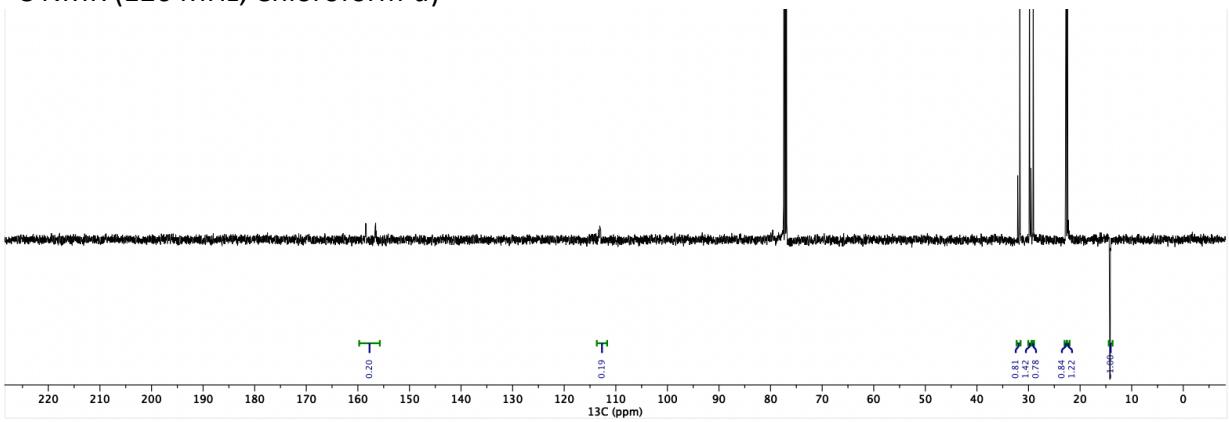
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



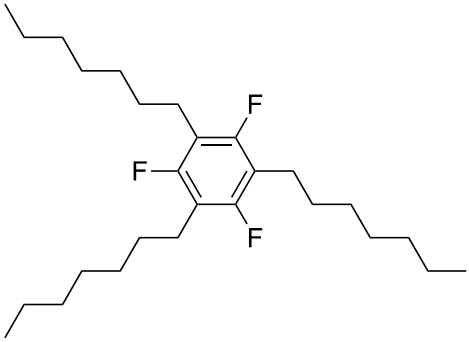
^{1}H NMR (500 MHz, Chloroform-*d*)



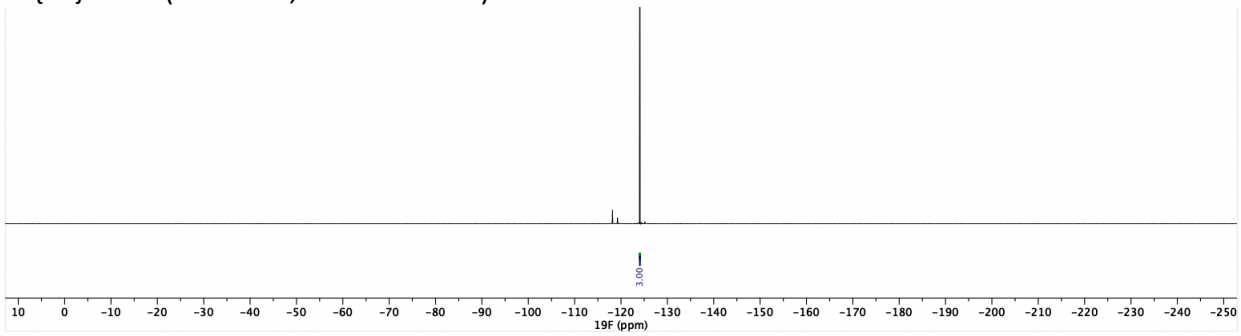
^{13}C NMR (126 MHz, Chloroform-*d*)



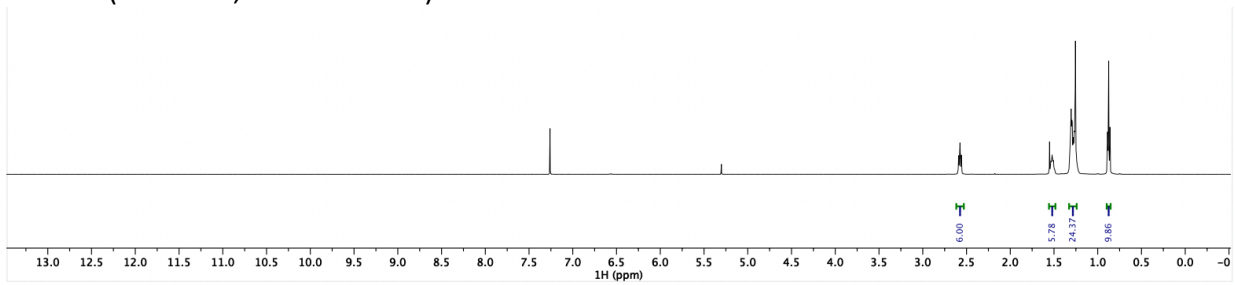
1,3,5-Trifluoro-2,4,6-triheptylbenzene (15b)



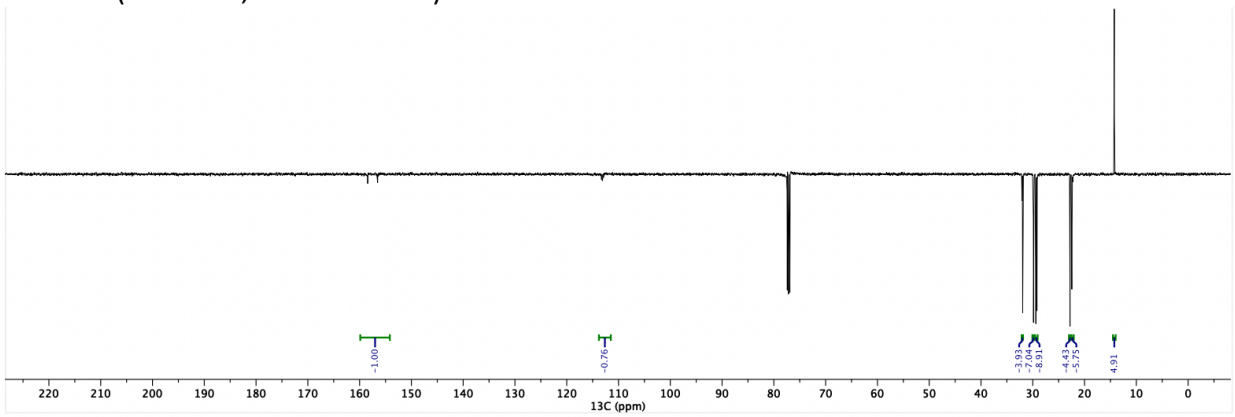
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



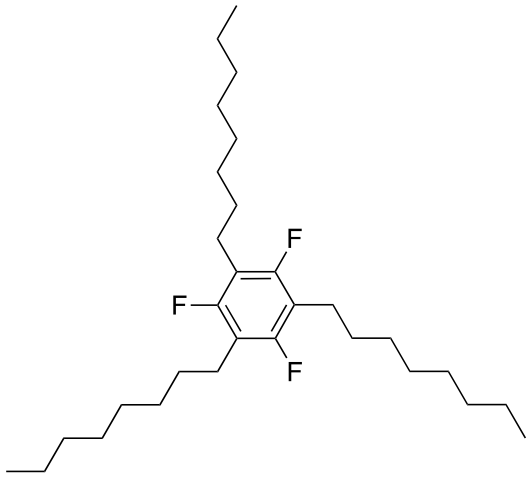
^{1}H NMR (500 MHz, Chloroform-*d*)



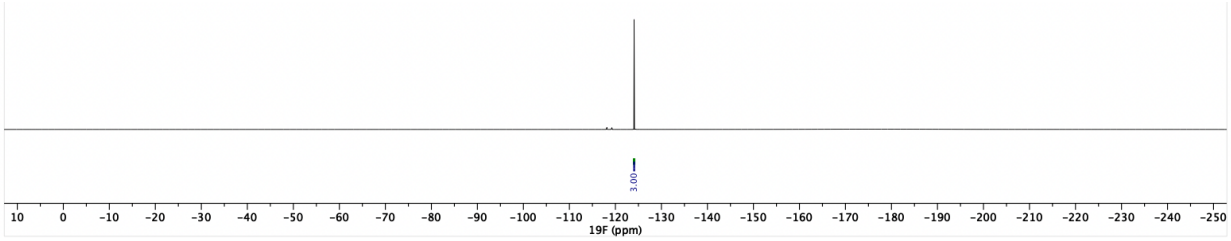
^{13}C NMR (126 MHz, Chloroform-*d*)



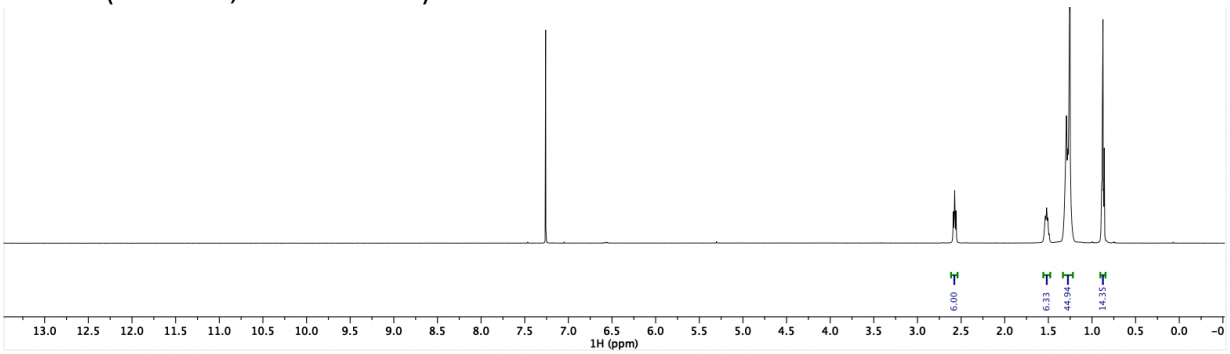
1,3,5-Trifluoro-2,4,6-trioctylbenzene (15c)



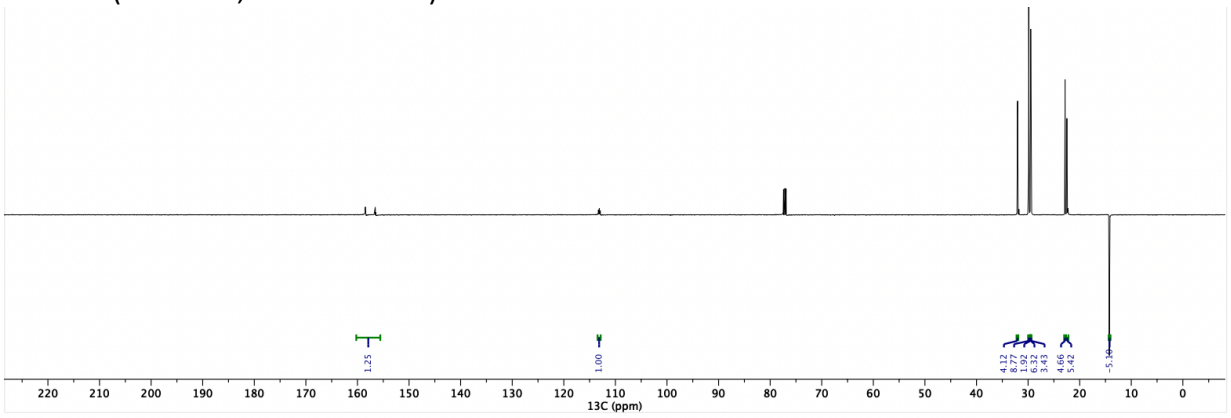
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



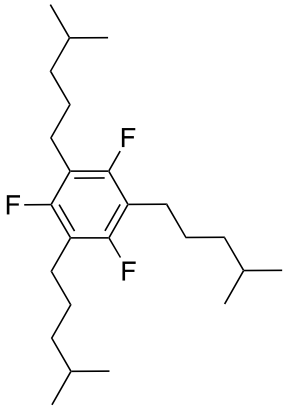
^{1}H NMR (500 MHz, Chloroform-*d*)



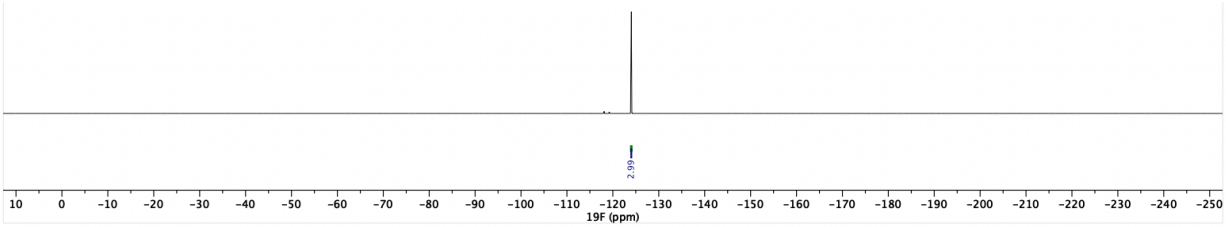
^{13}C NMR (126 MHz, Chloroform-*d*)



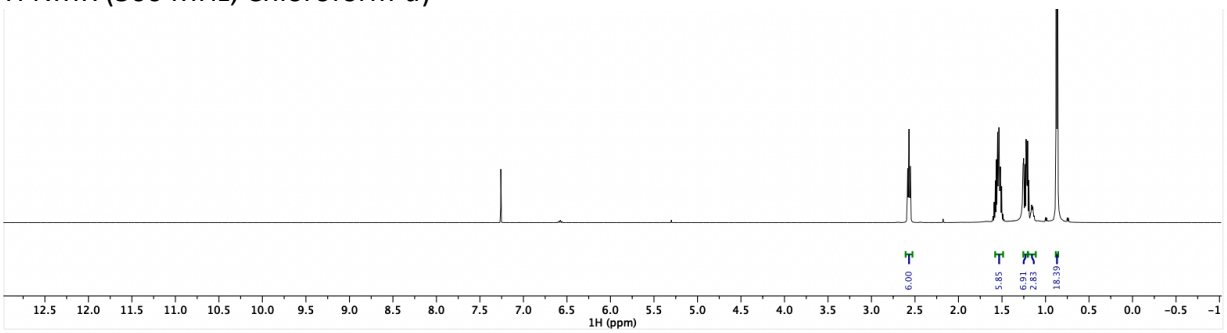
1,3,5-trifluoro-2,4,6-tris(4-methylpentyl)benzene (15d)



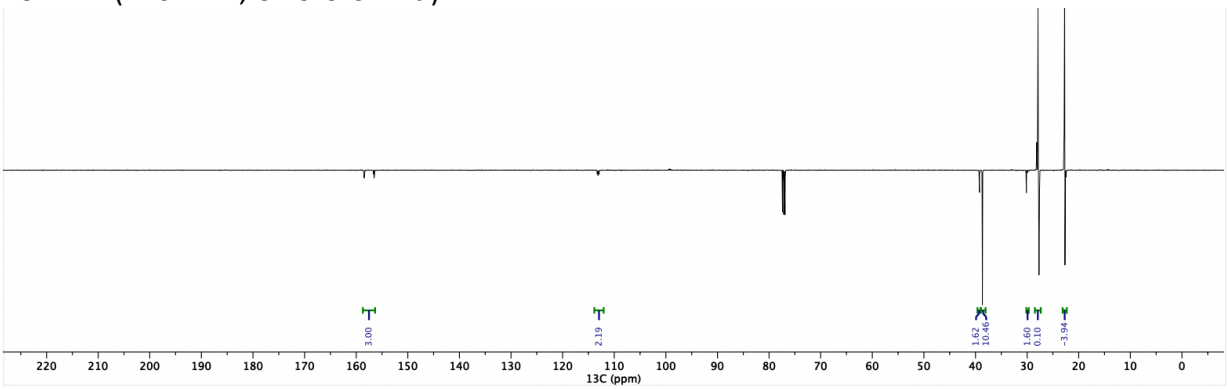
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



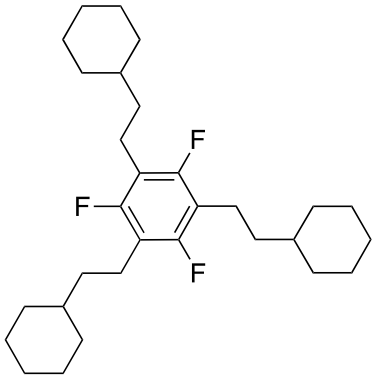
^{1}H NMR (500 MHz, Chloroform-*d*)



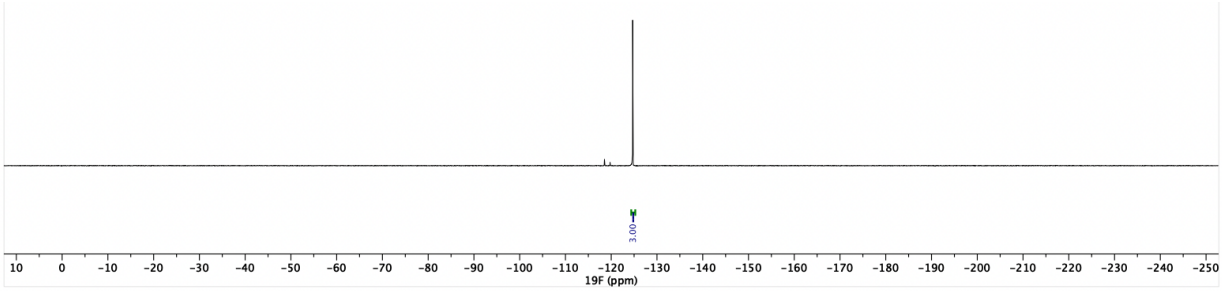
^{13}C NMR (126 MHz, Chloroform-*d*)



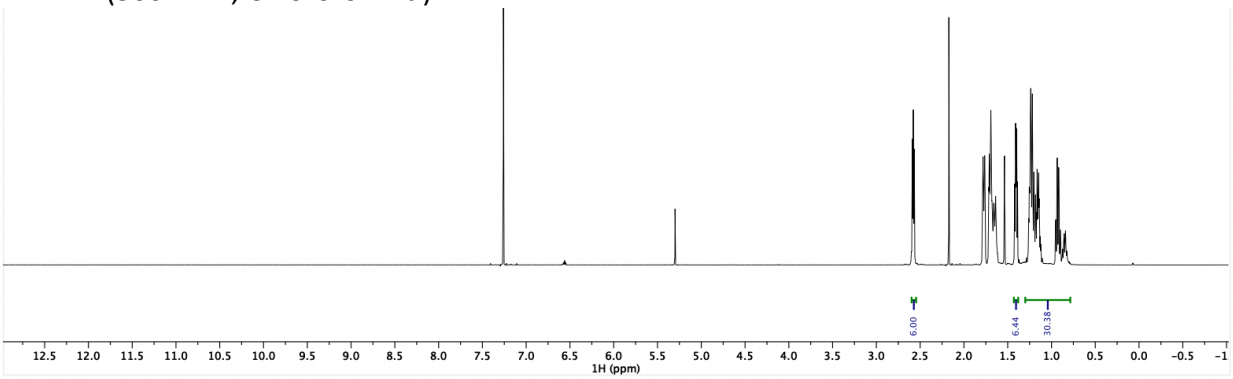
((2,4,6-Trifluorobenzene-1,3,5-triyl)tris(ethane-2,1-diyl))tricyclohexane (15e)



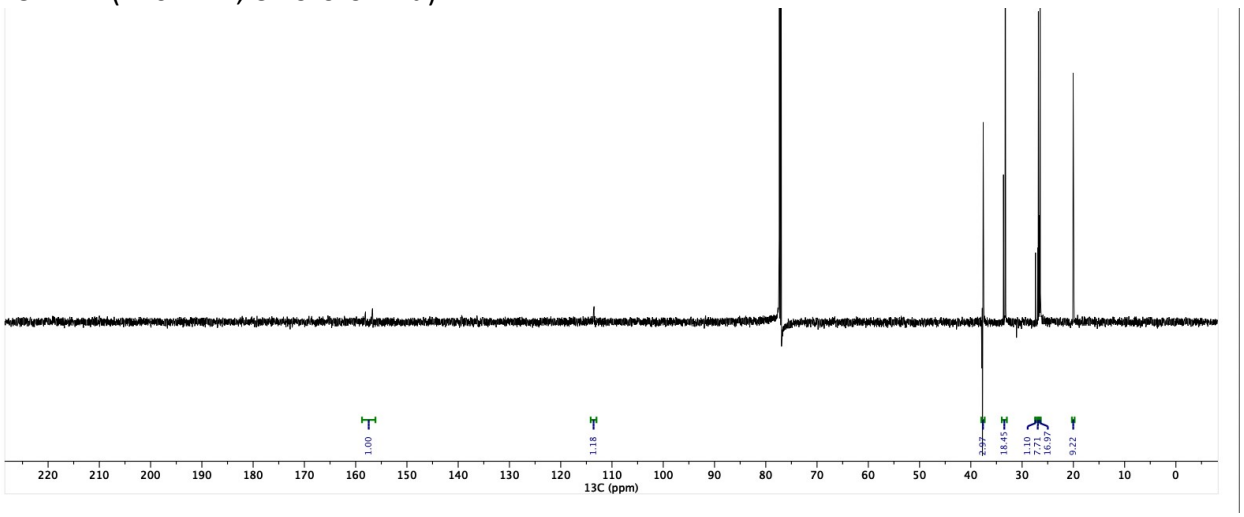
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



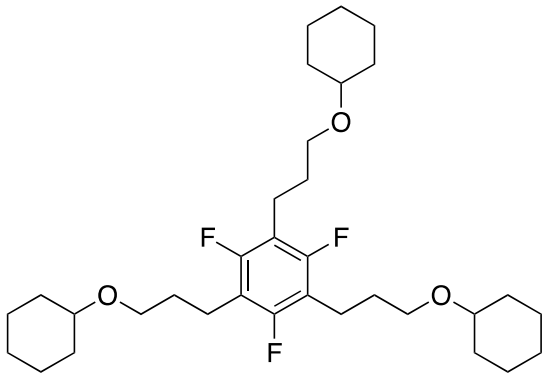
^{1}H NMR (500 MHz, Chloroform-*d*)



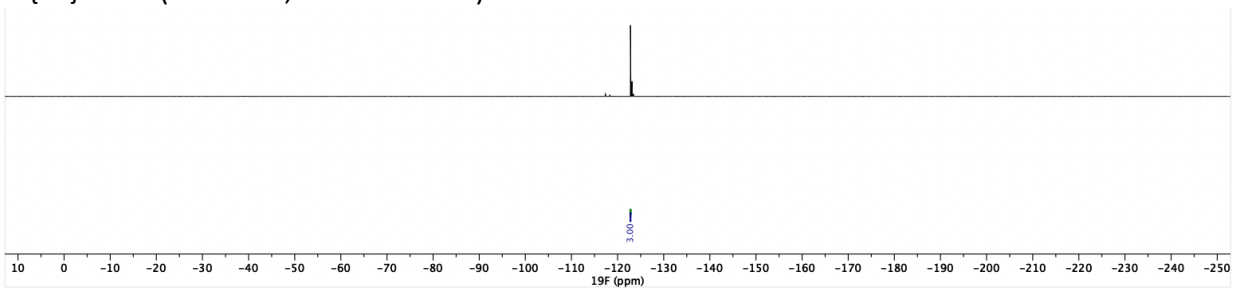
^{13}C NMR (126 MHz, Chloroform-*d*)



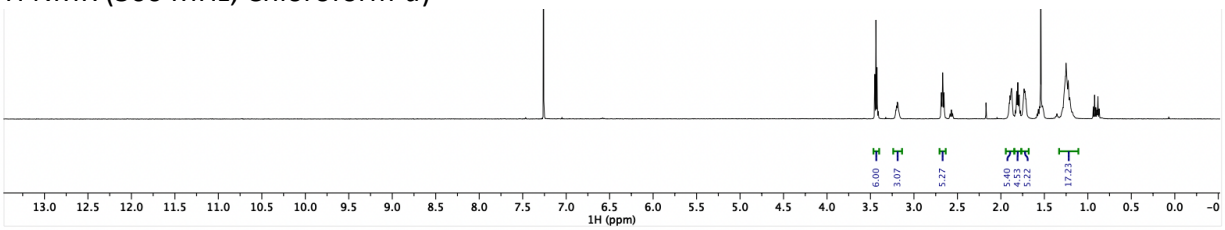
(((2,4,6-trifluorobenzene-1,3,5-triyl)tris(propane-3,1-diyl))tris(oxy))tricyclohexane (15f)



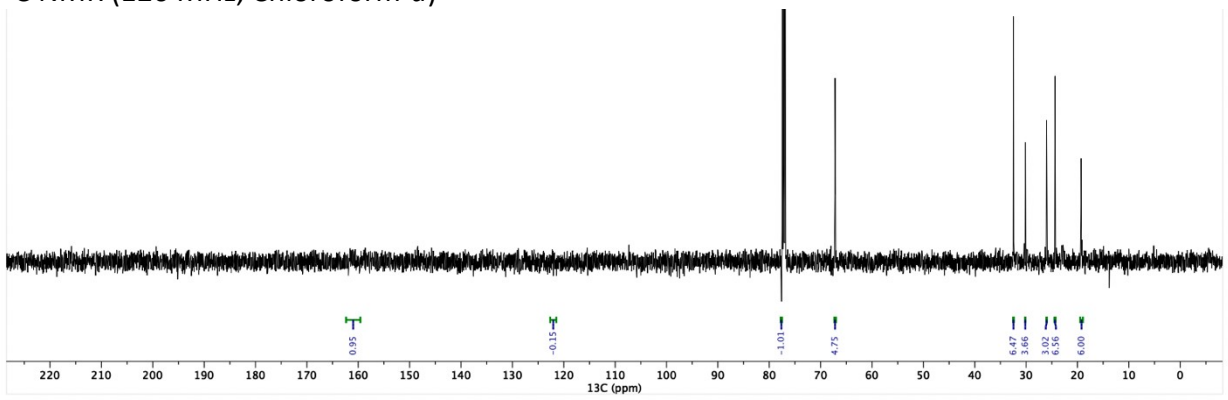
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



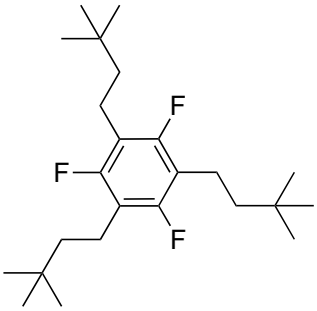
^{1}H NMR (500 MHz, Chloroform-*d*)



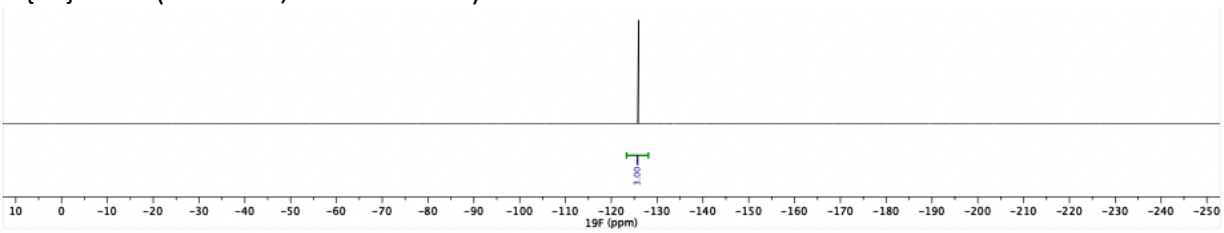
^{13}C NMR (126 MHz, Chloroform-*d*)



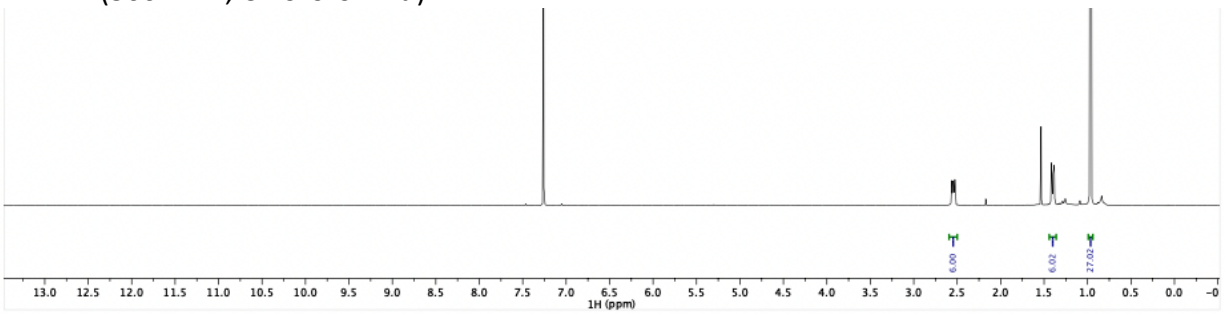
1,3,5-tris(3,3-dimethylbutyl)-2,4,6-trifluorobenzene (15g)



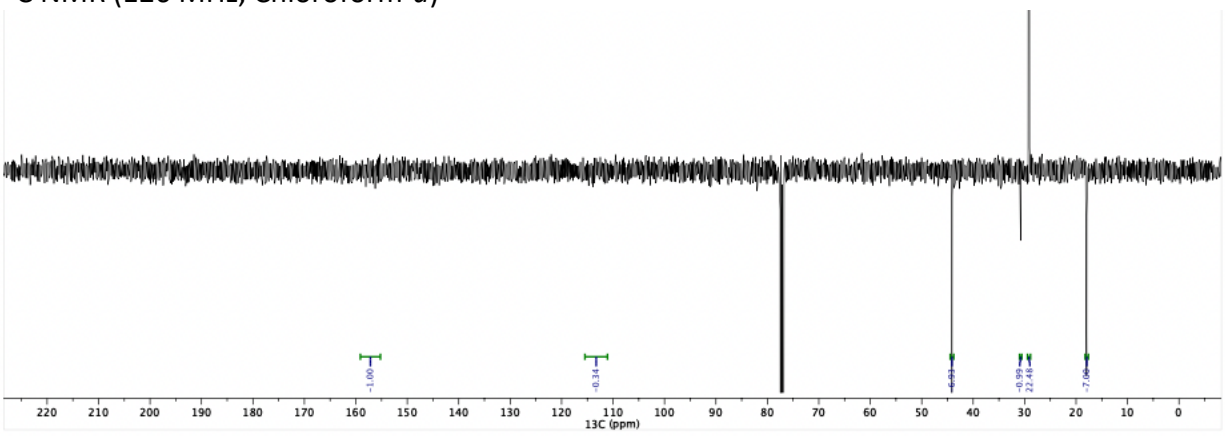
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



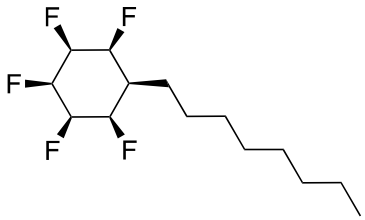
^{1}H NMR (500 MHz, Chloroform-*d*)



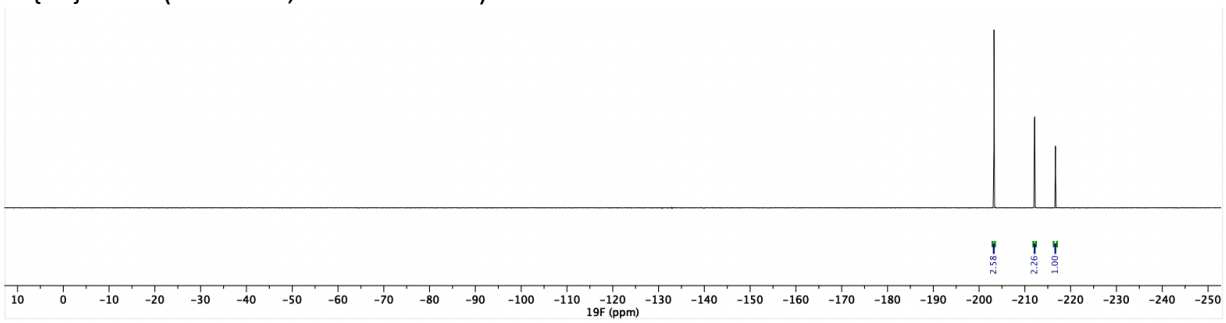
^{13}C NMR (126 MHz, Chloroform-*d*)



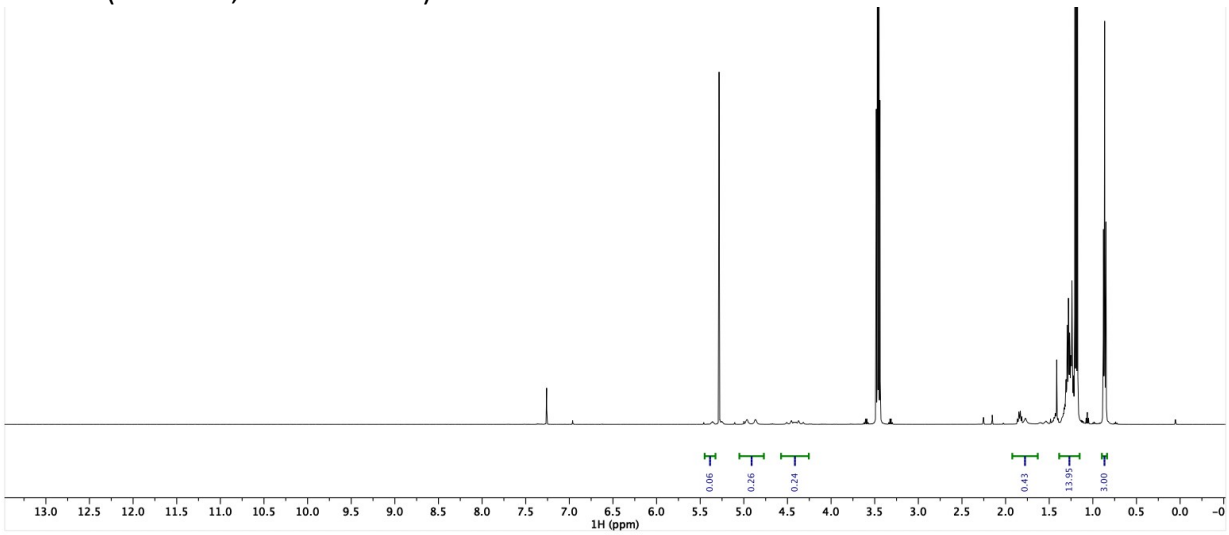
All-cis 1,2,3,4,5-pentafluoro-6-octylcyclohexane (8)



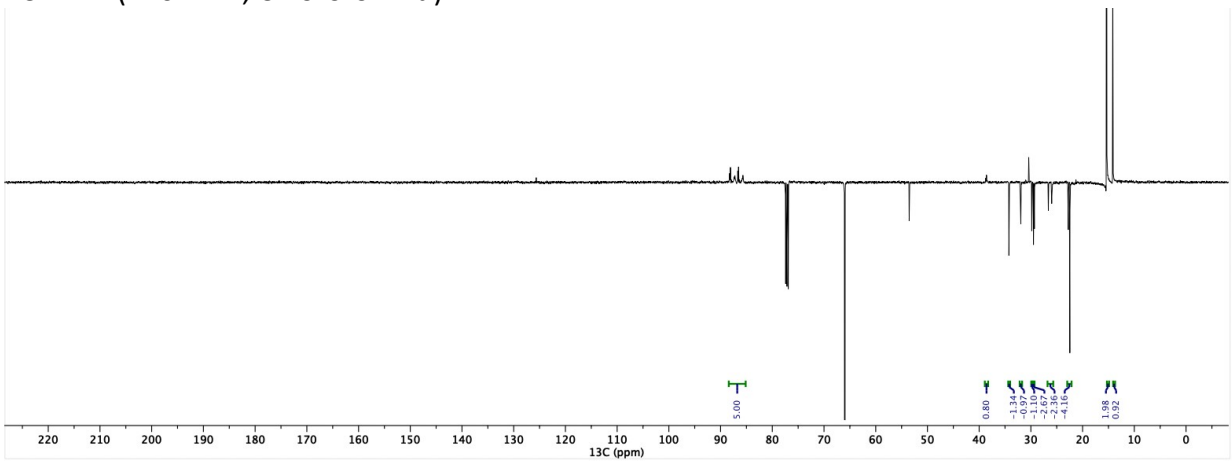
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



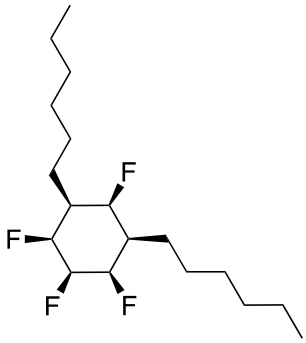
^{1}H NMR (500 MHz, Chloroform-*d*)



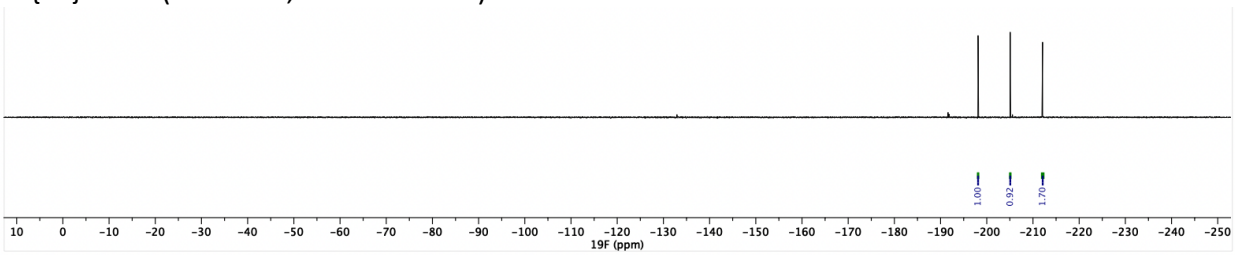
^{13}C NMR (126 MHz, Chloroform-*d*)



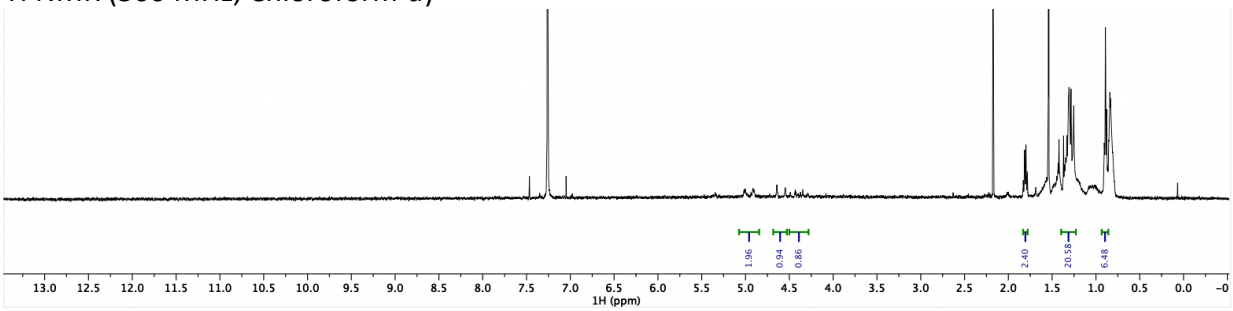
All-cis 1,2,3,5-tetrafluoro-4,6-dihexylcyclohexane (12a)



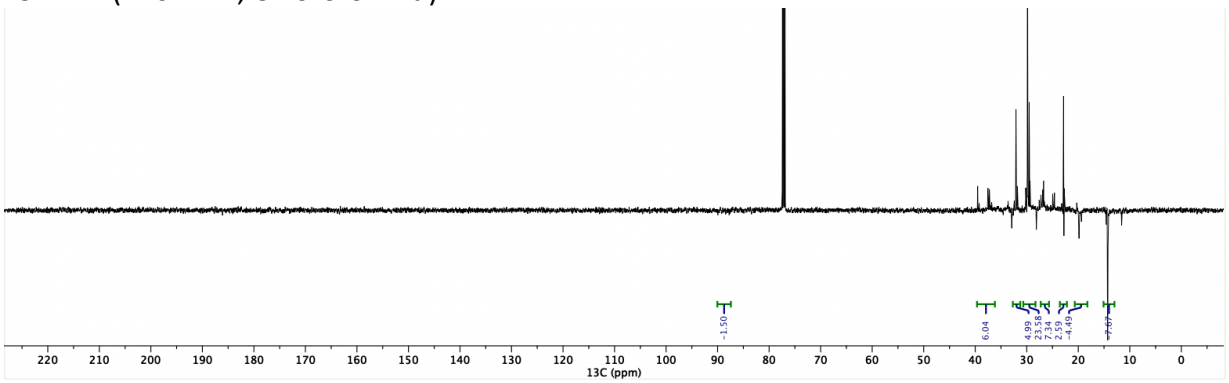
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



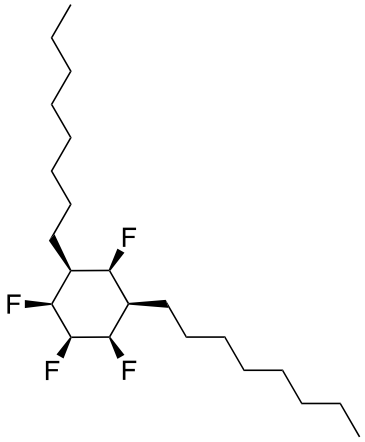
^{1}H NMR (500 MHz, Chloroform-*d*)



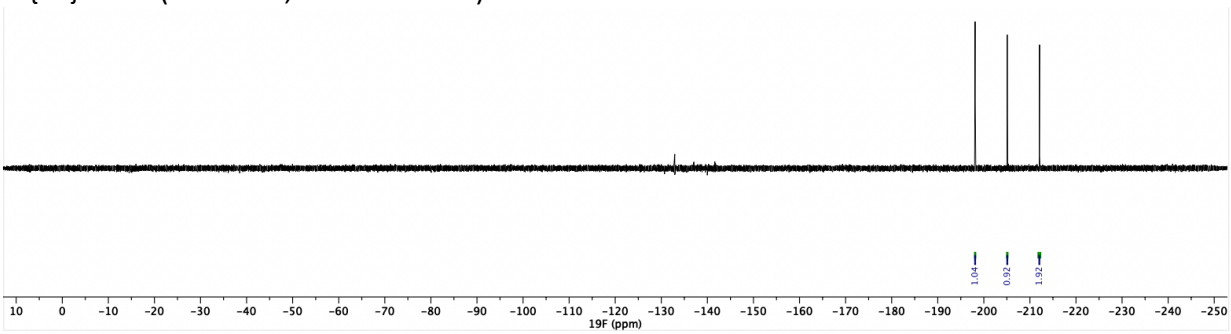
^{13}C NMR (126 MHz, Chloroform-*d*)



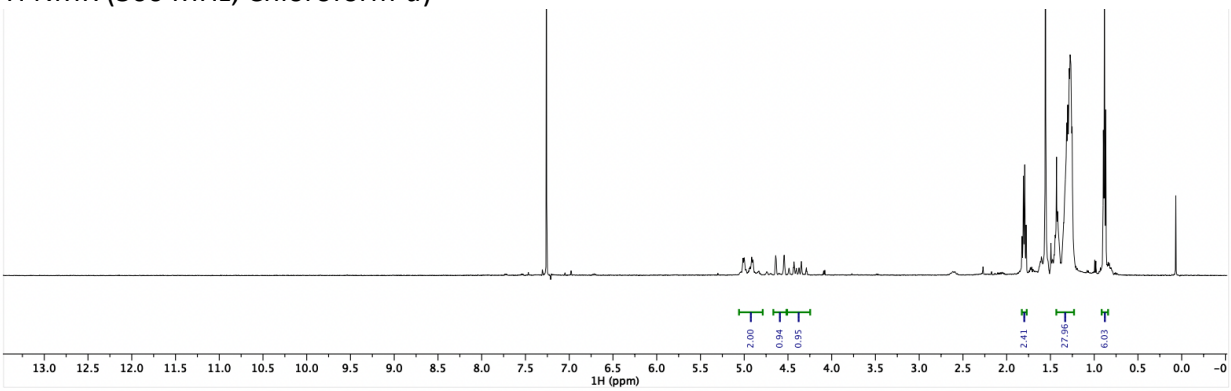
All-cis 1,2,3,5-tetrafluoro-4,6-dioctylcyclohexane (12b)



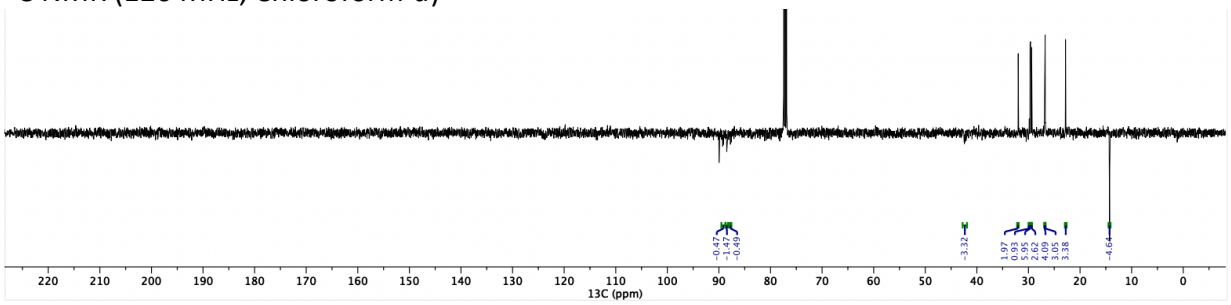
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



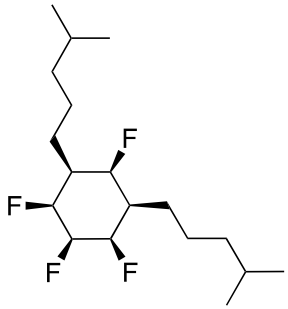
^{1}H NMR (500 MHz, Chloroform-*d*)



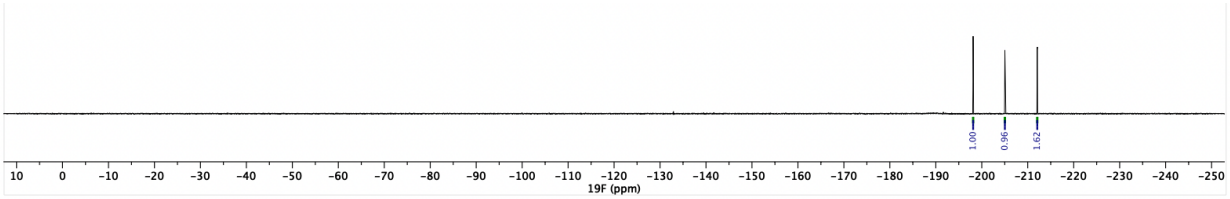
^{13}C NMR (126 MHz, Chloroform-*d*)



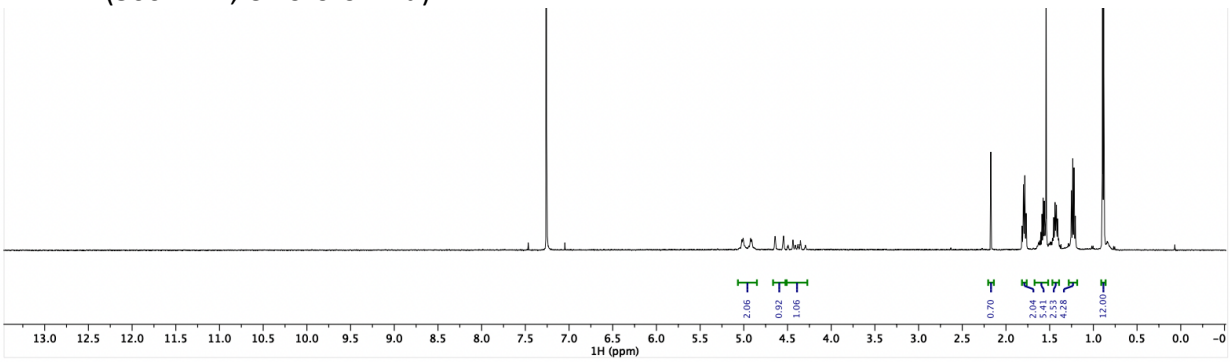
All-cis 1,2,3,5-tetrafluoro-4,6-bis(4-methylpentyl)cyclohexane (12c)



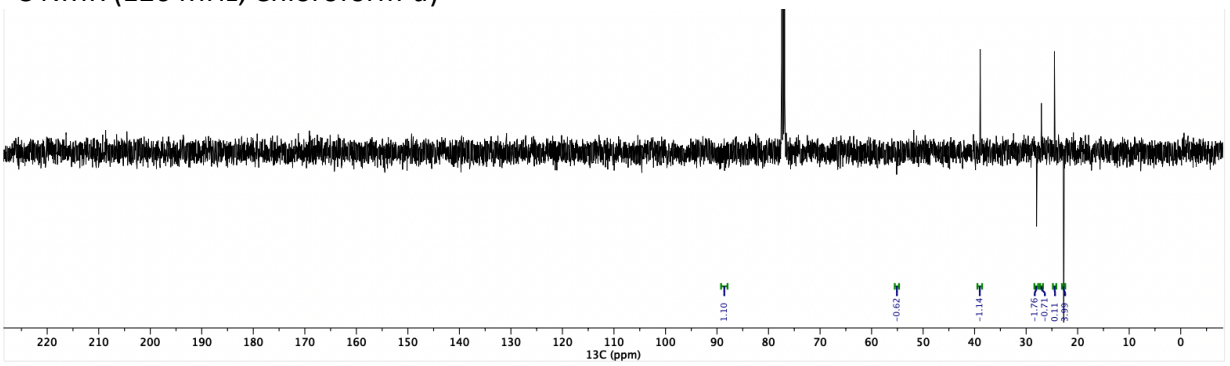
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



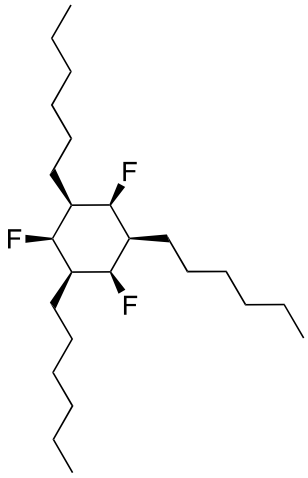
^{1}H NMR (500 MHz, Chloroform-*d*)



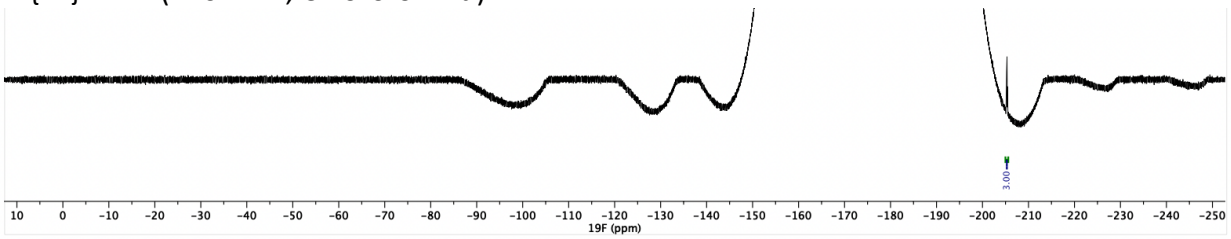
^{13}C NMR (126 MHz, Chloroform-*d*)



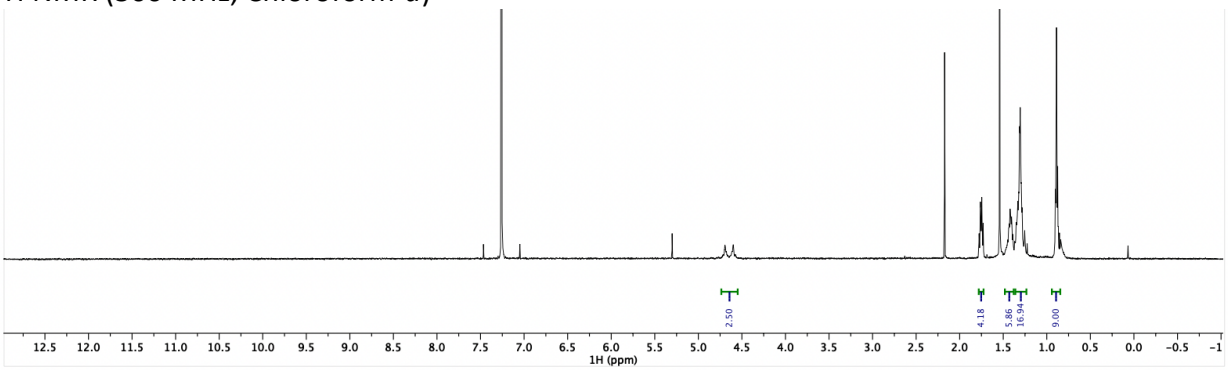
All-cis 1,3,5-trifluoro-2,4,6-trihexylcyclohexane (16a)



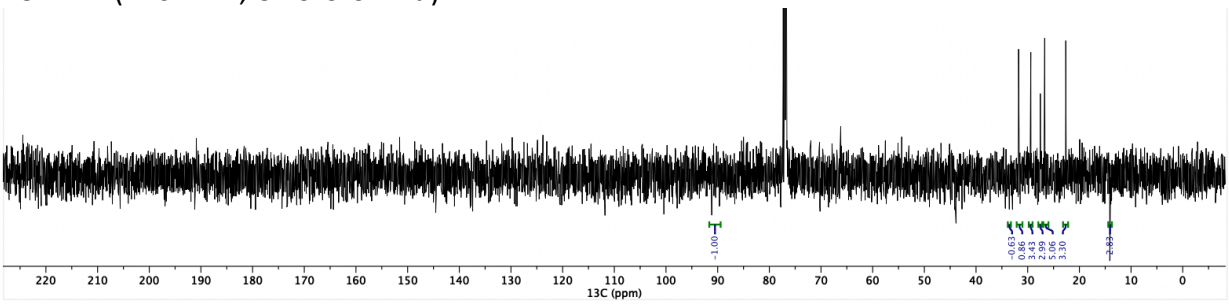
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



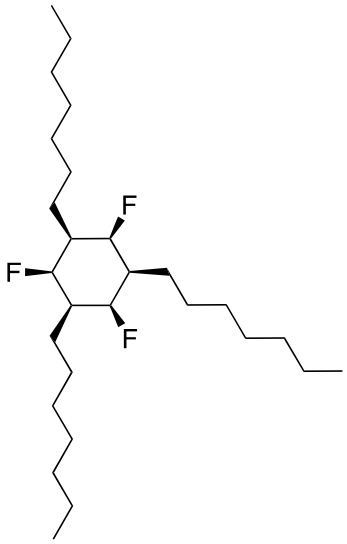
^{1}H NMR (500 MHz, Chloroform-*d*)



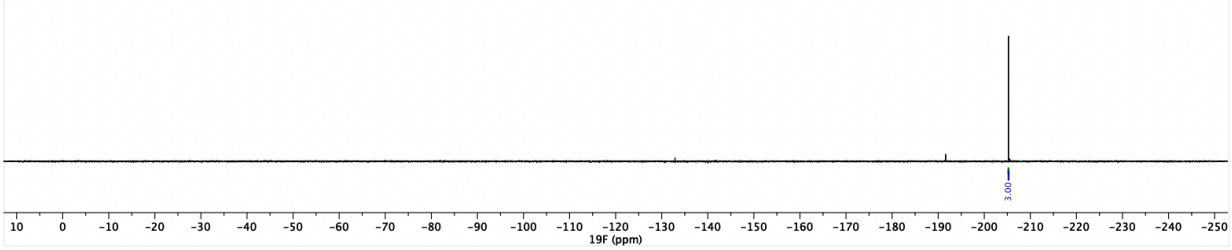
^{13}C NMR (126 MHz, Chloroform-*d*)



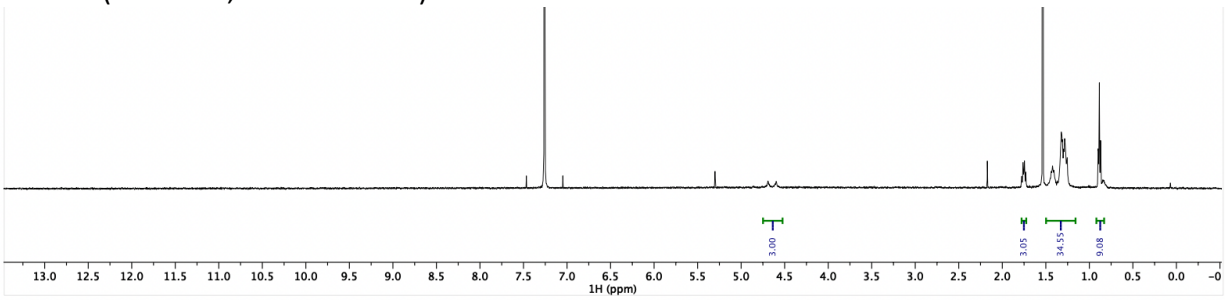
All-cis 1,3,5-trifluoro-2,4,6-triheptylcyclohexane (16b)



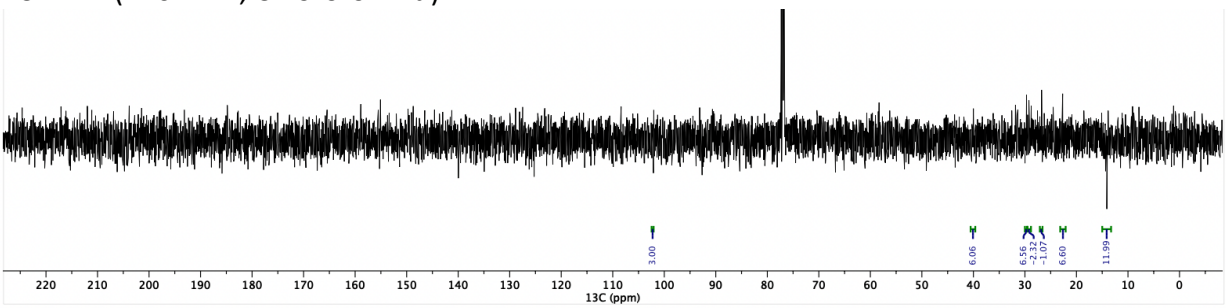
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



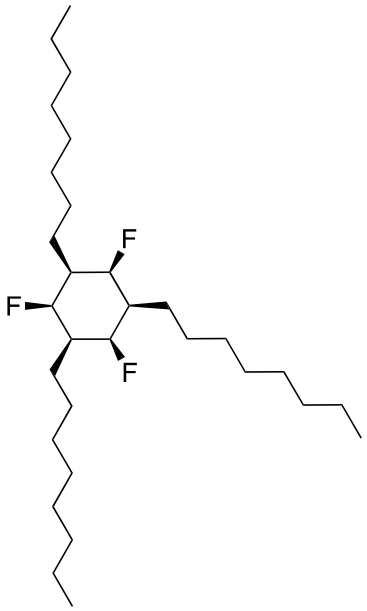
^{1}H NMR (500 MHz, Chloroform-*d*)



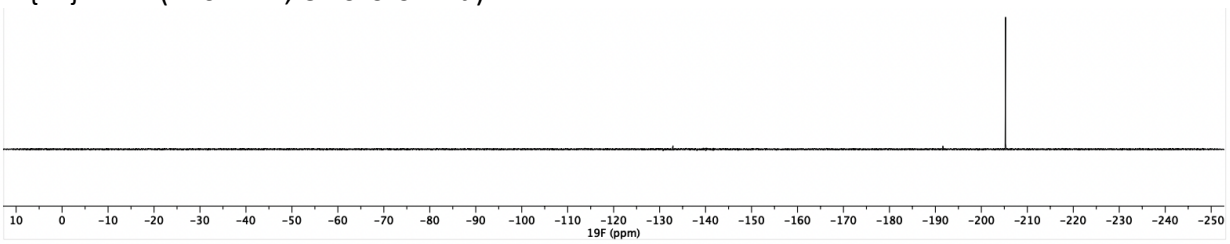
^{13}C NMR (126 MHz, Chloroform-*d*)



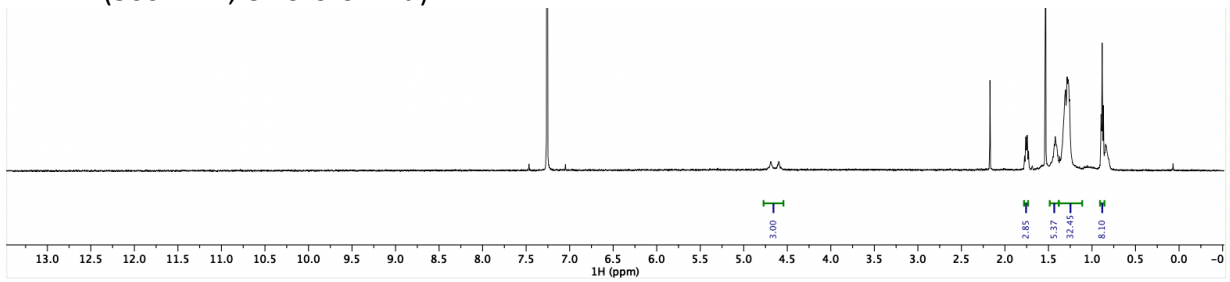
All-cis 1,3,5-trifluoro-2,4,6-trioctylcyclohexane (16c)



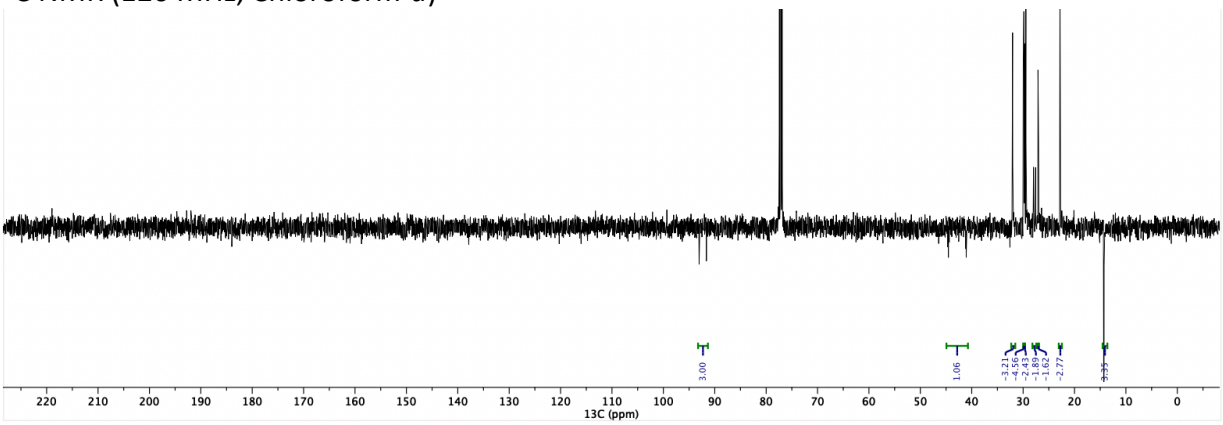
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



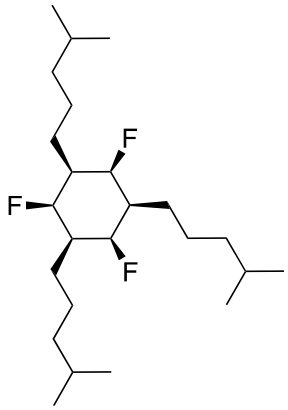
^{1}H NMR (500 MHz, Chloroform-*d*)



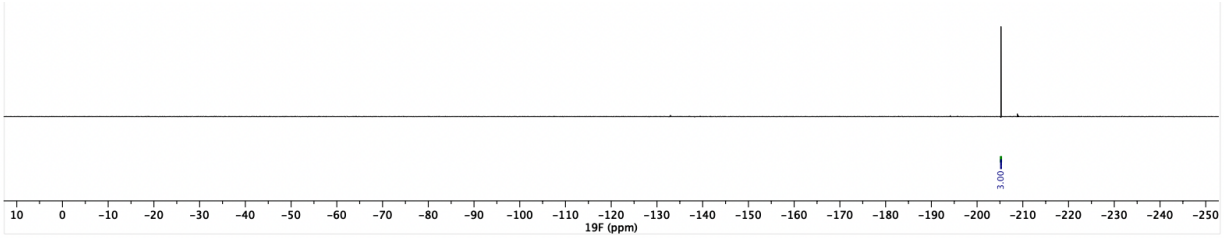
^{13}C NMR (126 MHz, Chloroform-*d*)



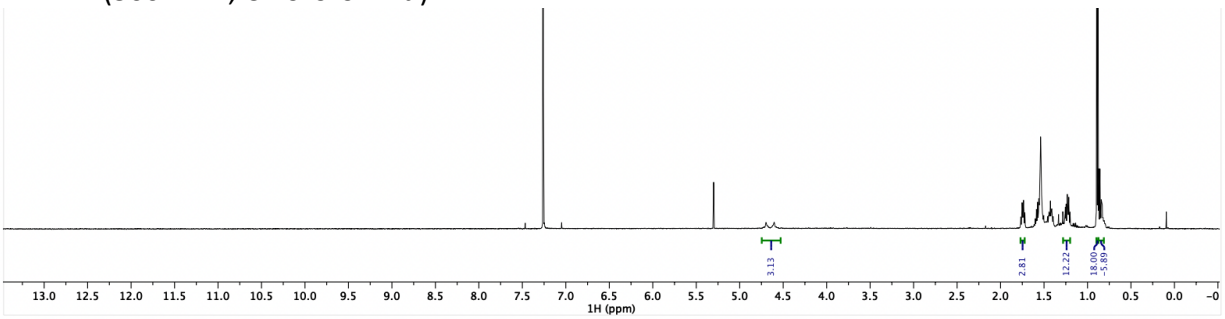
All-cis 1,3,5-trifluoro-2,4,6-tris(4-methylpentyl)cyclohexane (16d)



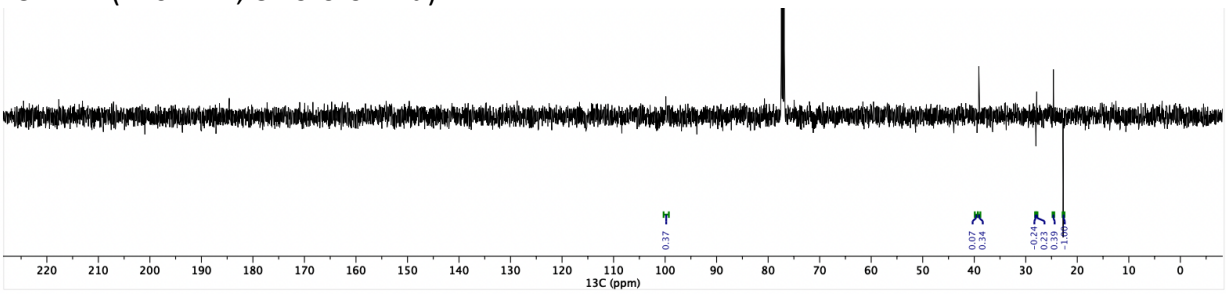
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



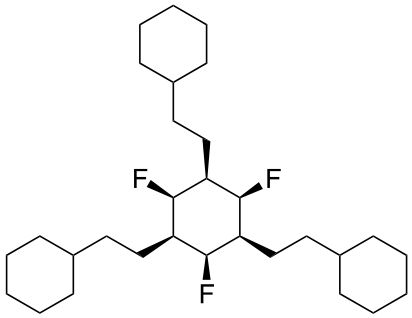
^{1}H NMR (500 MHz, Chloroform-*d*)



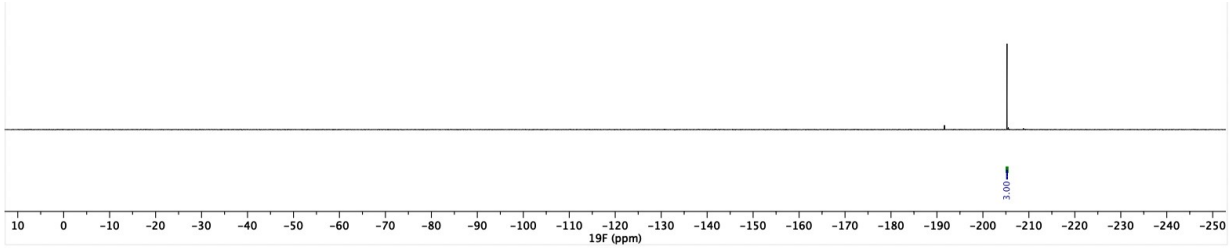
^{13}C NMR (126 MHz, Chloroform-*d*)



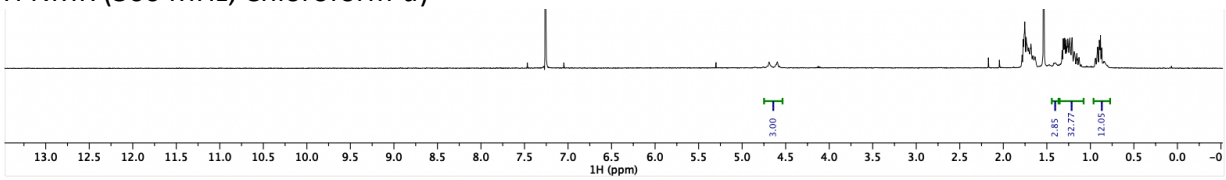
All-cis 2,4,6-trifluorocyclohexane-1,3,5-triyl)tris(ethane-2,1-diyl))tricyclohexane (16e)



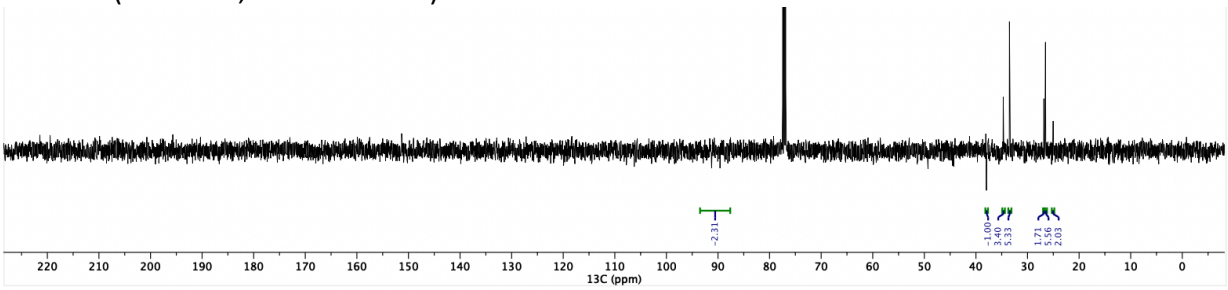
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



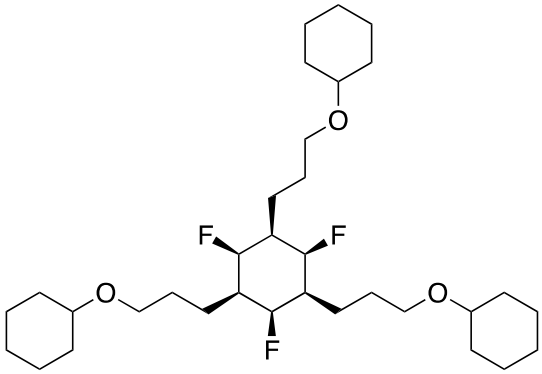
^{1}H NMR (500 MHz, Chloroform-*d*)



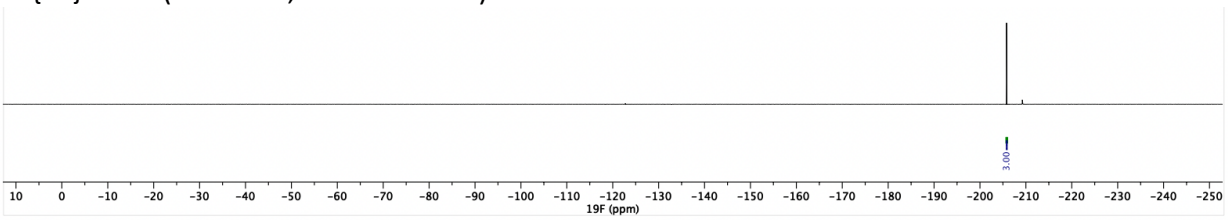
^{13}C NMR (126 MHz, Chloroform-*d*)



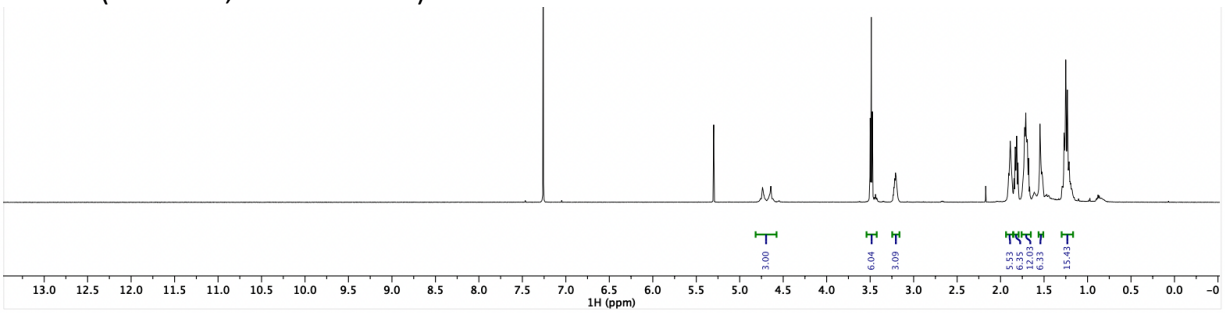
((((1*s*,2*s*,3*s*,4*s*,5*s*,6*s*)-2,4,6-trifluorocyclohexane-1,3,5-triyl)tris(propane-3,1-diyl))tris(oxy))tricyclohexane (16f)



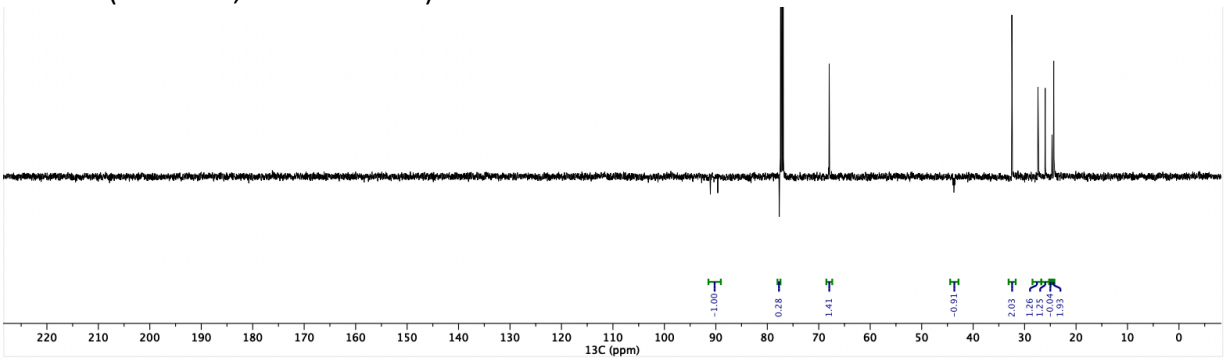
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



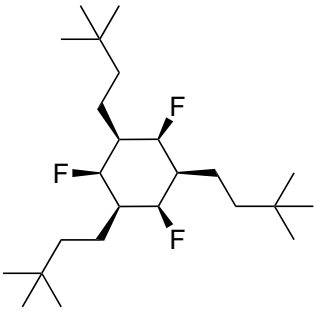
^{1}H NMR (500 MHz, Chloroform-*d*)



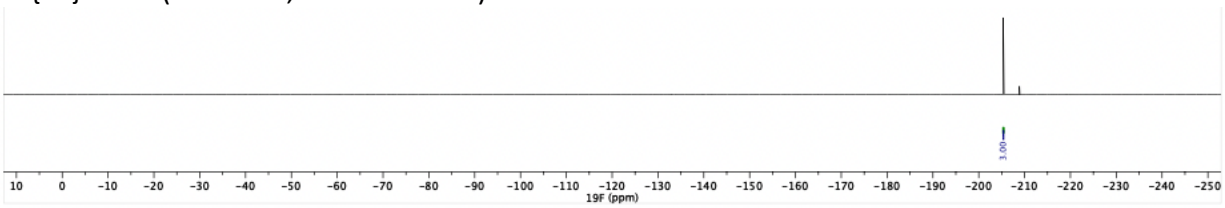
^{13}C NMR (126 MHz, Chloroform-*d*)



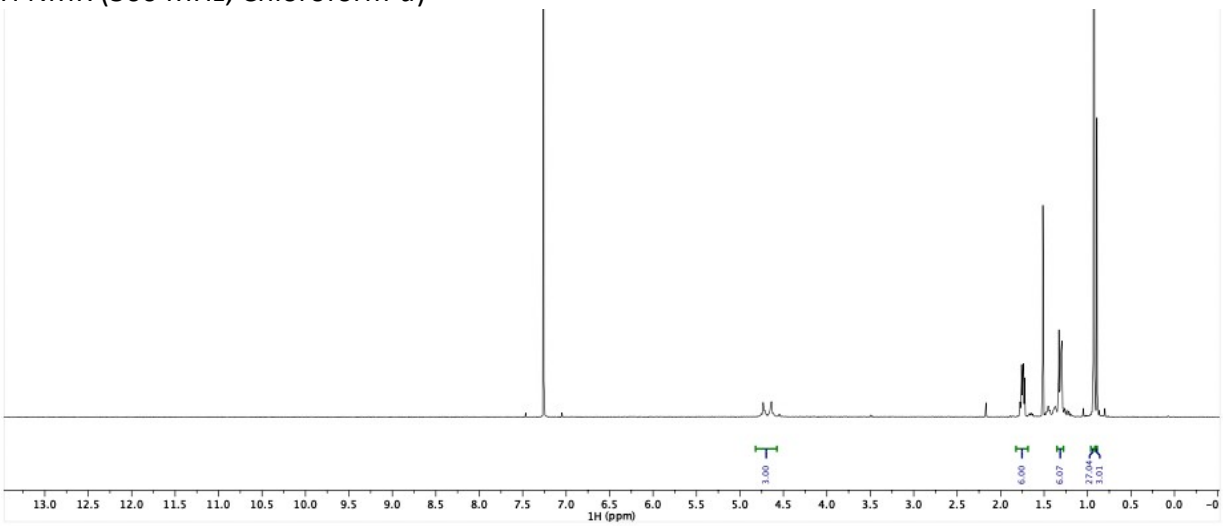
All-cis 1,3,5-tris(3,3-dimethylbutyl)-2,4,6-trifluorocyclohexane (16g)



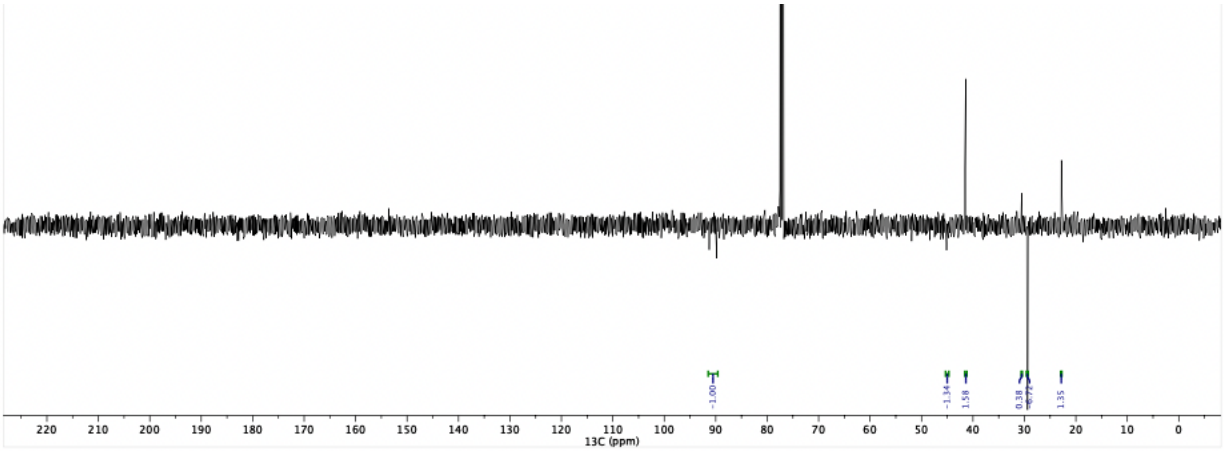
$^{19}F\{^{1}H\}$ NMR (470 MHz, Chloroform-*d*)



^{1}H NMR (500 MHz, Chloroform-*d*)



^{13}C NMR (126 MHz, Chloroform-*d*)

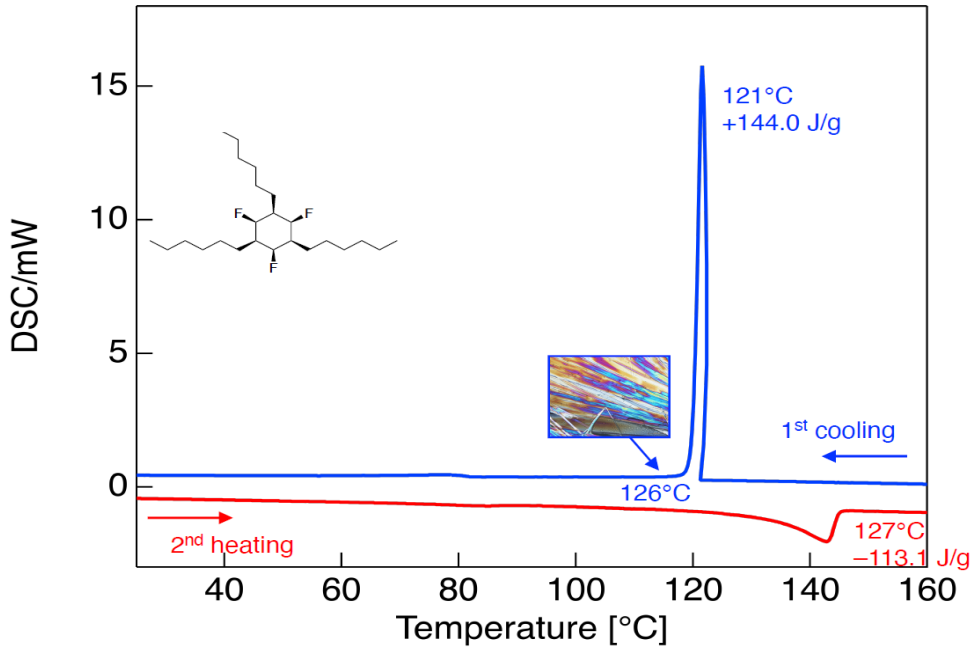


4 Differential Scanning Calorimetry (DSC) Profiles

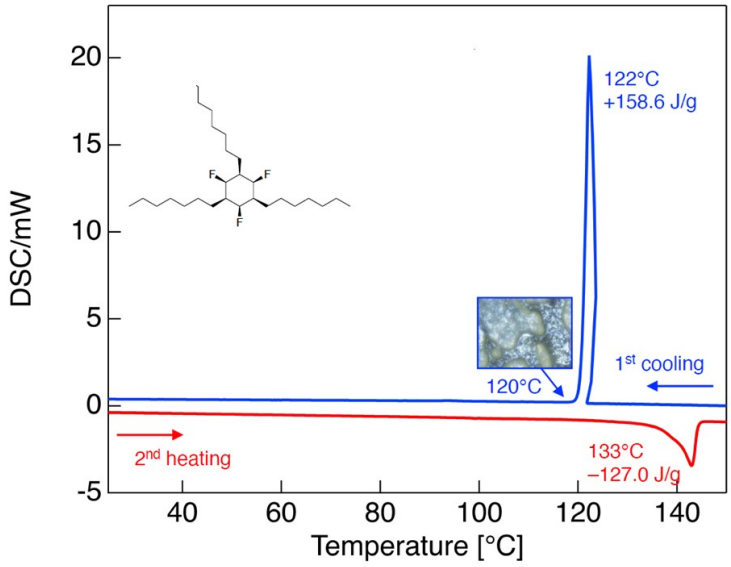
Some polarising optical microscopic (POMs) images included at key transitions.
The phase transition behaviour was studied via polarized optical microscopy (POM) using an Olympus BX53 microscope, equipped with a heating and cooling stage (Linkam Scientific Instruments, 10.002 L). The phase sequences and the phase transition enthalpies were determined using a differential scanning calorimeter (SHIMADZU DSC-60 Plus) with heating and cooling rates of 5.0 °C min−1 under a N_2 atmosphere.

The temperatures of the phase transitions are not mirror images during the heating and cooling cycles due to the hysteresis effect as free disordered chains have to become ordered. There is a kinetic barrier to achieving an ordered state in going from the melt to the solid (or between other transitions) which requires a lower 'freezing' temperature than going from the solid to the melt.

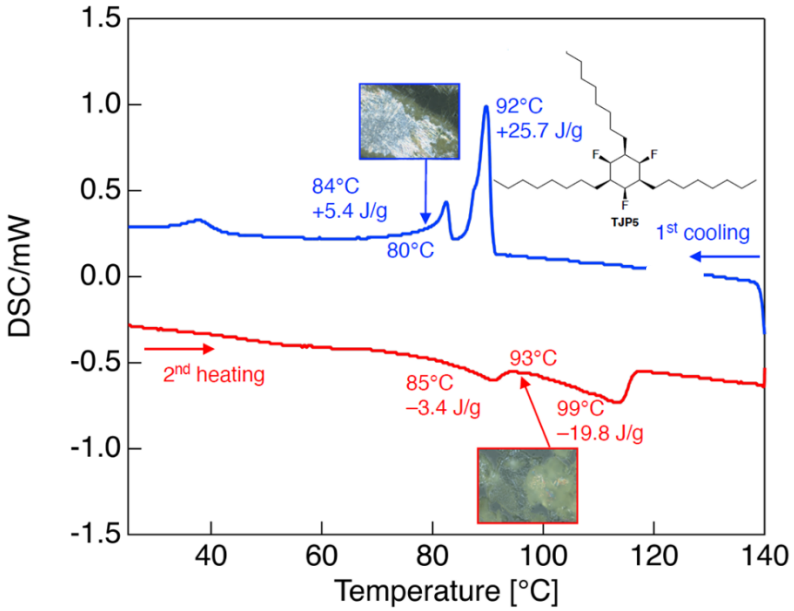
All-*cis* 1,3,5-trifluoro-2,4,6-trihexylcyclohexane (16a)



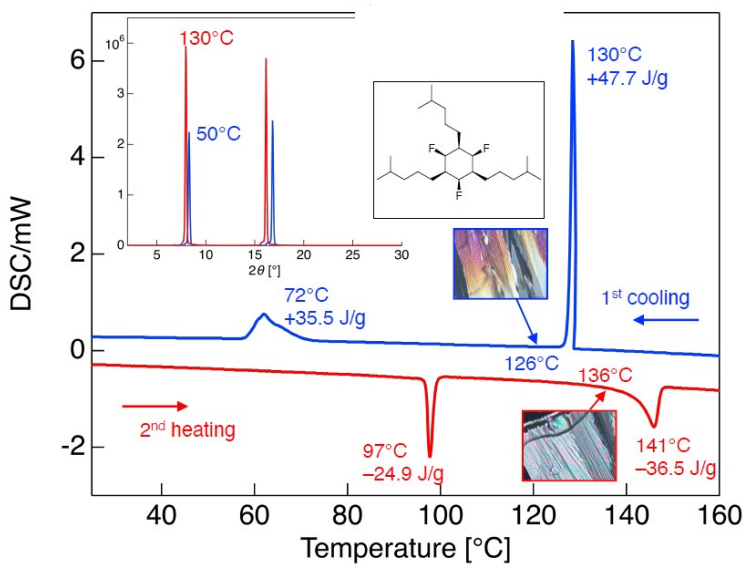
All-*cis* 1,3,5-trifluoro-2,4,6-triheptylcyclohexane (16b)



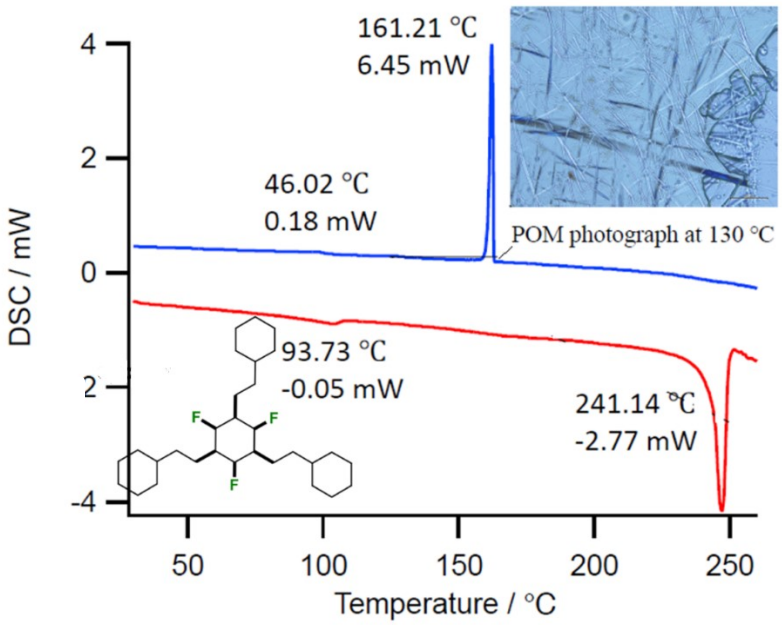
All-*cis* 1,3,5-trifluoro-2,4,6-trioctylcyclohexane (16c)



All-*cis* 1,3,5-trifluoro-2,4,6-tris(4-methylpentyl)cyclohexane (16d)



All-cis 2,4,6-trifluorocyclohexane-1,3,5-triyl)tris(ethane-2,1-diyl))tricyclohexane (16e)



5 Computational Details

The B3LYP-D3/def2-TZVP theoretical level accurately reproduces the geometries and molecular assemblies of *Janus face* compounds as demonstrated by the low RMSD calculated between calculated and X-ray diffraction geometries. Compounds **1**-**4** and dimeric and trimeric arrangements of compound **4** were optimized and harmonic frequency calculations were carried out at the B3LYP-D3/def2-TZVP theory level to identify each conformer as a true energy minima, showing no imaginary frequencies using Gaussian 16 Rev C.01 program.[1] Single point energies using the Domain-Based Local Pair Natural Orbital (DLPNO)[2] approximation for CCSD(T) and with the basis set extrapolated to completeness from Dunning's correlation-consistent polarized basis sets (cc-pVDZ, cc-pVTZ and cc-pVQZ) as implemented in ORCA 5.0.3[3] with TightPNO and TightSCF settings were calculated over the optimized geometries and considered as reference for a benchmark study. The Perdew-Burke-Ernzerhof hybrid functional (PBE0)[4] corrected with D3 empirical dispersion[5] and def2-TZVP basis set showed the lowest MAE (Mean Absolute Error) with respect to DLPNO-CCSD(T), and thus was chosen for subsequent calculations. Single point energies were obtained at the PBE0-D3/def2-TZVP theoretical level from the optimized geometries and corrected with the B3LYP-D3/def2-TZVP thermal correction to Gibbs free energies to afford the ring interconversion ΔG energy for compounds **2**-**4** equilibria. Molecular dipole moments were also obtained at the PBE0-D3/def2-TZVP level. The PBE0-D3/def2-TZVP electron density was further used for the electrostatic potential surface graphs, NCI[6] and QTAIM[7] calculations.

References for Computation

1. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E.

Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

2. C. Riplinger, F. Neese, *J. Chem. Phys.* **2013**, *138*, 034106.
3. F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.*, **2020**, *152*, 224108.
4. J. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.*, **1996**, *105*, 9982.
5. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, **2010**, *132*, 154104.
6. J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J. Piquemal, D. N. Beratan, W. Yang, *J. Chem. Theory Comput.*, **2011**, *7*, 3, 625-632.
7. R. F. W. Bader. *Atoms in Molecules: A Quantum Theory*, Claredon, Oxford, **1990**.

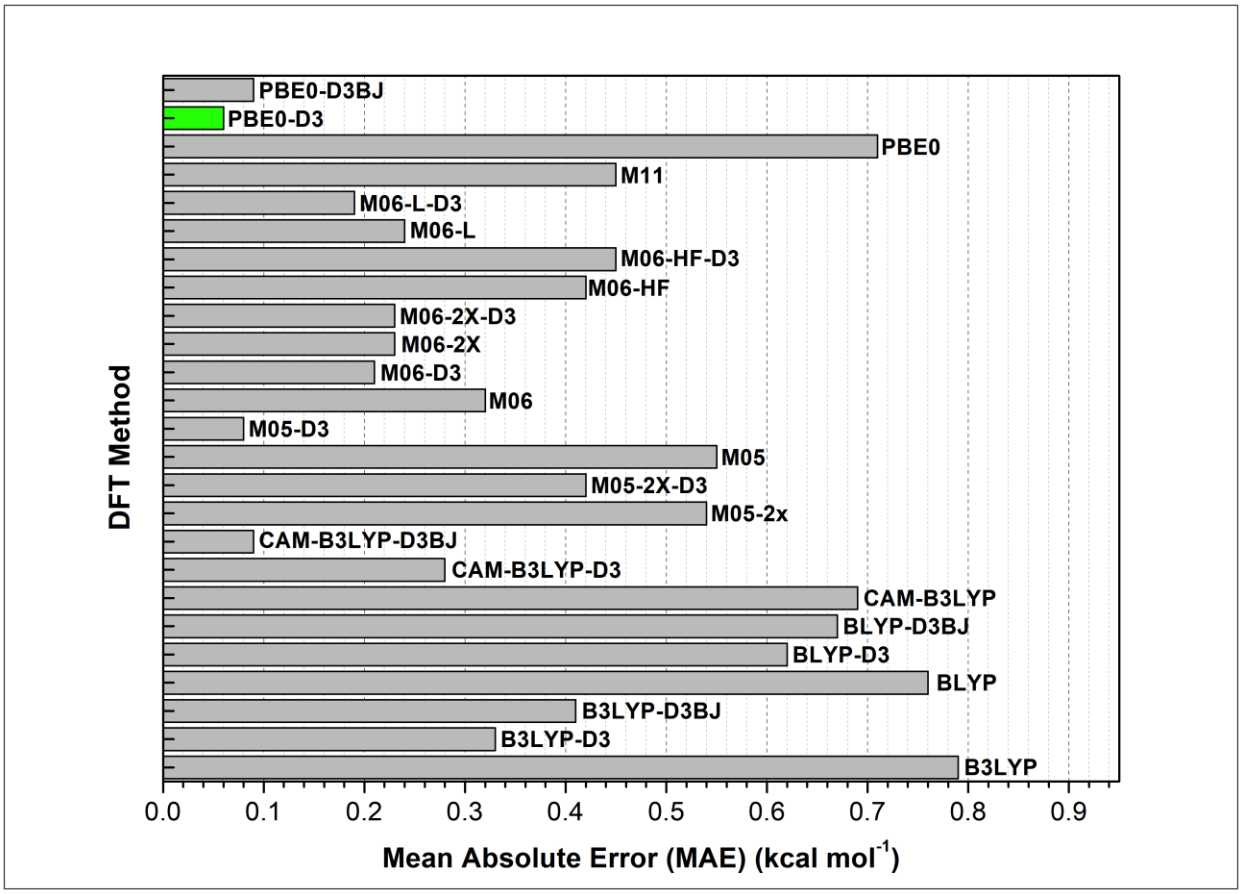


Figure S1. Mean Absolute Error (MAE) of single point energies (calculated over the B3LYP-D3/def2-TZVP optimized geometries) obtained in different DFT methods using the def2-TZVP

basis set with respect to the electronic energy obtained at the "golden standard" DLPNO-CCSD(T)/CBS level. Highlighted in green is the functional with the lowest MAE (0.06 kcal mol^{-1}).

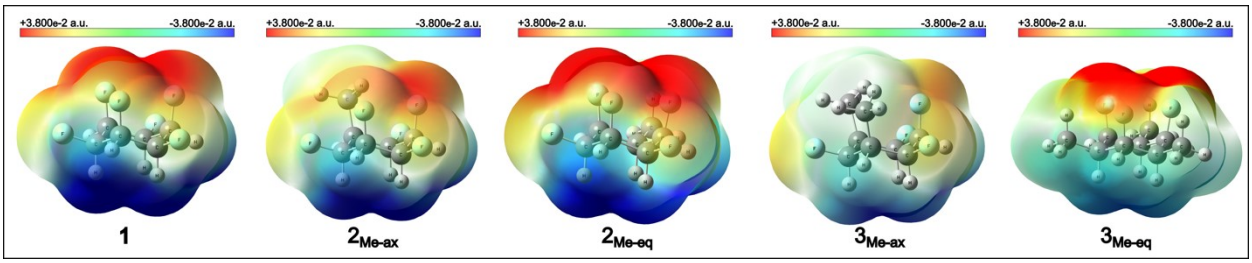


Figure S2. Electrostatic potential surface graphs for compounds **1**-**3** obtained from the PBE0-D3/def2-TZVP electron density over B3LYP-D3/def2-TZVP optimized geometries.

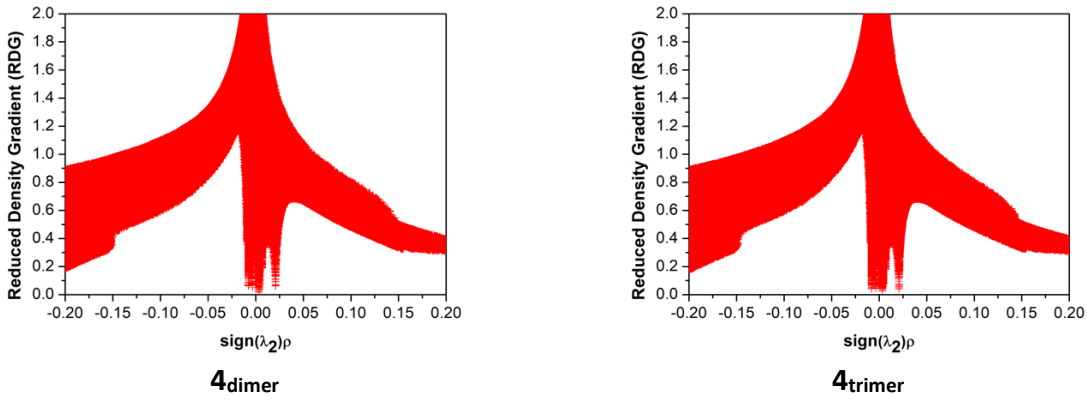


Figure S3. Reduced RDG versus sign(λ_2)ρ plots for dimeric (left) and trimeric (right) arrangements of compound **4**.

Table S1. Cartesian coordinates and Lowest harmonic vibrational frequencies of the optimized geometries for compounds **1**-**4** and dimeric and trimeric arrangements of **4** obtained at the B3LYP-D3/def2-TZVP level in the gas-phase. Electronic energies were calculated over the optimized geometries at PBE0-D3/def2-TZVP theoretical level.

1 **Energy (hartrees) = -830.802495** **No negative frequencies** **Lowest harmonic vibrational frequency (cm^{-1}) = 108.53**			
C	-0.31915100	1.39466200	-0.69020600
C	-1.40289200	0.43172700	-0.22444800
C	-1.04825000	-0.97398300	-0.68999500
C	0.32735800	-1.43070700	-0.22354600
C	1.36723800	-0.42128000	-0.69030500
C	1.07554200	0.99883700	-0.22453400
H	-2.36522400	0.72786100	-0.64739000
H	-0.32143400	1.40490400	-1.78588600
H	0.55224300	-2.41263100	-0.64534000
H	1.37678800	-0.42479300	-1.78598500
H	1.81327800	1.68396700	-0.64762300
H	-1.05554400	-0.98135400	-1.78567200
F	1.16588500	1.08236700	1.13657900
F	-1.52028700	0.46779800	1.13665700
F	0.35495700	-1.54853900	1.13771200
F	-0.60918500	2.66078200	-0.25690900

F	2.60875300	-0.80359600	-0.25742300
F	-2.00003200	-1.85808900	-0.25704900

$2_{Me\text{-}ax}$				$2_{Me\text{-}eq}$			
Energy (hartrees) = -770.902399				**Energy (hartrees) = -770.902469**			
No negative frequencies				**No negative frequencies**			
Lowest harmonic vibrational frequency (cm^{-1}) = 109.85				**Lowest harmonic vibrational frequency (cm^{-1}) = 98.09**			
C	0.66413600	-1.23583500	-0.74062700	C	-1.43565900	0.00000000	-0.70370500
C	1.46705100	-0.00002100	-0.31013500	C	-0.70011000	-1.27670700	-0.27227500
C	0.66417200	1.23581500	-0.74062900	C	0.76655700	-1.23688700	-0.68467400
C	-0.76918900	1.27535400	-0.21547600	C	1.50848900	-0.00000500	-0.18983600
C	-1.49034700	0.00002100	-0.64165500	C	0.76656000	1.23688000	-0.68467400
C	-0.76922600	-1.27533300	-0.21547300	C	-0.70010200	1.27671300	-0.27225900
H	2.37820400	-0.00003500	-0.91565700	H	-1.16979600	-2.14923100	-0.73718900
H	0.60461200	-1.26391500	-1.83599100	H	-1.43408400	0.00001600	-1.80072200
H	-1.28949400	2.14690200	-0.62130300	H	2.52988400	-0.00000400	-0.58129100
H	-1.54964100	0.00002000	-1.73689900	H	0.79926500	1.23125800	-1.78137500
H	-1.28955700	-2.14686600	-0.62130000	H	-1.16979300	2.14923700	-0.73717200
H	0.60464700	1.26389600	-1.83599400	H	0.79926900	-1.23126700	-1.78137500
C	1.88570400	-0.00002000	1.16257400	F	-0.80308400	1.45343200	1.09894600
H	2.48792600	-0.88457400	1.36558400	F	-0.80310700	-1.45342700	1.09893800
H	2.48800800	0.88448300	1.36555800	F	1.59755600	-0.00000800	1.18584700
H	1.03365200	0.00002900	1.83428000	C	-2.88310100	0.00001500	-0.21412400
F	1.32185200	2.39462600	-0.35023300	H	-3.41139200	0.88399500	-0.57468600
F	1.32178400	-2.39466600	-0.35023200	H	-3.41129000	-0.88418300	-0.57430100
F	-2.78404600	0.00004000	-0.15583100	H	-2.91315800	0.00023500	0.87352900
F	-0.78438000	-1.40299500	1.16205200	F	1.41795500	2.37987700	-0.25721200
F	-0.78434000	1.40301400	1.16205100	F	1.41793400	-2.37988700	-0.25720200

$3_{Me\text{-}ax}$				$3_{Me\text{-}eq}$			
Energy (hartrees) = -710.996591				**Energy (hartrees) = -711.000112**			
No negative frequencies				**No negative frequencies**			
Lowest harmonic vibrational frequency (cm^{-1}) = 106.99				**Lowest harmonic vibrational frequency (cm^{-1}) = 94.01**			
C	1.24126300	-0.77811200	-0.68835600	C	-1.28582800	-0.68696200	-0.69923900
C	1.31035500	0.70682500	-0.31356000	C	0.00000100	-1.43130700	-0.32364700
C	0.00000700	1.36021300	-0.78506700	C	1.28582900	-0.68696100	-0.69923900
C	-1.31034700	0.70683900	-0.31356000	C	1.27495400	0.77368700	-0.23727000
C	-1.24127200	-0.77809900	-0.68835600	C	0.00000000	1.47147700	-0.68238800
C	-0.00000800	-1.49969100	-0.17783600	C	-1.27495400	0.77368700	-0.23726900
H	2.10036500	1.14347100	-0.93218600	H	0.00000100	-2.40588000	-0.82438900
H	1.23640300	-0.87405700	-1.78094700	H	-1.30464200	-0.65933300	-1.79588100
H	-2.10035300	1.14349400	-0.93218400	H	2.13377100	1.30645000	-0.65816600
H	-1.23641200	-0.87404400	-1.78094800	H	-0.00000100	1.48437200	-1.77942300
H	-0.00001400	-2.53520500	-0.52705200	H	-2.13377100	1.30644900	-0.65816700
H	0.00000700	1.35335700	-1.88175600	H	1.30464300	-0.65933200	-1.79588100
C	1.69136100	0.97174100	1.14539700	F	-1.40361200	0.84597200	1.14352700
H	2.69807700	0.59758000	1.32729900	F	0.00000100	-1.70549700	1.04688100
H	1.68155500	2.04444300	1.33376400	F	1.40361100	0.84597200	1.14352800
H	1.02711600	0.48623400	1.85208800	C	2.53182700	-1.41925000	-0.20416700
C	-1.69134900	0.97175700	1.14539900	H	2.55144400	-2.44436100	-0.57831200
H	-1.68152400	2.04445800	1.33377000	H	3.43762000	-0.91475700	-0.54510300
H	-2.69807100	0.59761200	1.32730100	H	2.54331400	-1.45064000	0.88344500
H	-1.02711100	0.48623600	1.85208800	C	-2.53182600	-1.41925100	-0.20416700
F	0.00001400	2.70837000	-0.41784200	H	-3.43761900	-0.91475900	-0.54510200
F	2.37688600	-1.44393900	-0.23821100	H	-2.55144300	-2.44436200	-0.57831400
F	-2.37690200	-1.44391300	-0.23821200	H	-2.54331200	-1.45064400	0.88344500
F	-0.00000900	-1.55189700	1.21253100	F	0.00000000	2.79089500	-0.25436200

$4_{Me\text{-}ax}$				$4_{Me\text{-}eq}$			
Energy (hartrees) = -651.085226				**Energy (hartrees) = -651.095751**			
No negative frequencies				**No negative frequencies**			
Lowest harmonic vibrational frequency (cm^{-1}) = 98.74				**Lowest harmonic vibrational frequency (cm^{-1}) = 93.51**			
C	0.24189200	1.40882400	-0.73009000	C	-1.41584700	0.42071700	-0.69603600
C	-1.16064600	0.96478500	-0.29026500	C	-1.06689700	-1.01075400	-0.28895800
C	-1.34081400	-0.49494500	-0.73056800	C	0.34362600	-1.43639900	-0.69599200
C	-0.25526800	-1.48742600	-0.29020500	C	1.40883600	-0.41833500	-0.28917700
C	1.09928000	-0.91384700	-0.73030100	C	1.07199600	1.01609100	-0.69598200
C	1.41592900	0.52259800	-0.29032300	C	-0.34207400	1.42938100	-0.28844700
H	-1.86066000	1.54718100	-0.89802800	H	-1.79029100	-1.69622500	-0.74507300
H	0.24870900	1.44906900	-1.82550300	H	-1.42016800	0.42227100	-1.79347000
H	-0.40945600	-2.38521000	-0.89751800	H	2.36400200	-0.70203000	-0.74566500
H	1.13077300	-0.93998200	-1.82572300	H	1.07533900	1.01965700	-1.79342000
H	2.27027900	0.83789500	-0.89799800	H	-0.57409600	2.39884700	-0.74396800
H	-1.37876400	-0.50906100	-1.82599800	H	0.34469100	-1.44139000	-1.79342600

C	1.85391800	0.68404200	1.16682300
H	2.72952900	0.06296600	1.35143600
H	2.12069100	1.72405200	1.35053300
H	1.09166300	0.40531100	1.88611500
C	-1.52029800	1.26279300	1.16692500
H	-1.42163200	2.33173100	1.35179300
H	-2.55423300	0.97283800	1.34979000
H	-0.89796200	0.74270400	1.88702900
C	-0.33443700	-1.94680200	1.16721900
H	-1.30980900	-2.39523600	1.35185500
H	0.43320800	-2.69739700	1.35128300
H	-0.19537600	-1.14707700	1.88650900
F	-2.59247500	-0.95713200	-0.30529400
F	0.46782200	2.72376700	-0.30464600
F	2.12528600	-1.76662600	-0.30460000
F	-0.39232200	1.63802300	1.09542000
F	-1.22343500	-1.15907700	1.09474100
F	1.61604000	-0.47994800	1.09445200
C	0.67999600	-2.84083700	-0.19760800
H	-0.05533500	-3.56496600	-0.55360100
H	1.66393400	-3.15283600	-0.55305800
H	0.68512300	-2.86345300	0.89027600
C	-2.80053500	0.83173100	-0.19833800
H	-3.05960100	1.83069400	-0.55437200
H	-3.56260400	0.13578800	-0.55434800
H	-2.82335500	0.83853000	0.88954400
C	2.12053400	2.00951100	-0.19818300
H	3.11512800	1.73430200	-0.55433300
H	1.89904200	3.01757700	-0.55395900
H	2.13784400	2.02561400	0.88968000

4_{dimer}

Energy (hartrees) = -1302.206592

No negative frequencies

Lowest harmonic vibrational frequency (cm^{-1}) = 26.55

F	-3.46777500	1.52216300	-0.76659700
F	-3.47896600	-0.09281900	1.69179400
F	-3.47577400	-1.41557000	-0.93543200
C	-1.67735200	0.08396300	-1.46964300
H	-0.58406200	0.08039700	-1.45799200
C	-2.08253700	1.31294300	-0.66034800
H	-1.61485700	2.19817100	-1.10542200
C	-1.67916700	1.23060600	0.80936700
H	-0.58582200	1.21823900	0.80717400
C	-2.09222700	-0.08352500	1.46658700
H	-1.63122300	-0.14174500	2.45884200
C	-1.68621300	-1.31610200	0.66307500
H	-0.59275700	-1.31038200	0.66160600
C	-2.08945000	-1.22735100	-0.80635700
H	-1.62644700	-2.05836100	-1.34998000
C	-2.15954200	0.16810200	-2.91648500
H	-3.24718700	0.17344000	-2.95749600
H	-1.79311300	1.07993700	-3.39319300
H	-1.79800700	-0.68557700	-3.49395800
C	-2.17728300	-2.60819300	1.31268500
H	-1.81805900	-2.68408400	2.34136300
H	-3.26517200	-2.63907900	1.32656400
H	-1.81556900	-3.47912900	0.76173800
C	-2.16229900	2.44297400	1.60271400
H	-3.24998500	2.47953200	1.62046300
H	-1.80298100	2.39841400	2.63318400
H	-1.79457300	3.36879000	1.15482300
F	1.28151200	1.50590700	-0.75815100
F	1.27805500	-0.09558800	1.68126100
F	1.27678800	-1.40930400	-0.92180300
C	3.06972400	0.08095000	-1.47527300
H	4.16691300	0.07977100	-1.48477600
C	2.67001400	1.31009600	-0.66064000
H	3.12263000	2.20007500	-1.10985800
C	3.07146300	1.23407900	0.81153600
H	4.16865900	1.24026200	0.81705500
C	2.66735300	-0.08506700	1.46767300
H	3.11676300	-0.14208700	2.46439900
C	3.06842500	-1.32264000	0.66662300
H	4.16558800	-1.33188200	0.67065200
C	2.66613000	-1.23090500	-0.80435000
H	3.11520600	-2.06614300	-1.35154300
C	2.56765500	0.16286500	-2.91640000
H	1.47984600	0.16605300	-2.94267500
H	2.92395400	1.07441600	-3.39925000
H	2.92118100	-0.69007000	-3.49823000
C	2.57088000	2.44210500	1.60247800
H	1.48308700	2.46595300	1.61591600
H	2.92487200	2.40307800	2.63407700
H	2.92771600	3.37177000	1.15592800
C	2.56497700	-2.61082300	1.31662100
H	2.91954000	-2.68938300	2.34577700
H	1.47714100	-2.63271600	1.32813800
H	2.91885000	-3.48523500	0.76783800

4_{trimer}

Energy (hartrees) = -1953.319917

No negative frequencies

Lowest harmonic vibrational frequency (cm^{-1}) = 13.17

F	-5.81401000	1.60896200	-0.58230000
F	-5.83351500	-0.29872500	1.66314100
F	-5.82161300	-1.29049000	-1.11100600
C	-4.02064000	0.26391100	-1.44845500
H	-2.92777900	0.25840000	-1.43254600
C	-4.42813500	1.38474300	-0.49668400
H	-3.95744400	2.31676700	-0.82806700
C	-4.03019500	1.12206000	0.95286000
H	-2.93710300	1.10997400	0.95155700
C	-4.44493100	-0.26216500	1.44273900
H	-3.98623300	-0.44172400	2.42126900
C	-4.03700900	-1.38675900	0.49560300
H	-2.94379900	-1.38082500	0.49849400
C	-4.43460300	-1.11839300	-0.95306300
H	-3.96865400	-1.87605700	-1.59254000
C	-4.49688300	0.52477900	-2.87594400
H	-5.58445200	0.53536300	-2.92059500
H	-4.12806600	1.48792400	-3.23564000
H	-4.13207000	-0.25175400	-3.55196200
C	-4.52893900	-2.74890600	0.98050800
H	-4.17107400	-2.94990900	1.99275400
H	-5.61692900	-2.78292500	0.98829600
H	-4.16429300	-3.54513200	0.32775900
C	-4.51500800	2.22836900	1.88758100
H	-5.60281200	2.26354100	1.90752900
H	-4.15732300	2.05754300	2.90539600
H	-4.14515100	3.20158100	1.55723000
F	-1.09880500	1.59807800	-0.57061400
F	-1.10555300	-0.30477900	1.67432900
F	-1.10091400	-1.29955200	-1.09157800
C	0.69413200	0.25758200	-1.44348000
H	1.78715600	0.25581600	-1.43629400
C	0.29291800	1.37852500	-0.49022100
H	0.75353000	2.31277900	-0.82571700
C	0.69103000	1.12154500	0.95949900
H	1.78417700	1.11564300	0.95738500
C	0.28737200	-0.26438200	1.45170900
H	0.74266500	-0.44092500	2.43108900
C	0.69040900	-1.39134700	0.50649100
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C	0.29143500	-1.12488100	-0.94129800
H	0.74972700	-1.88403100	-1.58258500
C	0.20674400	0.51400900	-2.86843900
H	-0.88083800	0.52190200	-2.91071500
H	0.56937700	1.47732500	-3.23260300
H	0.56885700	-0.26250100	-3.54521600
C	0.20173100	2.22746400	1.89299400
H	-0.88592000	2.26098200	1.91807400
H	0.56152200	2.06069400	2.91025900
H	0.56536000	3.20167000	1.56012300
C	0.20042400	-2.75317900	0.99547200
H	0.56067100	-2.95200400	2.00682500
H	-0.88724100	-2.79277900	1.00804000
H	0.56329800	-3.55018900	0.34342700
F	3.62406500	1.58421200	-0.57357100

	F 3.62799600 -0.29371200 1.65558600 F 3.62393000 -1.28792300 -1.08343100 C 5.41514600 0.25975600 -1.45933500 H 6.51223800 0.26161800 -1.46986900 C 5.01518700 1.38232400 -0.50356000 H 5.46281100 2.32101600 -0.84497800 C 5.41985400 1.13258600 0.94815600 H 6.51696800 1.13878800 0.95140400 C 5.01876400 -0.25569300 1.44338100 H 5.46790500 -0.43010600 2.42620300 C 5.41990900 -1.38866100 0.50060600 H 6.51702800 -1.39557400 0.50152400 C 5.01514500 -1.12307200 -0.94826100 H 5.46243400 -1.88698300 -1.59205700 C 4.91229300 0.51131200 -2.88034900 H 3.82449200 0.51547500 -2.90630900 H 5.26654800 1.47435200 -3.25166700 H 5.26716000 -0.26557700 -3.55957700 C 4.92251200 2.23833200 1.87852600 H 3.83480400 2.26100500 1.89936600 H 5.28042200 2.07757300 2.89679400 H 5.27801900 3.21432900 1.54403600 C 4.92268900 -2.74688700 0.99404600 H 5.28126700 -2.94606600 2.00528800 H 3.83499800 -2.77545900 1.00667900 H 5.27781400 -3.54830800 0.34411700

6 Details of X-ray Crystallography

X-ray diffraction data for compounds **8**, **16e** and **16f** were collected at 173 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P100 diffractometer. Diffraction data for compounds **12c** and **16d** were collected at 125 K using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with XtaLAB P200 diffractometer. Intensity data were collected using Cu Kα radiation (λ = 1.54187 Å), with either just ω steps, or both ω and ϕ steps, accumulating area detector images spanning at least a hemisphere of reciprocal space. Data for all compounds analysed were collected using CrystalClear[1] and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro.[2] Structures were solved by dual-space methods (SHELXT[3]) and refined by full-matrix least-squares against F^2 (SHELXL-2018/3[4]). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. Compounds **12c** and **16e** showed non-merohedric twinning. All calculations were performed using either the Olex2[5] or the CrystalStructure[6] interface. Selected crystallographic data are presented in Table **S1**. Deposition numbers 2174305-2174309 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table S1. Selected crystallographic data.

	8	**12c**	**16d**	**16e**	**16f**
formula	$C_{14}H_{23}F_5$	$C_{18}H_{32}F_4$	$C_{24}H_{45}F_3$	$C_{30}H_{51}F_3$	$C_{33}H_{57}F_3O_3$
fw	286.32	324.44	390.61	468.73	558.78
crystal description	Colourless plate	Colourless plate	Colourless needle	Colourless needle	Colourless needle
crystal size [mm^3]	0.11×0.10×0.01	0.11×0.03×0.01	0.15×0.02×0.01	0.20×0.02×0.01	0.54×0.08×0.01
space group	$P2_1/n$	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1$
a [Å]	5.5262(16)	11.7685(6)	19.3963(11)	22.2117(8)	19.1482(8)
b [Å]	70.03(3)	4.7401(2)	4.7331(3)	4.74450(15)	4.7110(2)
c [Å]	11.417(4)	17.0705(10)	26.5239(15)	26.2704(8)	19.5670(9)
β [°]	101.86(3)	103.918(6)	95.933(5)	92.597(3)	117.937(6)
vol [Å]^3	4324(3)	924.30(9)	2422.0(2)	2765.62(16)	1559.39(14)
Z	12	2	4	4	2
ρ (calc) [g/cm^3]	1.319	1.166	1.071	1.126	1.190
μ [mm^{-1}]	1.044	0.786	0.608	0.611	0.694
F(000)	1824	352	864	1032	612
reflections collected	45738	9955	25361	28075	15777
independent reflections (R_{int})	8073 (0.3923)	3588 (0.0607)	4901 (0.0759)	4931 (0.0828)	5314 (0.0609)
parameters, restraints	518, 0	204, 1	250, 0	299, 0	352, 1
GoF on F^2	1.438	1.487	1.056	1.153	1.046
R_1 [$I > 2\sigma(I)$]	0.1646	0.1045	0.0850	0.0814	0.0786
wR_2 (all data)	0.4235	0.3408	0.2604	0.2436	0.2025
largest diff. peak/hole [e/Å^3]	0.75, -0.48	0.54, -0.39	1.07, -0.34	0.38, -0.29	1.03, -0.38
Flack parameter	-	0.4(3)	-	-	0.32(15)

Data for structures 8, 12c, 16d, 16e and 16f have been deposited at the CCDC as numbers 2174305-2174309 respectively.

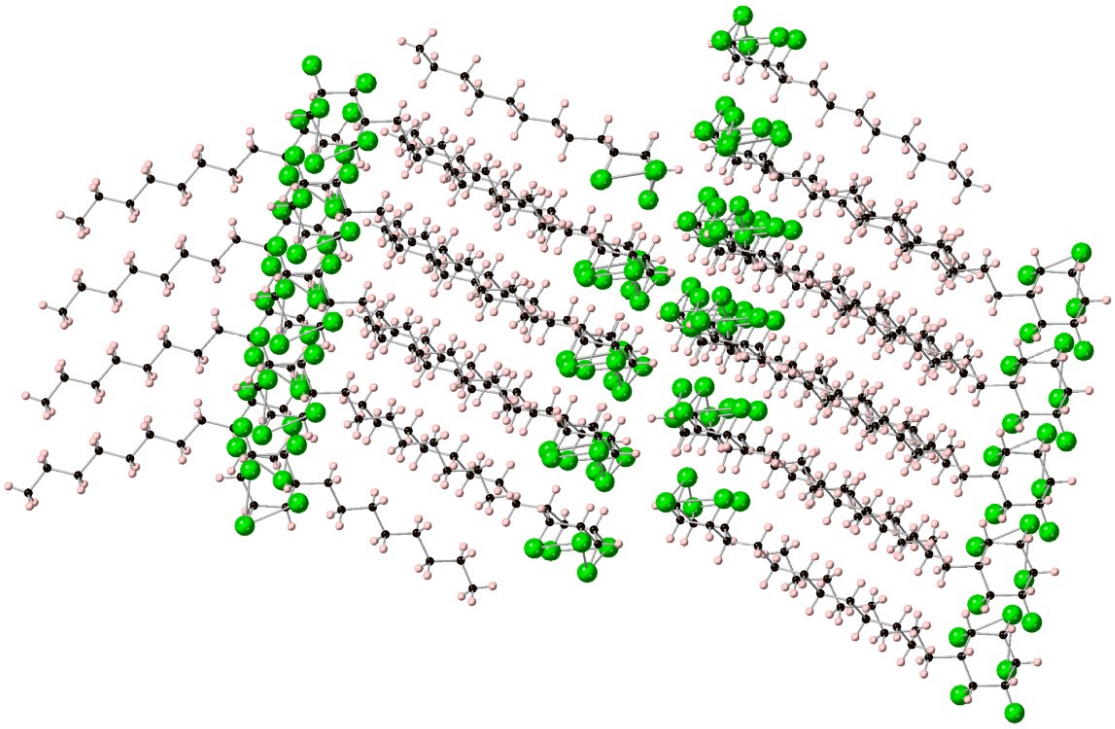

Figure S4 Molecular packing image for the structure of 8

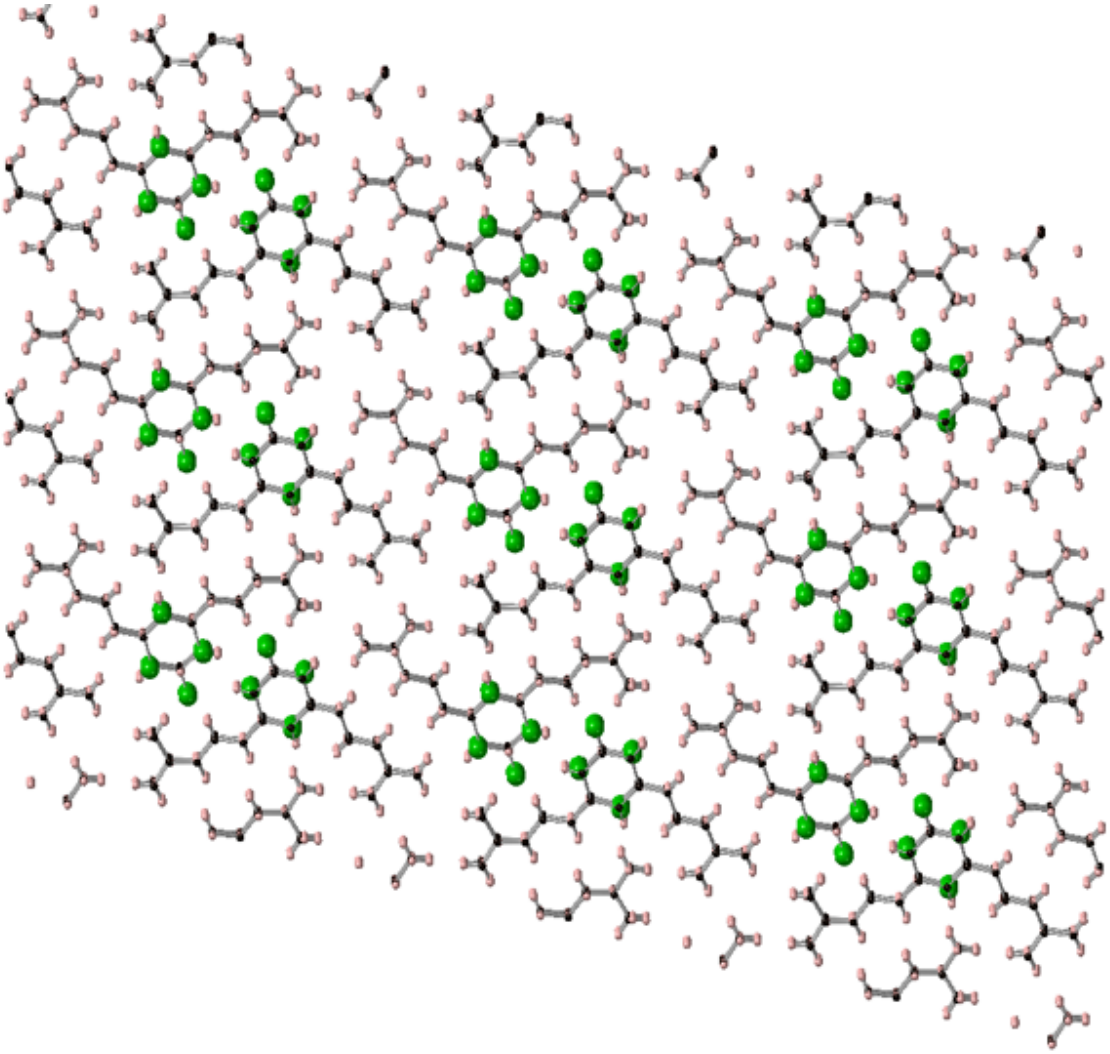

Figure S5 Molecular packing image for the structure of 12c

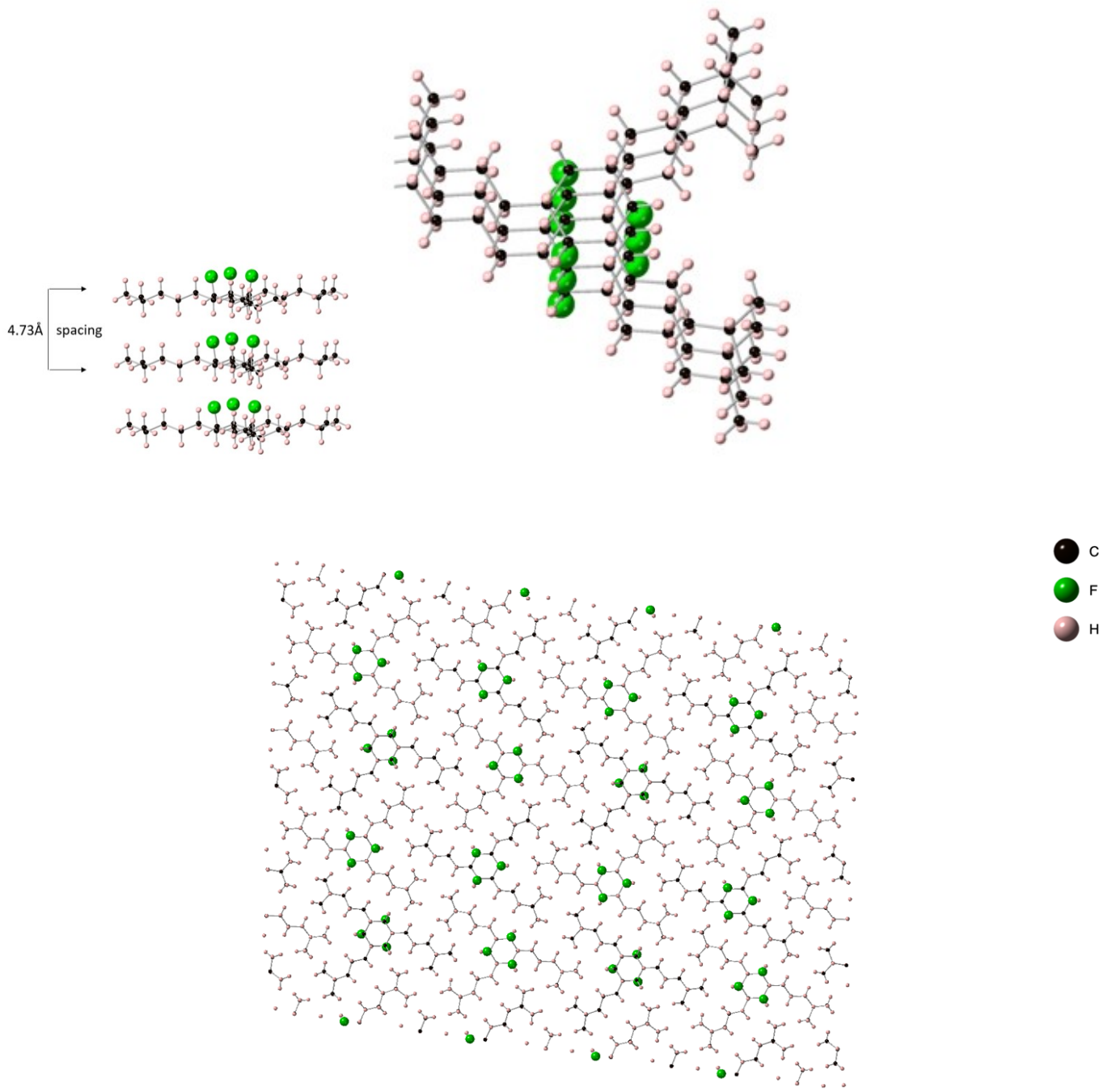

Figure S6 Molecular packing image for the structure of 16d

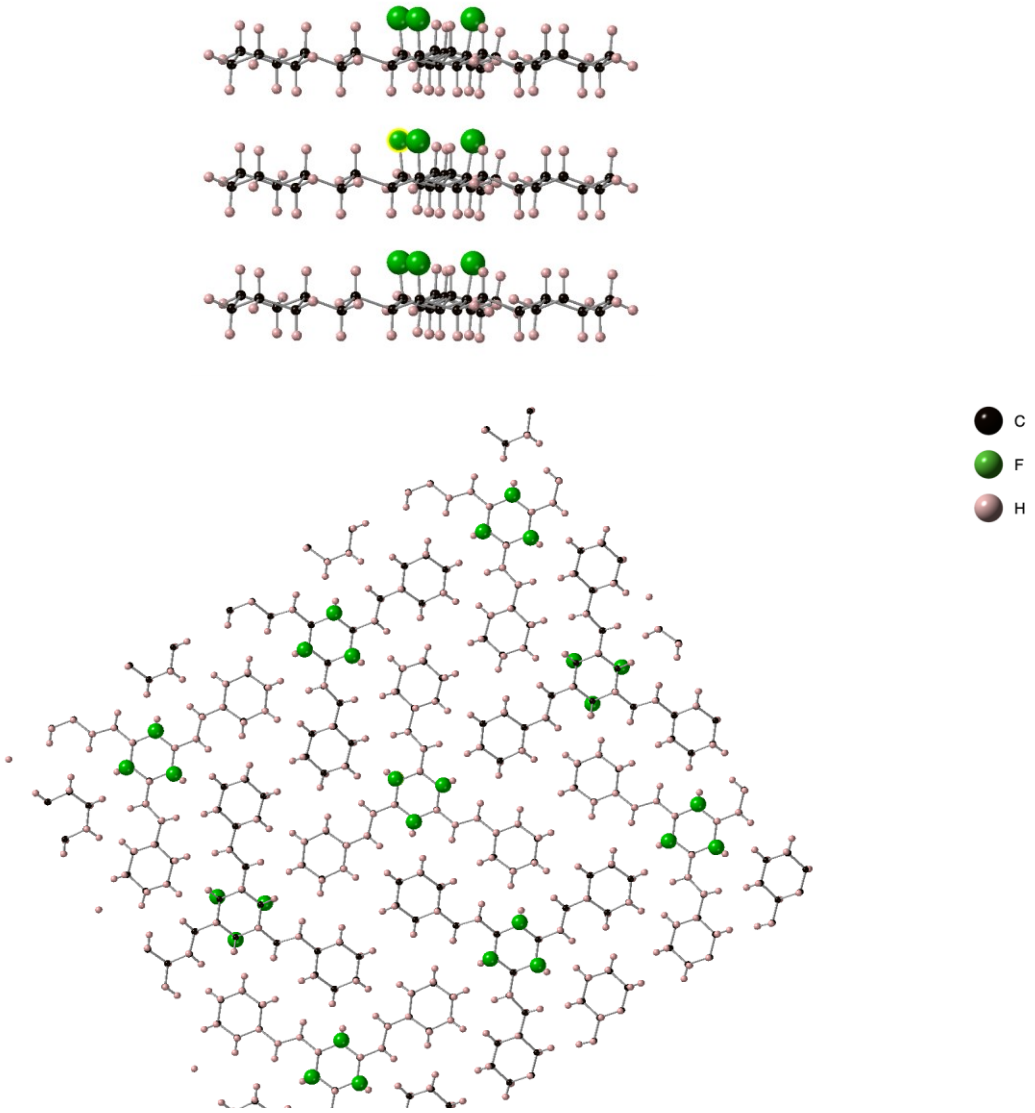

Figure S7 Molecular packing image for the structure of 16e

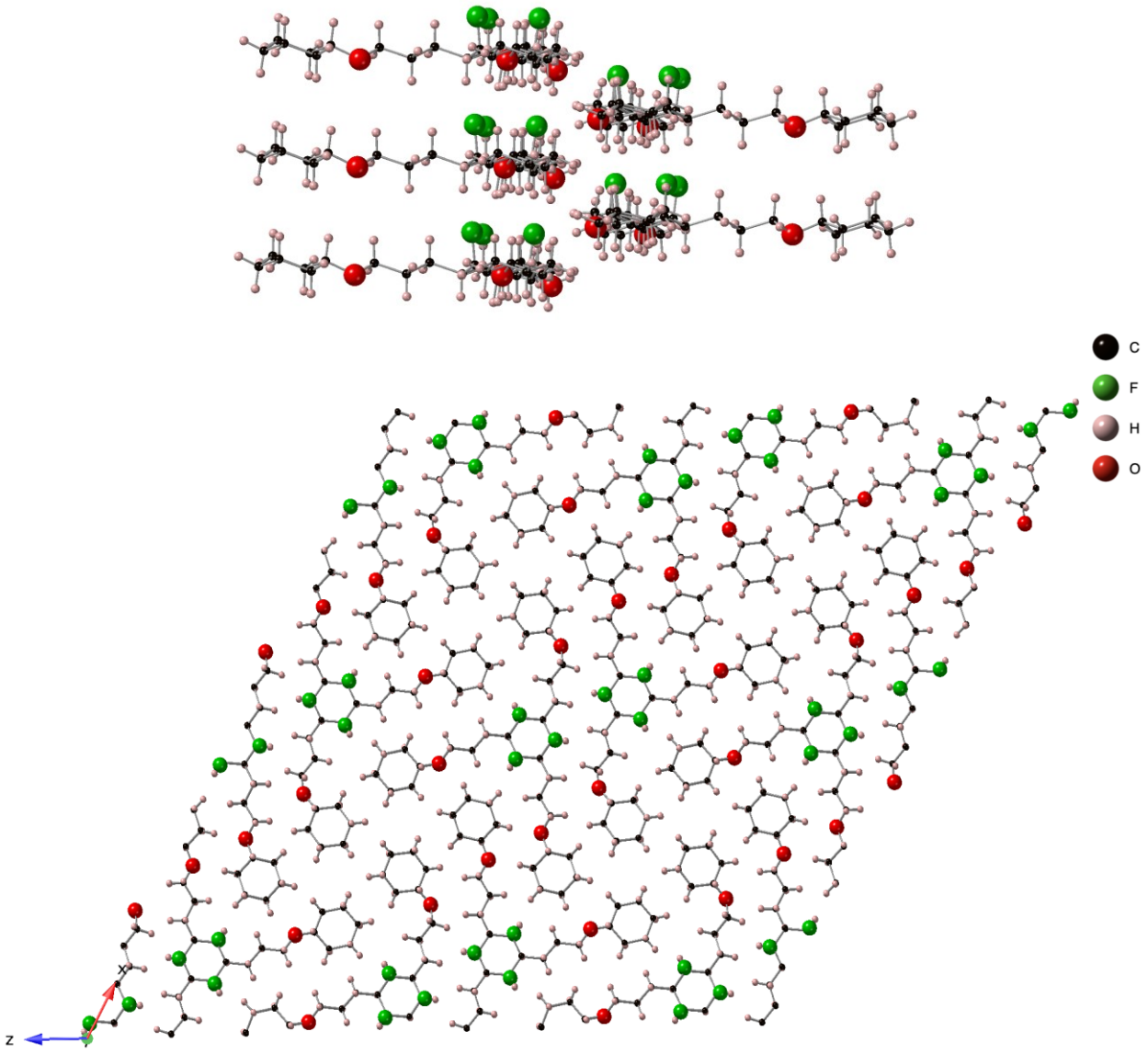

Figure S8 Molecular packing image for the structure of 16f

References for Crystallography

1. *CrystalClear-SM Exper*t v2.1. Rigaku Americas, *The Woodlands, Texas, USA*, and Rigaku Corporation, *Tokyo, Japan*, 2015.
2. CrysAlisPro v1.171.39.8d or v1.171.40.14a. Rigaku Oxford Diffraction, Rigaku Corporation, Oxford, U.K., 2015-2018.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv*. **2015**, *71*, 3-8. doi: 10.1107/S2053273314026370
4. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3-8. doi: 10.1107/S2053229614024218
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*., **2009**, *42*, 339-341. doi: 10.1107/S0021889808042726
6. CrystalStructure v4.3.0. Rigaku Americas, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan, 2018.