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# A new cycloadduct based on quadricyclane and perfluorocyclohexene: synthesis, metathesis polymerization and gas-transport properties of the obtained polymer

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## 1. Materials

All starting fluorine-containing compounds were purchased from SIA "P&M-Invest" Ltd. THF was distilled for three times, first over NaOH, for the second time over sodium and for the third time over sodium with benzophenone when persisted violet color was observed. Quadricyclane was synthesized as reported previously.[1]

## 2. Methods of characterization

NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer at 500.13 MHz ($^{1}$H NMR) and 125.76 MHz ($^{13}$C NMR), at 470.59 MHz for $^{19}$F NMR. Each sample was dissolved in a solvent ($CDCl_3$ or mixture $C_6D_6/C_6F_6$ was used due to poor solubility of **2** and hexafluorobenzene ($C_6F_6$) was applied also as an internal standard in $^{19}$F NMR) up to a concentration of 10%. Mass spectra were recorded on a Thermo Focus DSQ II (ionization energy 70 eV, source temperature 230°C). Differential scanning calorimetry (DSC) was performed on a Mettler TA4000 system at a heating rate 20°C/min. Thermal gravimetric measurements (TGA) were carried out using a Perkin-Elmer TGA-7 instrument.

## 3. Film casting

The films of the polymers studied were cast from the 2 weight % solution in $C_6F_6$. The solution was poured into a steal cylinder with a stretched cellophane bottom. The solvent was

allowed to evaporate slowly to yield the desired polymer films. After the films formation, cellophane was detached from the films. Before testing, the films were kept under vacuum until the constant weight is achieved. The thickness of the films was in the range of 50-80 μm.

**NMR description of 1.**

$^{1}$H NMR ($CDCl_3$; δ, ppm): 6.20 br.s (2H), 3.30 br.s (2H), 2.47-2.43 m (2H), 2.02 (d, $^{2}J$=10.1 Hz, 1H), 1.42 (d, $^{2}J$=10.1 Hz, 1H). $^{13}$C NMR ($CDCl_3$; δ, ppm): 137.98 s, 113.38-112.53 m, 111.39-110.36 m, 109.26-108.23 m, 107.12-106.13 m, 89.08-87.99 m, 86.87-86.00 m, 44.17-44.04 m, 43.56 d ($^{2}J$=3.6 Hz), 40-60-40.15 m. $^{19}$F NMR ($CDCl_3$; δ, ppm): -118.96-(-)119.11 m (1F), -119.55-(-)119.69 m (1F), -124.29-(-)124.49 m (1F), -124.86-(-)125.06 m (1F), -126.02-(-)126.19 m (1F), -126.00-(-)126.79 m (1F), -129.30-(-)129.51 m (1F), -129.87-(-)130.08 m (1F), -198.88 s (2F). m/z (EI): 354, $M^+$ (1%), 308 (4%), 91 (20%), 66 (100%).

**NMR description of 2.**

$^{1}$H NMR ($C_6D_6/C_6F_6$; δ, ppm): 5.93-5.34 m (2H), 3.92-3.53 m (0.5 H), 3.51-2.73 m (3.5 H), 2.47-2.10 m (1H), 1.80-1.47 m (1 H). $^{13}$C NMR ($C_6D_6/C_6F_6$; δ, ppm): 132.50-131.13 m, 118.91-117.67 m, 116.75-115.56 m, 114.45-113.53 m, 112.62-111.58 m, 110.95-109.49 m, 109.01-107.39 m, 106.90-105.77 m, 95.15-87.05 m, 47.93-46.33 m, 46.14-44.48 m, 43.27-40.53 m, 36.96-36.59 m. $^{19}$F NMR ($C_6D_6/C_6F_6$; δ, ppm): -120.89-(-)124.65 (2F), -125.06-(-)129.45 (4F), -129.50-(-)132.08 (2F), -181.84-(-)184.47 (2F).

# X-ray analysis of 1

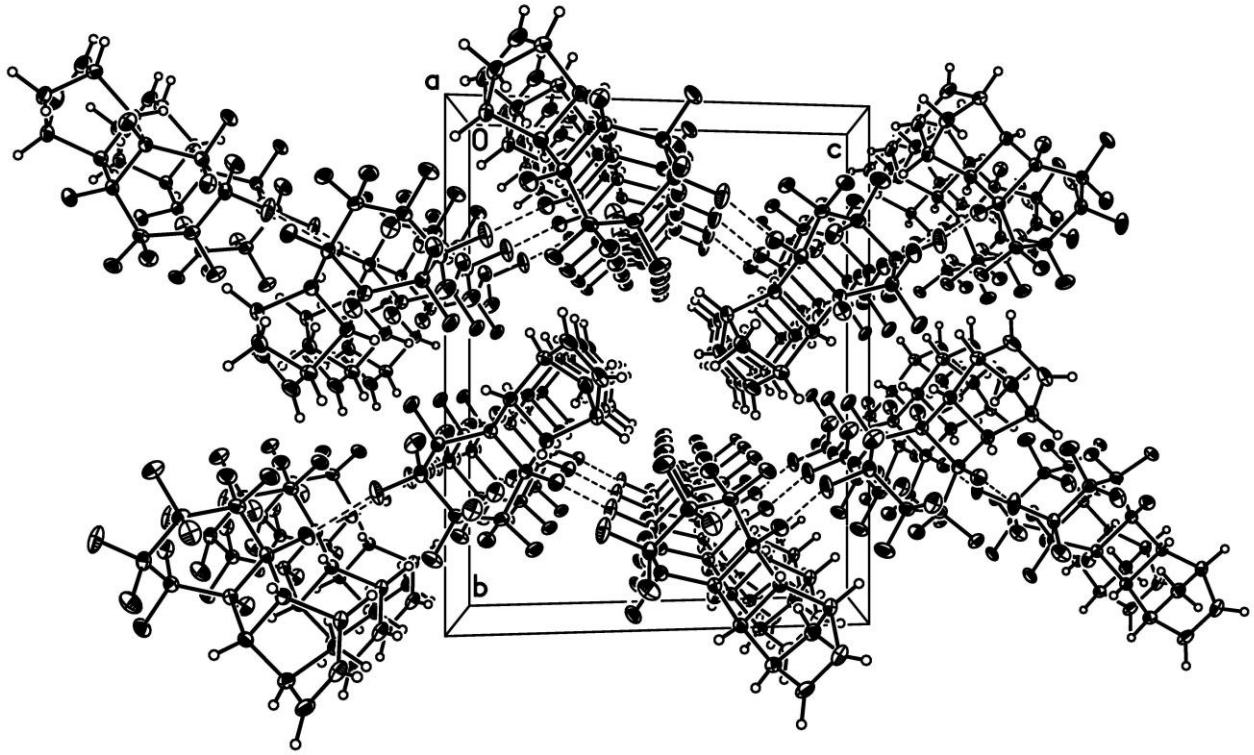


**Figure S1** A fragment of the crystal packing of the compound **1** along the crystallographic axis *a*.

**Table S1** Crystal data and structure refinement for **1**.

| | | |
|---|---|---|
| Identification code | I | |
| Empirical formula | C13 H8 F10 | |
| Formula weight | 354.19 | |
| Temperature | 120(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 6.1614(5) Å | α= 90°. |
| | b = 15.7377(13) Å | β= 100.198(2)°. |
| | c = 12.8181(11) Å | γ = 90°. |
| Volume | 1223.29(18) $Å^3$ | |
| Z | 4 | |

| | |
|---|---|
| Density (calculated) | 1.923 $Mg/m^3$ |
| Absorption coefficient | 0.219 $mm^{-1}$ |
| F(000) | 704 |
| Crystal size | 0.35 x 0.05 x 0.05 $mm^3$ |
| Theta range for data collection | 2.07 to 29.00°. |
| Index ranges | -8<=h<=8, -19<=k<=21, -17<=l<=17 |
| Reflections collected | 9998 |
| Independent reflections | 3255 [R(int) = 0.0253] |
| Completeness to theta = 29.00° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.981 and 0.923 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3255 / 0 / 208 |
| Goodness-of-fit on $F^2$ | 1.014 |
| Final R indices [for 2723 rfln with I>2sigma(I)] | R1 = 0.0354, wR2 = 0.0892 |
| R indices (all data) | R1 = 0.0442, wR2 = 0.0956 |
| Largest diff. peak and hole | 0.500 and -0.221 e. $Å^{-3}$ |

**Table S2** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 1934(2) | 1907(1) | 3051(1) | 14(1) |
| C(2) | 2806(2) | 1191(1) | 3862(1) | 14(1) |
| C(3) | 910(2) | 602(1) | 3341(1) | 15(1) |
| C(4) | 1503(2) | -128(1) | 2619(1) | 19(1) |
| C(5) | -748(3) | -400(1) | 2028(1) | 23(1) |
| C(6) | -1493(3) | 208(1) | 1332(1) | 23(1) |
| C(7) | 245(2) | 905(1) | 1444(1) | 20(1) |
| C(8) | 31(2) | 1320(1) | 2526(1) | 15(1) |
| C(9) | 2344(2) | 360(1) | 1729(1) | 21(1) |
| C(10) | 1283(2) | 2728(1) | 3549(1) | 15(1) |
| C(11) | -87(2) | 2616(1) | 4441(1) | 17(1) |
| C(12) | 783(2) | 1896(1) | 5258(1) | 17(1) |
| C(13) | 2850(2) | 1420(1) | 5023(1) | 15(1) |

| | | | | |
|---|---|---|---|---|
| F(1) | 3405(1) | 2146(1) | 2415(1) | 22(1) |
| F(2) | 4903(1) | 916(1) | 3806(1) | 19(1) |
| F(3) | 3134(1) | 3163(1) | 3968(1) | 21(1) |
| F(4) | 115(1) | 3228(1) | 2792(1) | 22(1) |
| F(5) | -90(2) | 3359(1) | 4958(1) | 31(1) |
| F(6) | -2182(1) | 2441(1) | 3996(1) | 25(1) |
| F(7) | 1286(2) | 2232(1) | 6229(1) | 30(1) |
| F(8) | -843(1) | 1326(1) | 5263(1) | 26(1) |
| F(9) | 4618(1) | 1919(1) | 5376(1) | 19(1) |
| F(10) | 3089(1) | 704(1) | 5619(1) | 22(1) |

**Table S3** Bond lengths [Å] and angles [°] for **1**.

| | | | |
|---|---|---|---|
| C(1)-F(1) | 1.3748(14) | C(10)-F(4) | 1.3531(15) |
| C(1)-C(10) | 1.5261(18) | C(10)-F(3) | 1.3567(15) |
| C(1)-C(8) | 1.5493(18) | C(10)-C(11) | 1.5469(19) |
| C(1)-C(2) | 1.5620(18) | C(11)-F(6) | 1.3436(16) |
| C(2)-F(2) | 1.3763(14) | C(11)-F(5) | 1.3442(16) |
| C(2)-C(13) | 1.5264(18) | C(11)-C(12) | 1.5713(19) |
| C(2)-C(3) | 1.5471(18) | C(12)-F(7) | 1.3382(16) |
| C(3)-C(4) | 1.5590(18) | C(12)-F(8) | 1.3448(16) |
| C(3)-C(8) | 1.5695(18) | C(12)-C(13) | 1.5526(18) |
| C(3)-H(3A) | 1.0000 | C(13)-F(9) | 1.3541(15) |
| C(4)-C(5) | 1.520(2) | C(13)-F(10) | 1.3541(15) |
| C(4)-C(9) | 1.5392(19) | F(1)-C(1)-C(10) | 105.40(10) |
| C(4)-H(4A) | 1.0000 | F(1)-C(1)-C(8) | 115.68(11) |
| C(5)-C(6) | 1.332(2) | C(10)-C(1)-C(8) | 116.85(11) |
| C(5)-H(5A) | 0.9500 | F(1)-C(1)-C(2) | 114.00(10) |
| C(6)-C(7) | 1.522(2) | C(10)-C(1)-C(2) | 114.68(11) |
| C(6)-H(6A) | 0.9500 | C(8)-C(1)-C(2) | 90.23(9) |
| C(7)-C(9) | 1.541(2) | F(2)-C(2)-C(13) | 105.67(10) |
| C(7)-C(8) | 1.5600(19) | F(2)-C(2)-C(3) | 115.70(10) |
| C(7)-H(7A) | 1.0000 | C(13)-C(2)-C(3) | 116.35(10) |
| C(8)-H(8A) | 1.0000 | F(2)-C(2)-C(1) | 114.01(10) |
| C(9)-H(9A) | 0.9900 | C(13)-C(2)-C(1) | 115.02(10) |
| C(9)-H(9B) | 0.9900 | C(3)-C(2)-C(1) | 90.05(10) |

| | | | |
|---|---|---|---|
| C(2)-C(3)-C(4) | 117.32(11) | C(4)-C(9)-C(7) | 94.35(10) |
| C(2)-C(3)-C(8) | 90.03(9) | C(4)-C(9)-H(9A) | 112.9 |
| C(4)-C(3)-C(8) | 102.99(10) | C(7)-C(9)-H(9A) | 112.9 |
| C(2)-C(3)-H(3A) | 114.4 | C(4)-C(9)-H(9B) | 112.9 |
| C(4)-C(3)-H(3A) | 114.4 | C(7)-C(9)-H(9B) | 112.9 |
| C(8)-C(3)-H(3A) | 114.4 | H(9A)-C(9)-H(9B) | 110.3 |
| C(5)-C(4)-C(9) | 99.66(11) | F(4)-C(10)-F(3) | 107.05(10) |
| C(5)-C(4)-C(3) | 102.37(11) | F(4)-C(10)-C(1) | 109.81(11) |
| C(9)-C(4)-C(3) | 102.56(11) | F(3)-C(10)-C(1) | 109.17(10) |
| C(5)-C(4)-H(4A) | 116.6 | F(4)-C(10)-C(11) | 107.78(11) |
| C(9)-C(4)-H(4A) | 116.6 | F(3)-C(10)-C(11) | 107.20(11) |
| C(3)-C(4)-H(4A) | 116.6 | C(1)-C(10)-C(11) | 115.49(11) |
| C(6)-C(5)-C(4) | 107.91(13) | F(6)-C(11)-F(5) | 107.59(11) |
| C(6)-C(5)-H(5A) | 126.0 | F(6)-C(11)-C(10) | 108.61(11) |
| C(4)-C(5)-H(5A) | 126.0 | F(5)-C(11)-C(10) | 108.26(11) |
| C(5)-C(6)-C(7) | 107.56(13) | F(6)-C(11)-C(12) | 108.89(11) |
| C(5)-C(6)-H(6A) | 126.2 | F(5)-C(11)-C(12) | 109.20(11) |
| C(7)-C(6)-H(6A) | 126.2 | C(10)-C(11)-C(12) | 114.10(11) |
| C(6)-C(7)-C(9) | 99.65(11) | F(7)-C(12)-F(8) | 108.00(11) |
| C(6)-C(7)-C(8) | 102.48(11) | F(7)-C(12)-C(13) | 107.98(11) |
| C(9)-C(7)-C(8) | 102.78(11) | F(8)-C(12)-C(13) | 108.47(11) |
| C(6)-C(7)-H(7A) | 116.5 | F(7)-C(12)-C(11) | 109.28(11) |
| C(9)-C(7)-H(7A) | 116.5 | F(8)-C(12)-C(11) | 108.52(11) |
| C(8)-C(7)-H(7A) | 116.5 | C(13)-C(12)-C(11) | 114.42(11) |
| C(1)-C(8)-C(7) | 117.32(11) | F(9)-C(13)-F(10) | 107.05(10) |
| C(1)-C(8)-C(3) | 89.69(10) | F(9)-C(13)-C(2) | 109.71(10) |
| C(7)-C(8)-C(3) | 102.55(10) | F(10)-C(13)-C(2) | 109.57(11) |
| C(1)-C(8)-H(8A) | 114.6 | F(9)-C(13)-C(12) | 107.14(10) |
| C(7)-C(8)-H(8A) | 114.6 | F(10)-C(13)-C(12) | 107.61(10) |
| C(3)-C(8)-H(8A) | 114.6 | C(2)-C(13)-C(12) | 115.41(11) |

Symmetry transformations used to generate equivalent atoms:

**Table S4** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 14(1) | 14(1) | 15(1) | 2(1) | 5(1) | 0(1) |
| C(2) | 11(1) | 14(1) | 16(1) | 1(1) | 3(1) | 1(1) |
| C(3) | 16(1) | 14(1) | 16(1) | 1(1) | 4(1) | -2(1) |
| C(4) | 23(1) | 14(1) | 19(1) | -1(1) | 4(1) | 1(1) |
| C(5) | 27(1) | 20(1) | 24(1) | -8(1) | 6(1) | -6(1) |
| C(6) | 23(1) | 26(1) | 20(1) | -9(1) | 1(1) | -2(1) |
| C(7) | 25(1) | 20(1) | 14(1) | -1(1) | 3(1) | -1(1) |
| C(8) | 15(1) | 15(1) | 15(1) | -1(1) | 1(1) | -1(1) |
| C(9) | 22(1) | 22(1) | 20(1) | -5(1) | 8(1) | 0(1) |
| C(10) | 15(1) | 12(1) | 18(1) | 2(1) | 0(1) | -1(1) |
| C(11) | 15(1) | 15(1) | 20(1) | -3(1) | 3(1) | 2(1) |
| C(12) | 14(1) | 21(1) | 15(1) | -1(1) | 4(1) | 0(1) |
| C(13) | 13(1) | 15(1) | 15(1) | 2(1) | 1(1) | 1(1) |
| F(1) | 24(1) | 22(1) | 22(1) | 3(1) | 12(1) | -5(1) |
| F(2) | 12(1) | 23(1) | 23(1) | -3(1) | 3(1) | 5(1) |
| F(3) | 20(1) | 17(1) | 26(1) | -1(1) | 1(1) | -7(1) |
| F(4) | 26(1) | 16(1) | 22(1) | 5(1) | -2(1) | 3(1) |
| F(5) | 44(1) | 18(1) | 33(1) | -8(1) | 13(1) | 4(1) |
| F(6) | 12(1) | 33(1) | 28(1) | 5(1) | 1(1) | 4(1) |
| F(7) | 29(1) | 45(1) | 14(1) | -8(1) | 2(1) | 11(1) |
| F(8) | 17(1) | 28(1) | 35(1) | 9(1) | 10(1) | -2(1) |
| F(9) | 13(1) | 25(1) | 19(1) | -3(1) | -1(1) | -2(1) |
| F(10) | 27(1) | 21(1) | 18(1) | 8(1) | 2(1) | 5(1) |

**Table S5** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for **1**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3A) | -137 | 434 | 3819 | 18 |
| H(4A) | 2481 | -589 | 2977 | 23 |
| H(5A) | -1493 | -913 | 2134 | 28 |
| H(6A) | -2861 | 206 | 854 | 28 |
| H(7A) | 184 | 1300 | 827 | 23 |
| H(8A) | -1480 | 1532 | 2571 | 18 |
| H(9A) | 2598 | -13 | 1141 | 25 |
| H(9B) | 3677 | 702 | 1991 | 25 |

**Table S6** Torsion angles [°] for **1**.

| | | | |
|---|---|---|---|
| F(1)-C(1)-C(2)-F(2) | -0.06(15) | C(3)-C(4)-C(5)-C(6) | 72.00(14) |
| C(10)-C(1)-C(2)-F(2) | -121.70(12) | C(4)-C(5)-C(6)-C(7) | -0.13(16) |
| C(8)-C(1)-C(2)-F(2) | 118.37(11) | C(5)-C(6)-C(7)-C(9) | 33.41(14) |
| F(1)-C(1)-C(2)-C(13) | 122.22(12) | C(5)-C(6)-C(7)-C(8) | -72.10(14) |
| C(10)-C(1)-C(2)-C(13) | 0.58(15) | F(1)-C(1)-C(8)-C(7) | 12.95(16) |
| C(8)-C(1)-C(2)-C(13) | -119.35(11) | C(10)-C(1)-C(8)-C(7) | 137.96(12) |
| F(1)-C(1)-C(2)-C(3) | -118.43(11) | C(2)-C(1)-C(8)-C(7) | -104.00(12) |
| C(10)-C(1)-C(2)-C(3) | 119.93(11) | F(1)-C(1)-C(8)-C(3) | 116.95(11) |
| C(8)-C(1)-C(2)-C(3) | 0.01(9) | C(10)-C(1)-C(8)-C(3) | -118.04(11) |
| F(2)-C(2)-C(3)-C(4) | -12.20(16) | C(2)-C(1)-C(8)-C(3) | -0.01(9) |
| C(13)-C(2)-C(3)-C(4) | -137.14(12) | C(6)-C(7)-C(8)-C(1) | 164.70(11) |
| C(1)-C(2)-C(3)-C(4) | 104.67(12) | C(9)-C(7)-C(8)-C(1) | 61.63(14) |
| F(2)-C(2)-C(3)-C(8) | -116.88(11) | C(6)-C(7)-C(8)-C(3) | 68.46(13) |
| C(13)-C(2)-C(3)-C(8) | 118.18(11) | C(9)-C(7)-C(8)-C(3) | -34.62(13) |
| C(1)-C(2)-C(3)-C(8) | -0.01(9) | C(2)-C(3)-C(8)-C(1) | 0.01(9) |
| C(2)-C(3)-C(4)-C(5) | -165.02(11) | C(4)-C(3)-C(8)-C(1) | -118.10(10) |
| C(8)-C(3)-C(4)-C(5) | -68.14(12) | C(2)-C(3)-C(8)-C(7) | 117.98(10) |
| C(2)-C(3)-C(4)-C(9) | -62.02(14) | C(4)-C(3)-C(8)-C(7) | -0.13(12) |
| C(8)-C(3)-C(4)-C(9) | 34.86(13) | C(5)-C(4)-C(9)-C(7) | 50.30(12) |
| C(9)-C(4)-C(5)-C(6) | -33.25(14) | C(3)-C(4)-C(9)-C(7) | -54.80(12) |

| | | | |
|---|---|---|---|
| C(6)-C(7)-C(9)-C(4) | -50.40(12) | F(5)-C(11)-C(12)-F(8) | 117.03(12) |
| C(8)-C(7)-C(9)-C(4) | 54.86(12) | C(10)-C(11)-C(12)-F(8) | -121.69(12) |
| F(1)-C(1)-C(10)-F(4) | 67.21(13) | F(6)-C(11)-C(12)-C(13) | 121.08(12) |
| C(8)-C(1)-C(10)-F(4) | -62.82(14) | F(5)-C(11)-C(12)-C(13) | -121.70(12) |
| C(2)-C(1)-C(10)-F(4) | -166.57(10) | C(10)-C(11)-C(12)-C(13) | -0.42(16) |
| F(1)-C(1)-C(10)-F(3) | -49.87(13) | F(2)-C(2)-C(13)-F(9) | 48.66(13) |
| C(8)-C(1)-C(10)-F(3) | -179.90(10) | C(3)-C(2)-C(13)-F(9) | 178.56(10) |
| C(2)-C(1)-C(10)-F(3) | 76.36(13) | C(1)-C(2)-C(13)-F(9) | -78.02(13) |
| F(1)-C(1)-C(10)-C(11) | -170.71(11) | F(2)-C(2)-C(13)-F(10) | -68.60(12) |
| C(8)-C(1)-C(10)-C(11) | 59.26(15) | C(3)-C(2)-C(13)-F(10) | 61.30(14) |
| C(2)-C(1)-C(10)-C(11) | -44.48(15) | C(1)-C(2)-C(13)-F(10) | 164.73(10) |
| F(4)-C(10)-C(11)-F(6) | 45.61(14) | F(2)-C(2)-C(13)-C(12) | 169.77(10) |
| F(3)-C(10)-C(11)-F(6) | 160.55(10) | C(3)-C(2)-C(13)-C(12) | -60.33(15) |
| C(1)-C(10)-C(11)-F(6) | -77.55(14) | C(1)-C(2)-C(13)-C(12) | 43.10(15) |
| F(4)-C(10)-C(11)-F(5) | -70.93(13) | F(7)-C(12)-C(13)-F(9) | -42.37(14) |
| F(3)-C(10)-C(11)-F(5) | 44.00(14) | F(8)-C(12)-C(13)-F(9) | -159.18(10) |
| C(1)-C(10)-C(11)-F(5) | 165.90(11) | C(11)-C(12)-C(13)-F(9) | 79.53(13) |
| F(4)-C(10)-C(11)-C(12) | 167.27(11) | F(7)-C(12)-C(13)-F(10) | 72.45(13) |
| F(3)-C(10)-C(11)-C(12) | -77.80(13) | F(8)-C(12)-C(13)-F(10) | -44.35(14) |
| C(1)-C(10)-C(11)-C(12) | 44.10(16) | C(11)-C(12)-C(13)-F(10) | -165.64(11) |
| F(6)-C(11)-C(12)-F(7) | -117.73(12) | F(7)-C(12)-C(13)-C(2) | -164.87(11) |
| F(5)-C(11)-C(12)-F(7) | -0.51(15) | F(8)-C(12)-C(13)-C(2) | 78.32(14) |
| C(10)-C(11)-C(12)-F(7) | 120.77(12) | C(11)-C(12)-C(13)-C(2) | -42.96(15) |
| F(6)-C(11)-C(12)-F(8) | -0.19(14) | | |

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Symmetry transformations used to generate equivalent atoms:

1. C. D. Smith, *Org. Syn.*, 1971, **51**, 133.