CF_2H, a Hydrogen Bond Donor

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1. Materials and Methods

General

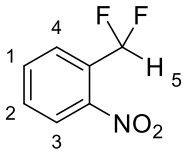
Reagents were purchased from commercial sources and used as received. Anhydrous solvents were purchased from commercial sources and stored in an MBraun dry box. Reaction mixtures were monitored by thin-layer chromatography (TLC) on pre-coated, aluminum-backed silica gel 60 F254 plates. Column chromatography was performed on silica gel 60 (230-400 mesh). *o*-Nitro-α,α-difluorotoluene and *p*-bromo-α,α-difluorotoluene were purchased from commercial sources.

Instrumentation

A ThermoNicolet Avatar 360 spectrometer was used to collect IR spectra and the data were processed with OMNIC software. Melting points were determined using a Stanford Research Systems OptiMelt. NMR spectra were recorded on a 400 MHz Bruker AVANCE-400 NMR spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0.00 ppm). ^{1}H and ^{13}C NMR spectra were referenced internally to residual solvent peaks. ^{19}F spectra were referenced externally to $CFCl_3$ (0.00 ppm). Low-resolution EI-MS spectra were obtained with an Agilent 5973N gas chromatograph/mass spectrometer using He carrier gas. High-resolution mass spectra were collected on a Bruker Daltonics APEXIV 4.7 tesla Fourier transform ion cyclotron resonance mass spectrometer with a direct analysis in real time (DART) ionization source at the MIT Department of Chemistry Instrumentation Facility.

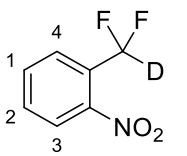
2. Synthetic Procedures

o-Nitro-α,α-difluorotoluene (1-CF_2H)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (H3, dd, *J* = 8.1, 0.7 Hz, 1H), 7.91 (H4, d, *J* = 7.8 Hz, 1H), 7.78 (H1, t, *J* = 7.6 Hz, 1H), 7.68 (H2, t, *J* = 7.8 Hz, 1H), 7.39 (H5, t, *J* = 54.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.5 (d, *J* = 54.9 Hz). IR (CCl_4): ν 3118 (vw), 3089 (w), 3071 (w), 3049 (vw), 3013 (w, CF_2–H), 2867 (w), 1981 (vw), 1952 (vw), 1849 (vw), 1538 (vs), 1370 (m), 1344 (s), 1209 (m), 1103 (m), 1066 (s).

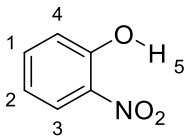
o-Nitro-α-deutero-α,α-difluorotoluene (1-CF_2D)



Tetramethylammonium hydroxide pentahydrate (97 mg, 108 mmol), **1-CF_2H** (94 mg, 54 mmol), and D_2O (270 μL, 15 mmol, 99.9 atom%) were mixed in DMSO-d_6 (2.25 mL, 99.9 atom %). The reaction was stirred for 48 h at room temperature. The reaction mixture was acidified with DCl (162 mmol in 10 mL D_2O, 99.9%). The reaction mixture was then extracted with pentane (10 mL × 3). The combined organic phase was washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed under vacuum. The crude product was purified by column chromatography using pentane:CH_2Cl_2 (2:1 to 1:1) to give a colorless solid (50 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (H4, d, *J* = 8.1 Hz, 1H), 7.91 (H3, d, *J* = 7.8 Hz, 1H), 7.79 (H1, t, *J* = 7.6 Hz, 1H), 7.72 – 7.64 (H2, m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −116.1 (t, *J* = 8.4 Hz).

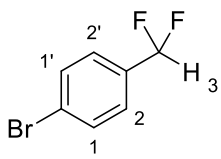
IR (CCl_4): ν 3115 (vw), 3086 (w), 3068 (w), 3046 (vw), 2967 (vw), 2925 (vw), 2870 (w), 2276 and 2237 (w, CF_2–D), 1977 (vw), 1948 (vw), 1842 (vw), 1538 (vs), 1348 (s), 1282 (m), 1271 (m), 1250 (m), 1209 (m), 1093 (s), 1056 (m), 964 (m).

_o_-Nitrophenol (1-OH)



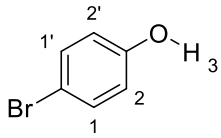
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.12 (dd, J = 8.5, 1.5 Hz, 1H), 7.59 (ddd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.16 (dd, J = 8.6, 1.1 Hz, 1H), 7.00 (ddd, J = 8.6, 7.2, 1.3 Hz, 1H). IR (CCl_4): ν 3236 (m, br, O–H), 3108 (vw), 3086 (w), 3071 (w), 3045 (vw), 1959 (w), 1932 (w), 1902 (w), 1622 (s), 1593 (s), 1541 (s), 1477 (s), 1458 (s), 1330 (s), 1253 (m), 1190 (m), 1154 (m), 1133 (m), 1078 (m), 1030 (m).

_p_-Bromo-α,α-difluorotoluene (2-CF_2H)



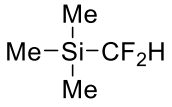
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (H1,1', d, J = 8.7 Hz, 2H), 7.39 (H2,2', d, J = 8.6 Hz, 2H), 6.61 (H3, t, J = 56.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.6 (d, J = 56.3 Hz). IR (CCl_4): 3056 (vw), 2969 (w, CF_2–H), 1607 (m), 1491 (m), 1411 (m), 1370 (m), 1213 (m), 1077 (s), 1041 (s), 1015 (m).

_p_-Bromophenol (2-OH)



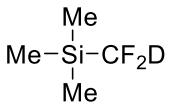
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (H1,1', m, 2H), 6.77 – 6.68 (H2,2', m, 2H), 4.78 (H3, s, 1H). IR (CCl_4): ν 3608 (m, O–H), 3473 (w, br), 3067 (vw), 3031 (w), 1590 (m), 1491 (vw), 1421 (m), 1319 (m), 1260 (s), 1176 (s), 1089 (m), 1070 (m), 1008 (w).

$TMSCF_2H$

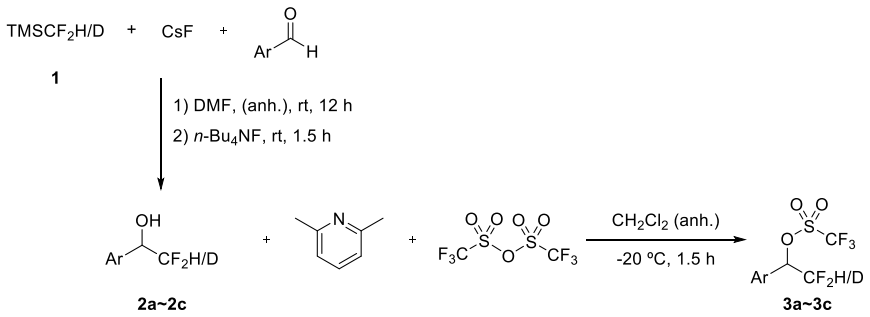


$TMSCF_2H$ was prepared according to a literature procedure.[1] $TMSCF_3$ (12.50 g, 88.00 mmol) was used to give $TMSCF_2H$ as a colorless liquid (4.51 g, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (CF_2H, t, $^2J_{H\text{-}F}$ = 46.2 Hz, 1H), 0.17 (Me, s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −139.6 (d, $^2J_{F\text{-}H}$ = 46.3 Hz). IR (CCl_4): ν 2961 (w), 2899 (w, CF_2–H), 1319 (w), 1253 (m), 1081 (m), 993(m).

$TMSCF_2D$

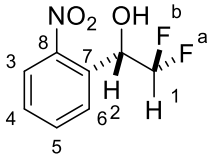


$TMSCF_2D$ was prepared by a modified literature procedure.[1] Under N_2, $NaBD_4$ (1.23 g, 29.50 mmol) was mixed with dry diglyme (25 mL) and cooled in an ice bath. $TMSCF_3$ (12.50 g, 88.00 mmol) was then added dropwise to the mixture. The mixture was stirred for two hours and gradually warmed to room temperature. The reaction mixture was purified by distillation and fractions with boiling points below 80 °C were collected. The distillate was redistilled with a 10-cm Vigreux column, collecting fractions with boiling points of 62-66 °C to give a colorless liquid (3.30 g, 30% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (Me, t, $^4J_{H\text{-}F}$ = 0.5 Hz, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 123.6 (tt, $^1J_{C\text{-}F}$ = 253.0, $^1J_{C\text{-}D}$ = 25.0 Hz), −5.3 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ −140.3 (pseudo t, $^2J_{F\text{-}D}$ = 7.3 Hz, 2F). IR (CCl_4): ν 2960 (w), 2925(vw), 2901(vw), 2167 (vw, CF_2–D), 1253 (m), 1149 (w), 1132 (w), 1030 (m), 982 (w).



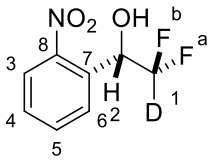
Scheme S1. Synthesis of 2,2-difluoro-1-(aryl)ethan-1-ol (**2**) and 2,2-difluoro-1-arylethyl triflate (**3**).

2,2-Difluoro-1-(2-nitrophenyl)ethan-1-ol (3-NO_2)



3-NO_2 was prepared according to a literature procedure.[2] 2-Nitrobenzaldehyde (453 mg, 3.0 mmol) and $TMSCF_2H$ (745 mg, 6.0 mmol) were mixed in anhydrous DMF (6 mL). CsF (64 mg, 0.4 mmol) was added to the reaction mixture under positive N_2 flow. The mixture was stirred overnight at room temperature. A solution of *n*-Bu_4NF (3.0 mL, 1 M in THF) was then added and the mixture was stirred for one hour at room temperature. The mixture was then diluted with water (15 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic phase was washed with water (20 mL) and dried over Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by silica gel chromatography using hexanes:EtOAc (5:1 to 4:1) to give a slightly yellow solid (268 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.2, 1.1 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.73 (td, J = 7.7, 1.1 Hz, 1H), 7.55 (ddd, J = 7.8, 7.1, 1.4 Hz, 1H), 6.08 (H1, ddd, $^2J_{H1\text{-}Fa}$ = 55.8, $^2J_{H1\text{-}Fb}$ = 55.1, $^3J_{H1\text{-}H2}$ = 2.6 Hz, 1H), 5.65 (H2, ddt, $^3J_{H2\text{-}Fa}$ = 16.2 Hz, $^3J_{H2\text{-}Fb}$ = 6.0 Hz, $^3J_{H1\text{-}H2}$ = 3.0 Hz, $^3J_{H1\text{-}OH}$ = 3.0 Hz, 1H), 2.78 (O*H*, d, $^3J_{OH\text{-}H2}$ = 1.9 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.3, 134.0, 131.3 (dd, $^3J_{C7\text{-}Fa}$ = 4.9, $^3J_{C7\text{-}Fb}$ = 2.5 Hz), 129.74 (t, $J_{C6\text{-}F,through\text{-}space}$ = 1.2 Hz), 129.72, 124.8, 114.7 (dd, $^1J_{C1\text{-}Fa}$ = 246.2, $^1J_{C1\text{-}Fb}$ = 245.4 Hz), 69.0 (dd, $^2J_{C2\text{-}Fa}$ = 25.0, $^2J_{C2\text{-}Fb}$ = 22.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.8 (Fb, ddd, $^2J_{Fb\text{-}Fa}$ = 281.9, $^2J_{Fb\text{-}H1}$ = 55.1, $^3J_{Fb\text{-}H2}$ = 6.3 Hz, 1F), −133.6 (Fa, ddd, $^2J_{Fa\text{-}Fb}$ = 282.0, $^2J_{Fa\text{-}H1}$ = 55.9, $^3J_{Fa\text{-}H2}$ = 16.3 Hz, 1F). IR (CCl_4): ν 3612 (m, O–H), 3114 (vw), 3085 (w), 3067 (w), 3012, (w, CF_2–H), 2957 (w), 2924 (w), 2858 (w), 1539 (vs), 1353 (m), 1303 (w), 1185 (w), 1138 (m), 1075 (m), 1053 (m). Mp = 53.4-55.4 °C.

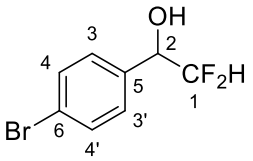
2,2-Difluoro-2-deutero-1-(2-nitrophenyl)ethan-1-ol (3-NO_2-D)



3-NO_2-D was prepared as described above for **3-NO_2** using $TMSCF_2D$ and 2-nitrobenzaldehyde on a 2.0 mmol-scale to obtain a slightly yellow solid (153 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, $^4J_{H3\text{-}H4}$ = 8.2 Hz, $^4J_{H3\text{-}H5}$ = 1.1 Hz, 1H), 7.92 (d, $^3J_{H6\text{-}H5}$ = 7.9 Hz, 1H), 7.73 (td, $^3J_{H5\text{-}H4,6}$ = 7.7 Hz, $^4J_{H5\text{-}H3}$ = 1.1 Hz, 1H), 7.55 (dd, $^3J_{H4\text{-}H3}$ = 7.8, $^3J_{H4\text{-}H5}$ = 7.1 Hz, $^4J_{H4\text{-}H6}$ = 1.4 Hz, 1H), 5.65 (H2, ddd, $^3J_{H2\text{-}Fa}$ = 16.3, $^3J_{H2\text{-}Fb}$ = 6.2 Hz, $^3J_{H2\text{-}OH}$ = 4.4 Hz, 1H), 2.74 (O*H*, d, $^3J_{OH\text{-}H2}$ = 4.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −126.4 (Fb, ddt, $^2J_{Fb\text{-}Fa}$ = 282.4, $^3J_{Fb\text{-}H2}$ = 8.2, $^2J_{Fb\text{-}D}$ = 7.3

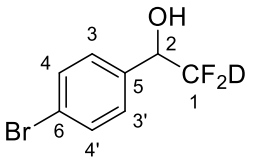
Hz, 1F), −134.3 (Fa, ddt, $^{2}J_{Fa\text{-}Fb}$ = 281.7, $^{3}J_{Fa\text{-}H2}$ = 16.7, $^{2}J_{Fa\text{-}D}$ = 8.1 Hz, 1F). IR (CCl_4): ν 3605 (m, br, O–H), 3114 (vw), 3082 (w), 3067 (w), 2954 (w), 2927 (w), 2866 (w), 2250 and 2188 (w, CF_2–D), 1529 (vs), 1346 (m), 1207 (m), 1186 (m), 1123 (m), 1093 (m), 1060 (m).

1-(4-Bromophenyl)-2,2-difluoroethan-1-ol (3-Br)



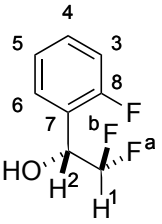
3-Br was prepared as described above for **3-NO$_2$** using $TMSCF_2H$ and 4-bromobenzaldehyde on a 0.85 mmol-scale to afford a colorless liquid (133 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (H4,4', m, 2H), 7.31 (H3,3', m, 2H), 5.72 (H1, td, $^{2}J_{H1\text{-}F}$ = 56.0 Hz, $^{3}J_{H1\text{-}H2}$ = 4.9 Hz, 1H), 4.81 (H2, tt, $^{3}J_{H2\text{-}Fa,b}$ = 9.5 Hz, $^{3}J_{H1\text{-}H2}$ = 4.2 Hz, $^{3}J_{H1\text{-}O\mathit{H}}$) = 4.2 Hz, 1H), 2.41 (O*H*, d, $^{3}J_{O\mathit{H}\text{-}H2}$ = 3.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.8 (C5, t, $^{3}J_{C5\text{-}F}$ = 3.2 Hz), 131.9 (C4,4'), 128.9 (C3,3', t, $^{4}J_{C3,3'\text{-}F}$ = 0.8 Hz), 123.2 (C6), 115.6 (C1, t, $^{1}J_{C1\text{-}F}$ = 245.8 Hz), 73.1 (C2, t, $^{2}J_{C2\text{-}F}$ = 24.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −127.58 (Fa, dd, $^{2}J_{Fa\text{-}H1}$ = 56.1, $^{3}J_{Fa\text{-}H2}$ = 10.4 Hz, 1F), −127.64 (Fb, dd, $^{2}J_{Fb\text{-}H1}$ = 55.8, $^{3}J_{Fb\text{-}H2}$ = 9.6 Hz, 1F). IR (CCl_4): ν 3618 (m, br, O–H), 3481 (w, br), 3085 (vw), 3052 (vw), 3034 (vw), 2972 (w, CF_2–H), 2899 (w), 1900 (w), 1594 (m), 1491 (m), 1403 (m), 1377 (m), 1187 (m), 1115 (m), 1081 (s), 1052 (m), 1012 (m).

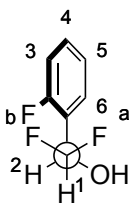
1-(4-Bromophenyl)-2,2-difluoroethan-2-deutero-1-ol (3-Br-D)



3-Br-D was prepared as described above for **3-NO$_2$** using $TMSCF_2D$ and 4-bromobenzaldehyde on a 1.27 mmol-scale to give a colorless liquid (232 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (H4,4', m, 2H), 7.29 (H3,3', m, 2H), 4.81 (H2, td, $^{3}J_{H2\text{-}Fa,b}$ = 10.0 Hz, $^{3}J_{H2\text{-}O\mathit{H}}$ = 3.1 Hz, 1H), 2.45 (O*H*, d, $^{3}J_{O\mathit{H}\text{-}H2}$ = 3.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −128.30 (Fa, dt, $^{3}J_{Fa\text{-}H}$ = 9.7 Hz, $^{2}J_{Fa\text{-}D}$ = 8.7 Hz, 1F), −128.36 (Fb, dt, $^{3}J_{Fa\text{-}H}$ = 9.0 Hz, $^{2}J_{Fa\text{-}D}$ = 9.0 Hz, 1F). IR (CCl_4): ν 3618 (m, br, O–H), 3470 (w, br), 3082 (vw), 3050 (vw), 3031 (vw), 2971 (vw), 2892 (w), 2248 and 2183 (w, CF_2–D), 1900 (w), 1593 (m), 1488 (m), 1403 (m), 1213 (m), 1179 (m), 1118 (s), 1067 (s), 1012 (s).

2,2-Difluoro-1-(2-fluorophenyl)ethan-1-ol (3-F)

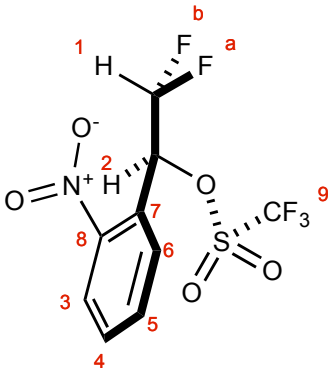




3-F was prepared as described above for **3-NO$_2$** using $TMSCF_2H$ and 2-fluorobenzaldehyde on a 1.14 mmol-scale to afford a slightly yellow liquid (150 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (H6, td, $^{3}J_{H6\text{-}H5}$ = 7.2 Hz, $^{4}J_{H6\text{-}F(Ar)}$ = 7.2 Hz, $^{4}J_{H6\text{-}H4}$ = 1.7 Hz, 1H), 7.37 (H4, dddd, $^{3}J_{H4\text{-}H3}$ = 8.2, $^{3}J_{H4\text{-}H5}$ = 7.3, $^{4}J_{H4\text{-}F(Ar)}$ = 5.4, $^{4}J_{H4\text{-}H6}$ = 1.9 Hz, 1H), 7.22 (H5, td, $^{3}J_{H5\text{-}H4}$ = 7.4 Hz, $^{3}J_{H5\text{-}H6}$ = 7.4 Hz, $^{4}J_{H5\text{-}H3}$ = 1.1 Hz, 1H), 7.09 (ddd, $^{3}J_{H3\text{-}F(Ar)}$ = 10.5 Hz, $^{3}J_{H3\text{-}H4}$ = 8.3 Hz, $^{4}J_{H3\text{-}H5}$ = 1.1 Hz, 1H), 5.90 (dddd, $^{2}J_{H1\text{-}Fa}$ = 56.1 Hz, $^{2}J_{H1\text{-}Fb}$ = 55.2 Hz, $^{3}J_{H1\text{-}H2}$ = 4.0 Hz, $J_{H1\text{-}F(Ar),\ through\ space}$ = 1.0 Hz, 1H), 5.19 (ddt, $^{3}J_{H2\text{-}Fa}$ = 13.0 Hz, $^{3}J_{H2\text{-}Fb}$ = 8.5 Hz, $^{3}J_{H2\text{-}H1}$ = 4.4 Hz, $^{3}J_{H2\text{-}O\mathit{H}}$ = 4.4 Hz, 1H), 2.47 (d, $^{3}J_{O\mathit{H}\text{-}H2}$ = 5.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.2 (F(Ar), dddd, $J_{F(Ar)\text{-}H2,\ through\ space}$ = 13.1 Hz, $^{3}J_{F(Ar)\text{-}H3}$ = 10.4 Hz, $J_{F(Ar)\text{-}Fb,\ through\ space}$ = 5.9 Hz, $J_{F(Ar)\text{-}Fa,\ through\ space}$ =

3.4 Hz, 1F), −127.9 (Fb, dddd, $^{2}J_{\text{Fb-Fa}}$ = 283.6 Hz, $^{2}J_{\text{Fb-H1}}$ = 55.2 Hz, $^{3}J_{\text{Fb-H2}}$ = 7.6 Hz, $J_{\text{Fb-F(Ar), through space}}$ = 5.8 Hz, 1F), −129.8 (Fa, dddd, $^{2}J_{\text{Fa-Fb}}$ = 283.8 Hz, $^{2}J_{\text{Fa-H1}}$ = 56.2 Hz, $^{3}J_{\text{Fa-H2}}$ = 13.4 Hz, $J_{\text{Fa-F(Ar), through space}}$ = 3.3 Hz, 1F). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −118.0 (F(Ar), dd, $J_{\text{F(Ar)-Fb, through space}}$ = 5.9 Hz, $J_{\text{F(Ar)-Fa, through space}}$ = 3.3 Hz, 1F), −127.3 (Fb, dd, $^{2}J_{\text{Fb-Fa}}$ = 283.7 Hz, $^{3}J_{\text{Fb-F(Ar)}}$ = 5.9 Hz, 1F), −129.6 (Fa, dd, $^{2}J_{\text{Fa-Fb}}$ = 283.7 Hz, $^{3}J_{\text{Fa-F(Ar)}}$ = 3.3 Hz, 1F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4 (C8, d, $^{1}J_{\text{C8-F(Ar)}}$ = 247.2 Hz), 130.7 (C4, d, $^{3}J_{\text{C4-F(Ar)}}$ = 8.4 Hz), 128.7 (C6, dt, $^{3}J_{\text{C6-F(Ar)}}$ = 3.5 Hz, $J_{\text{C6-Fa,b,through space}}$ = 0.8 Hz), 124.7 (C5, d, $^{4}J_{\text{C5-F(Ar)}}$ = 3.5 Hz), 123.2 (C7, ddd, $^{2}J_{\text{C7-F(Ar)}}$ = 13.2 Hz, $^{3}J_{\text{C7-Fa}}$ = 3.9 Hz, $^{3}J_{\text{C7-Fb}}$ = 2.8 Hz), 115.7 (C3, d, $^{2}J_{\text{C3-F(Ar)}}$ = 21.6 Hz), 115.1 (C1, ddd, $^{1}J_{\text{C1-Fa}}$ = 245.8 Hz, $^{1}J_{\text{C1-Fb}}$ 245.0 Hz, $J_{\text{C1-F(Ar), through space}}$ = 2.8 Hz), 68.2 (C2, ddd, $^{2}J_{\text{C2-Fa}}$ = 26.1 Hz, $^{2}J_{\text{C2-Fb}}$ = 23.9 Hz, $^{3}J_{\text{C2-F(Ar)}}$ = 2.3 Hz). IR (CCl_4): ν 3609 (m, br, O–H), 3484 (w, br), 3088 (w), 3070 (w), 3045 (w), 2968 (w), 2921 (w), 2851 (vw), 1617 (m), 1588 (m), 1492 (m), 1453 (m), 1385 (m, br), 1236 (m), 1082 (s), 1050 (s).

2,2-Difluoro-1-(2-nitrophenyl)ethyl triflate (4-NO_2)



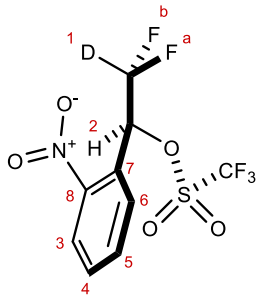
3-NO_2 (102 mg, 0.50 mmol) and 2,6-lutidine (116 µL, 1.00 mmol) were mixed in anhydrous CH_2Cl_2 (1 mL) under an inert atmosphere. The reaction mixture was cooled to −20 °C before adding triflic anhydride (134 µL, 0.80 mmol) dropwise. The reaction mixture was stirring for 25 min at −20 °C and was then warmed to room temperature. The crude product was mixed with cold Et_2O (25 mL) and was quickly washed with cold brine (10 mL), cold HCl (2 M, 10 mL), and cold water (10 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under vacuum to give a colorless liquid (156 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (H3, m, 1H), 7.85 (H5, H6, m, 2H), 7.71 (H4, ddd, $^{3}J_{\text{H4-H3}}$ = 8.4 Hz, $^{3}J_{\text{H4-H5}}$ = 6.2 Hz, $^{4}J_{\text{H4-H6}}$ = 2.8 Hz, 1H), 6.67 (H2, ddd, $^{3}J_{\text{H2-Fa}}$ = 15.6 Hz, $^{3}J_{\text{H2-Fb}}$ = 5.6 Hz, $^{3}J_{\text{H2-H1}}$ = 1.7 Hz, 1H), 6.25 (H1, ddd, $^{3}J_{\text{H1-Fa}}$ = 53.5 Hz, $^{3}J_{\text{H1-Fb}}$ = 53.1 Hz, $^{3}J_{\text{H1-H2}}$ = 1.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −74.3 (CF_3, d, $J_{\text{CF3-Fb,through space}}$ = 4.1 Hz, 3F), −124.5 (Fb, dddq, $^{2}J_{\text{Fb-Fa}}$ = 285.7 Hz, $^{2}J_{\text{Fb-H1}}$ = 53.7 Hz, $^{3}J_{\text{Fb-H2}}$ = 5.6 Hz, $J_{\text{Fb-CF3,through space}}$ = 4.1 Hz, 1F), −133.7 (Fa, ddd, $^{2}J_{\text{Fa-Fb}}$ = 285.5, $^{2}J_{\text{Fa-H1}}$ = 53.8 Hz, $^{3}J_{\text{Fa-H2}}$ = 15.6 Hz, 1F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.3 (C8), 135.0 (C5), 131.7 (C4), 129.6 (C6, t, $^{4}J_{\text{C6-Fa,b}}$ = 1.4 Hz), 125.9 (C7, d, $^{3}J_{\text{C7-Fb}}$ = 5.0 Hz), 125.7 (C3), 118.4 (C9, q, $^{1}J_{\text{C-F}}$ = 319.7 Hz), 111.6 (C1, dd, $^{1}J_{\text{C1-Fa}}$ = 250.6 Hz, $^{1}J_{\text{C1-Fb}}$ = 249.2 Hz), 79.9 (C2, dd, $^{2}J_{\text{C2-Fa}}$ = 25.5 Hz, $^{2}J_{\text{C2-Fb}}$ 21.2 Hz). IR (CCl_4): ν 3114 (vw), 3088 (vw), 3070 (vw), 3050 (vw), 3008 (w, CF_2–H), 2964 (vw), 2924 (w), 2862 (w), 1533 (vs), 1427 (s), 1350 (s), 1247 (s), 1214 (vs), 1141 (vs), 1093 (s), 1002 (m). DART-HRMS(+) *m/z* calculated for $C_9H_{10}F_5N_2O_5S^+$ ($[M+NH_4]^+$) = 353.0225, found 353.0226.

Note 1: The product was unstable at room temperature and was stored immediately after preparation at −80 °C or in liquid nitrogen. The compound was stable for up to a few days at −80 °C and for several weeks at −196 °C.

Note 2: H3 is a multiplet consisting a triplet (8.23 ppm, t, J = 0.8 Hz, 0.5H) and a doublet of doublets (8.21 ppm, J = 1.2, 0.5 Hz, 0.5H). Although this multiplet may be assigned to two species undergoing a very slow exchange

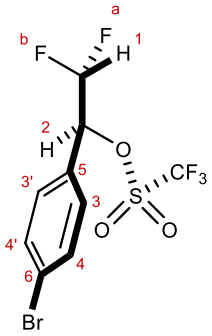
on the NMR timescale, such an assignment is not supported by theoretical calculations, which do not show any high rotational barriers on the PES. We currently cannot provide a conclusive explanation for this observation. This unsolved multiplet, however, does not change the major conclusions of the manuscript.

2,2-Difluoro-2-deutero-1-(2-nitrophenyl)ethyl triflate (4-NO_2-D)



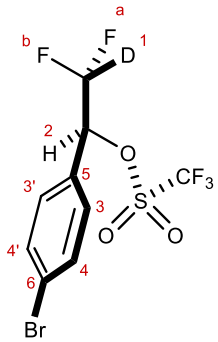
4-NO_2-D was prepared as described above for **4-NO_2** using **3-NO_2-D** on a 0.25 mmol-scale to give a colorless liquid (73 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (H3, d, $^3J_{H3\text{-}H4}$ = 8.1 Hz, 1H), 7.85 (H5, H6, m, 2H), 7.71 (H4, ddd, $^3J_{H4\text{-}H3}$ = 8.7, $^3J_{H4\text{-}H5}$ = 6.1, $^4J_{H4\text{-}H6}$ = 2.7 Hz, 1H), 6.67 (H2, dd, $^3J_{H2\text{-}Fb}$ = 15.5 Hz, $^3J_{H2\text{-}Fa}$ = 5.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −74.3 (CF_3, d, $J_{CF3\text{-}Fb,through\ space}$ = 4.1 Hz, 3F), −125.3 (Fb, ddtq, $^2J_{Fb\text{-}Fb}$ = 285.8 Hz, $^3J_{Fb\text{-}H2}$ 5.5 Hz, $^2J_{Fb\text{-}D}$ = 8.8 Hz, $J_{Fb\text{-}CF3,through\ space}$ = 4.2 Hz, 1F), −134.3 (Fa, ddt, $^3J_{Fa\text{-}Fb}$ = 282.6 Hz, $^3J_{Fa\text{-}H2}$ = 15.9 Hz, $^3J_{Fa\text{-}D}$ = 8.2 Hz, 1F). IR (CCl_4): ν 3614 (w), 3116 (vw), 3072 (vw), 3051 (vw), 3012 (vw), 2931 (w), 2868 (w), 2260 and 2200 (vw, CF_2–D), 1537 (vs), 1429 (s), 1352 (s), 1248 (s), 1221 (vs), 1142 (s), 1138 (m), 1018 (m), 989 (s), 964 (m).

1-(4-Bromophenyl)-2,2-difluoroethyl triflate (4-Br)



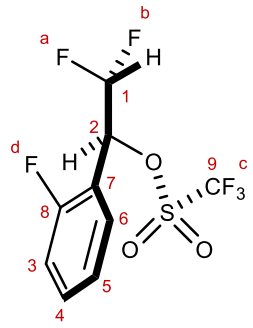
4-Br was prepared as described above for **4-NO_2** using **3-Br** on a 0.30 mmol-scale to give a white solid (91 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.56 (H4,4', m, 2H), 7.37 – 7.27 (H3,3', m, 2H), 5.98 (H1, td, $^1J_{H1\text{-}Fa,b}$ = 54.2 Hz, $^2J_{H1\text{-}H2}$ = 4.1 Hz, 1H), 5.68 (H2, td, $^3J_{H2\text{-}Fa,b}$ = 9.6 Hz, $^3J_{H2\text{-}H1}$ = 4.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.2 (CF_3, pseudo t, $J_{CF3\text{-}Fa,b,through\ space}$ = 1.7 Hz, 3F), −126.9 (Fa, dddq, $^2J_{Fa\text{-}Fb}$ = 293.0 Hz, $^2J_{Fa\text{-}H1}$ = 54.6 Hz, $^3J_{Fa\text{-}H2}$ = 10.1 Hz, $J_{Fa\text{-}CF3,through\ space}$ = 2.4 Hz, 1F), −128.4 (Fb, dddq, $^2J_{Fb\text{-}Fa}$ = 292.2 Hz, $^2J_{Fb\text{-}H1}$ = 54.0 Hz, $^3J_{Fb\text{-}H2}$ = 8.9 Hz, $J_{Fb\text{-}CF3,through\ space}$ = 1.1 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.8 (C4,4', s), 129.5 (C3,3', t, $^4J_{C3,3'\text{-}Fa,b}$ = 0.9 Hz), 128.6 (C5, t, $^3J_{C5\text{-}Fa,b}$ = 2.4 Hz), 125.8 (C6, s), 118.4 (CF_3, q, $^1J_{C\text{-}F}$ = 319.6 Hz), 112.0 (C1, dd, $^1J_{C1\text{-}Fa\ or\ Fb}$ = 249.7 Hz, $^1J_{C1\text{-}Fa\ or\ Fb}$ = 247.6 Hz), 84.2 (C2, dd, $^2J_{C2\text{-}Fa\ or\ Fb}$ = 28.6 Hz, $^2J_{C2\text{-}Fa\ or\ Fb}$ = 26.2 Hz). IR (CCl_4): ν 2972 (w, CF_2–H), 2910 (vw), 1907 (w), 1597 (m), 1491 (m), 1432 (s), 1388 (m), 1246 (s), 1220 (vs), 1140 (vs), 1099 (s), 1074 (m), 1012 (m).

1-(4-Bromophenyl)-2,2-difluoroethyl-2-deutero triflate (4-Br-D)



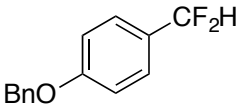
4-Br-D was prepared as described above for **4-NO_2** using **3-Br-D** on a 0.25 mmol-scale to give a white solid (79 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (H4,4', m, 2H), 7.32 (H3,3', m, 2H), 5.68 (H2, t, $^3J_{H2\text{-}Fa,b}$ = 9.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −74.6 (CF_3, s, 3F), −127.1 (Fa, dt, $^2J_{Fa\text{-}Fb}$ = 292.3 Hz, $^2J_{Fa\text{-}D}$ = 8.2 Hz, 1F), −128.6 (Fb, dt, $^2J_{Fb\text{-}Fa}$ = 292.3 Hz, $^2J_{Fb\text{-}D}$ = 8.2 Hz, 1F). IR (CCl_4): ν 2966 (w), 2926 (w), 2854 (vw), 2206 (w, CF_2–D), 1903 (w), 1595 (m), 1492 (m), 1427 (vs), 1248 (s), 1221 (vs), 1144 (vs), 1074 (m), 1014 (m), 972 (s).

2,2-Difluoro-1-(2-fluorophenyl)ethyl triflate (4-F):



4-F was prepared as described above for **4-NO$_2$** using **3-F** on a 0.50 mmol-scale to give a colorless liquid (99 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (H4,6, m, 2H), 7.29 (H5, td, $^{3}J_{H5\text{-}H4,6}$ = 7.6 Hz, $^{4}J_{H5\text{-}H3}$ = 1.2 Hz, 1H), 7.19 (H3, ddd, $^{3}J_{H3\text{-}F(Ar)}$ = 10.0 Hz, $^{3}J_{H3\text{-}H4}$ =8.8 Hz, $^{4}J_{H3\text{-}H5}$ = 1.1 Hz, 1H), 6.12 (H1, tdd, $^{2}J_{H1\text{-}Fa,b}$ = 54.7 Hz, $^{3}J_{H1\text{-}H2}$ = 4.2 Hz, $J_{H1\text{-}Fd,through\ space}$ = 0.8 Hz, 1H), 6.06 (H2, td, $^{3}J_{H2\text{-}Fa,b}$ = 9.3 Hz, $^{3}J_{H2\text{-}H1}$ = 4.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.2 (Fc, t, $J_{Fc\text{-}Fa,b,through\ space}$ = 1.8 Hz, 3F), −116.9 (Fd, dtt, $^{3}J_{Fd\text{-}H3}$ = 9.4 Hz, $^{4}J_{Fd\text{-}H4,6}$ = 6.1 Hz, $J_{Fd\text{-}Fa,b,through\ space}$ = 3.0 Hz, 1F), −127.7 (Fa and Fb, m, 2F). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −75.2 (Fc, t, $J_{Fc\text{-}Fa,b,through\ space}$ = 1.8 Hz, 3F), −116.9 (Fd, t, $J_{Fd\text{-}Fa,b,through\ space}$ = 3.0 Hz, 1F), −127.73 (Fa, dq, $J_{Fa\text{-}Fd,through\ space}$ = 2.8 Hz, $J_{Fa\text{-}Fc,through\ space}$ = 2.2 Hz, 1F), −127.75 (Fb, dq, $J_{Fb\text{-}Fd,through\ space}$ = 3.8 Hz, $J_{Fb\text{-}Fc,through\ space}$ = 2.1 Hz, 1F). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3 (C8, d, $^{1}J_{C8\text{-}Fd}$ = 250.9 Hz), 133.2 (C4, d, $^{3}J_{C2\text{-}Fd}$ = 8.5 Hz), 129.4 (C6, m), 125.3 (C5, d, $^{4}J_{C1\text{-}Fd}$ = 3.7 Hz), 118.4 (C9, q, $^{1}J_{C9\text{-}Fc}$ = 319.6 Hz), 117.5 (C3, dt, $^{2}J_{C3\text{-}Fd}$ = 12.7 Hz, $J_{C3\text{-}Fa,b,through\ space}$ = 2.7 Hz), 116.4 (C7, d, $^{2}J_{C7\text{-}Fd}$ = 21.0 Hz), 111.7 (C1, td, $^{1}J_{C1\text{-}Fa,b}$ = 248.1 Hz, $J_{C1\text{-}Fd,through\ space}$ = 3.0 Hz), 79.4 (C2, td, $^{2}J_{C2\text{-}Fa,b}$ = 28.4 Hz, $J_{C2\text{-}Fd,through\ space}$ = 2.6 Hz). IR (CCl_4): ν 3088 (vw), 3070 (vw), 3046 (vw), 2971 (w, CF_2–H), 2924 (w), 2848 (vw), 1621 (m), 1588 (m), 1492 (m), 1459 (m), 1433 (s), 1247 (s), 1218 (vs), 1145 (vs), 1101 (s), 951 (m).

1-(Benzyloxy)-4-(difluoromethyl)benzene (5-CF$_2$H):



5-CF$_2$H was prepared by treating 4-(benzyloxy)-1-benzaldehyde (2.0 mmol, 424 mg) in anhydrous CH_2Cl_2 (2.0 mL) with (diethylamino)sulfur trifluoride (DAST; 6.8 mmol, 1094 mg, 0.90 mL) in a PTFE vial. A portion of CH_3OH (20 μL) was added as a catalyst and the reaction was stirred at room temperature overnight. The reaction was quenched carefully with sat. Na_2CO_3(aq). The mixture was extracted with ethyl acetate (20 mL × 3) and the organic phase was dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (CH_2Cl_2:hexanes = 15:85 to 20:80 to 30:70) to give a white solid (220 mg, 47% yield). Colorless crystals were obtained by slow evaporation from a CH_2Cl_2 and hexanes solution. MP 73.9 – 74.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.33 (m, 7H, Ar-*H*), 7.03 (pseudo d, *J* = 8.9 Hz, 2H, Ar-*H*), 6.60 (t, *J* = 56.7 Hz, 1H, CF_2H), 5.11 (s, 2H, CH_2). ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.9 (d, *J* = 56.8 Hz, CF_2H). These data are consistent with published results.[3]

3. NMR Spectroscopy Studies

3.1 Concentration Dependence of NMR Chemical Shifts of 1-CF_2H and 1-OH

The concentration dependence of the NMR chemical shifts of **1-CF_2H** and **1-OH** was investigated in $CDCl_3$ at concentrations of 1, 5, 20, 100, and 500 mM at room temperature. The chemical shift of the CF_2H proton and the OH proton is independent of concentration from 1 to 100 mM. Slightly upfield shifts were observed at concentrations of 500 mM. This result indicates that hydrogen bonding interactions are predominantly intramolecular at concentrations less than 100 mM.

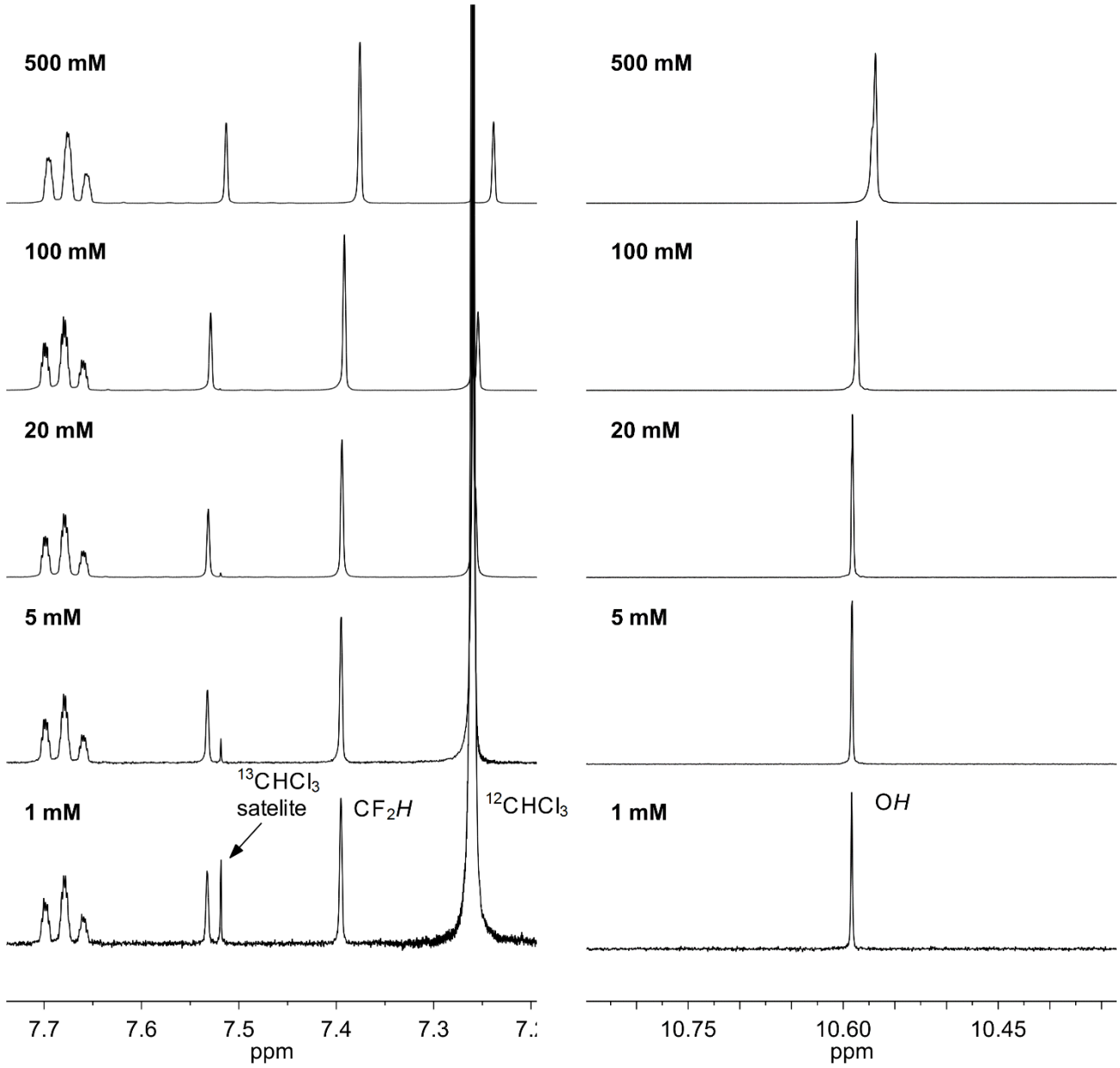


Figure S1. ^1H NMR spectra of **1-CF_2H** (left) and **1-OH** (right) in $CDCl_3$ at different concentrations.

3.2 Solvent Dependence of the Conformation of 4-NO_2

The conformation of **4-NO_2** was investigated at a concentration of 50 mM in four different solvents, including CCl_4 (ε = 2.22), $CDCl_3$ (ε = 4.71), CD_3NO_2 (ε = 36.6), and CD_3CN (ε = 35.7).[4] Although DMF-d_7 was also used in NMR studies, the compound decomposed rapidly in DMF-d_7 at room temperature. The four solvents were chosen not only because of their different dielectric constants, but are also due to their ability to facilitate various specific interactions, such as hydrogen and halogen bonding. As shown in Figure S2, although the ^{1}H NMR chemical shift of the CF_2H moiety varies in different solvents, the value, relative to that of the benzylic proton, is almost solvent independent. Other than in CCl_4, the multiplicity of the benzylic proton and the corresponding coupling constants do not change in different solvents. More importantly, the through-space coupling between the CF_3 group and the F^b nucleus is a good indicator of the conformation of **4-NO_2**. The coupling constants are only ca. 30% higher in non-polar solvents than those in highly polar solvents, suggesting only a minor change in conformational distribution. In summary, the conformation of **4-NO_2** is insensitive to solvents, which in turn suggests that the intramolecular CF_2-H···O bonding is not significantly perturbed by weak intermolecular forces.

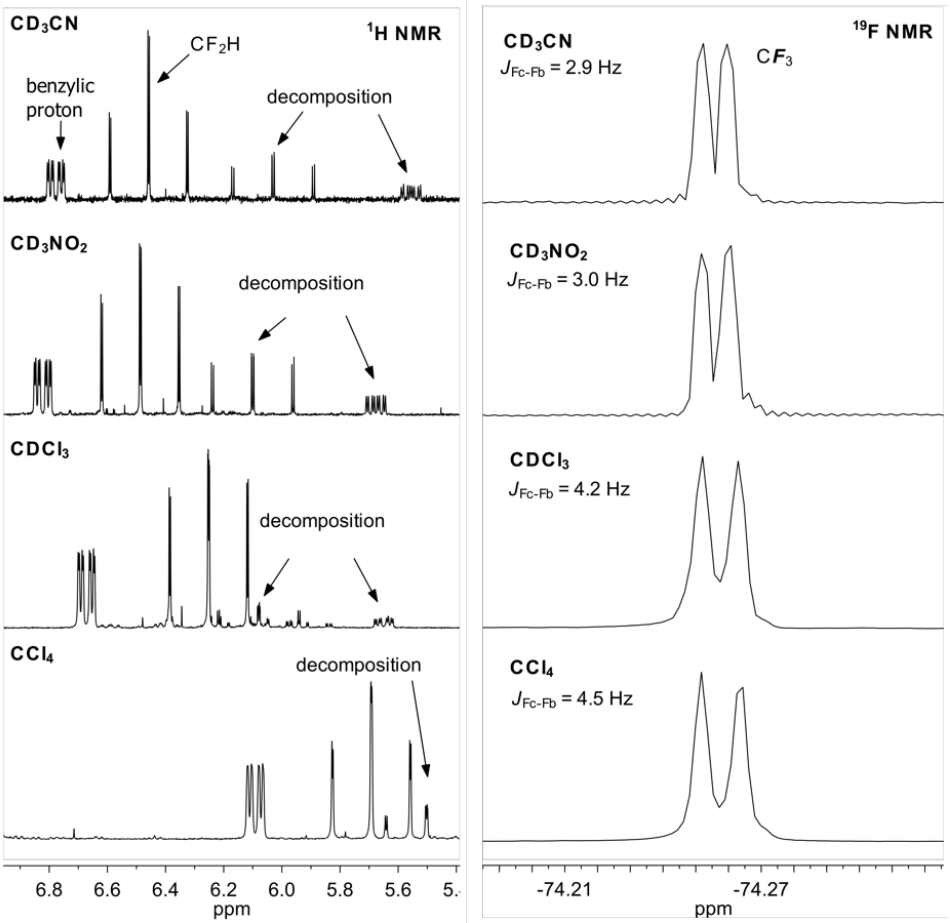


Figure S2. ^{1}H and ^{19}F NMR spectra of **4-NO_2** in various solvents.

3.3 Concentration Dependence of the Conformation of 4-NO_2

To investigate whether there are significant intermolecular $CF_2H\cdots O$ interactions, we performed NMR studies of **4-NO_2** in $CDCl_3$ at different concentrations. As illustrated in Figure S3, ^1H and ^{19}F NMR spectra of **4-NO_2** do not show any noticeable differences at concentrations spanning from 10 mM to 100 mM. These results indicate that **4-NO_2** experiences rather weak intermolecular interactions, if any.

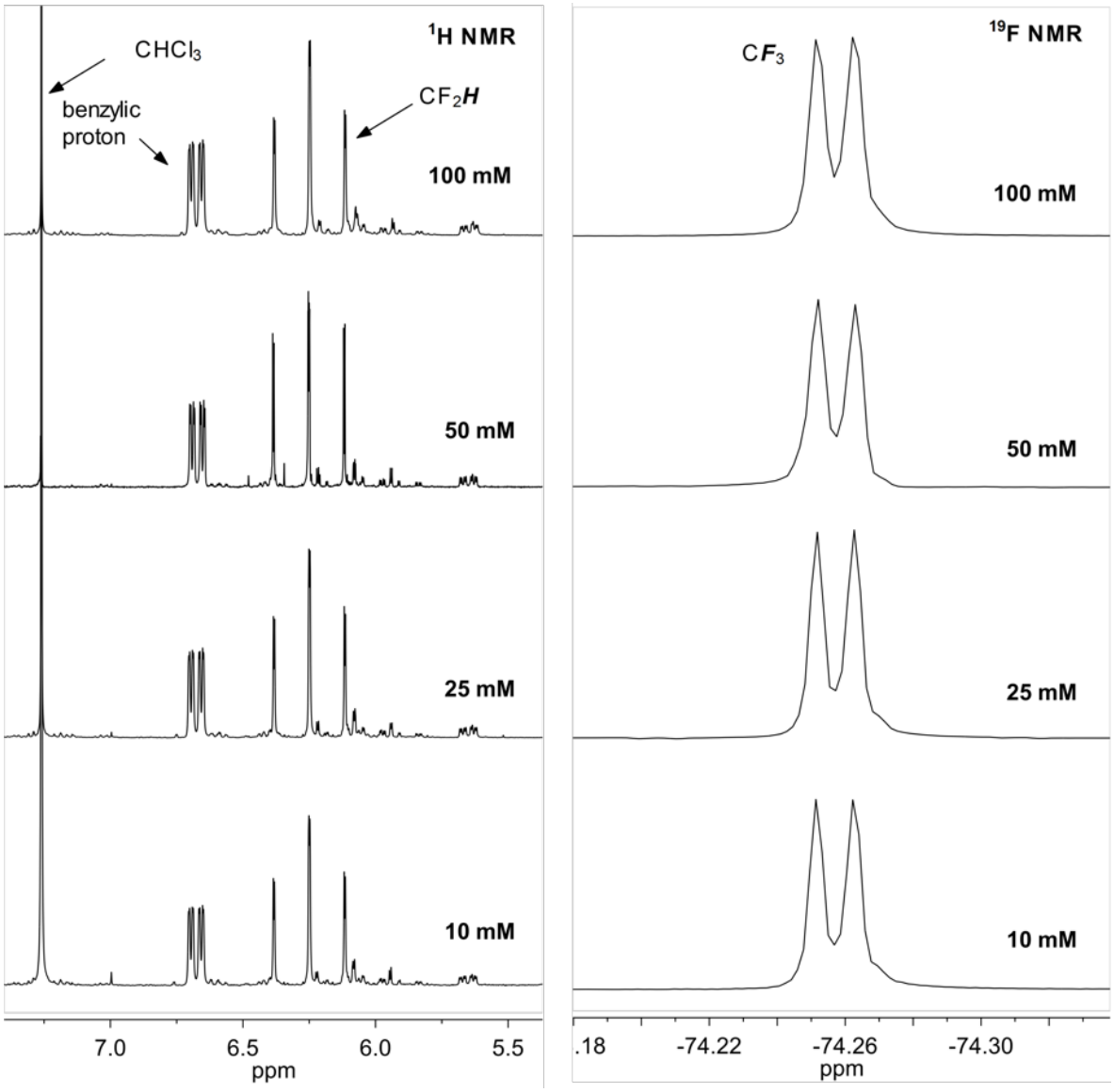


Figure S3. ^1H and ^{19}F NMR spectra of **4-NO_2** in $CDCl_3$ at various concentrations.

4. IR Spectroscopy Studies

Spectroscopic studies were performed at a concentration of 100 mM in anhydrous CCl_4. To identify the CF_2−H bond stretch, the corresponding CF_2−D-containing compounds were synthesized.

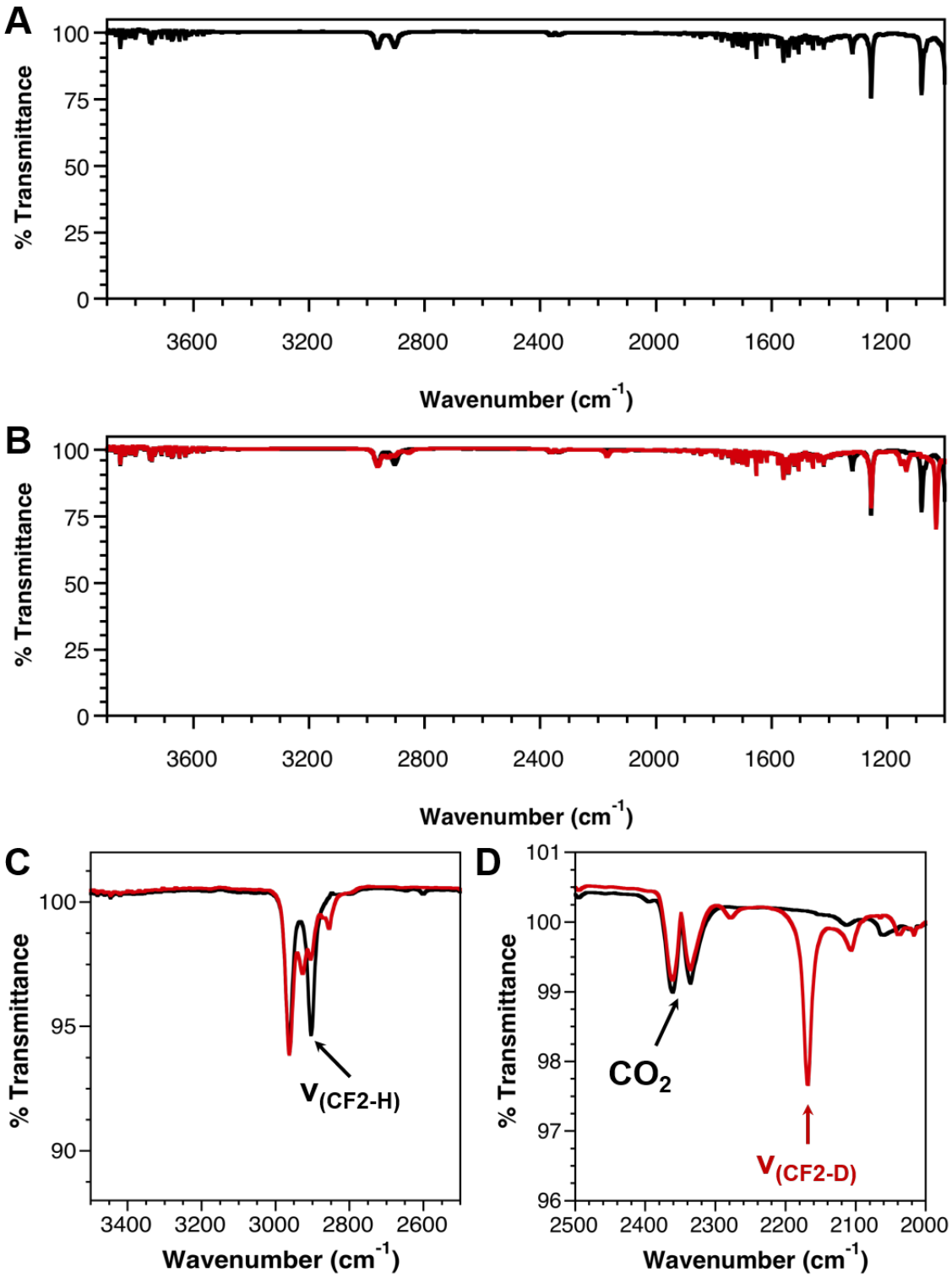


Figure S4. A) IR spectrum of $TMSCF_2H$. B) Superimposed IR spectra of $TMSCF_2H$ (black) and $TMSCF_2D$ (red). C) and D) Expansion of superimposed IR spectra of $TMSCF_2H$ (black) and $TMSCF_2D$ (red).

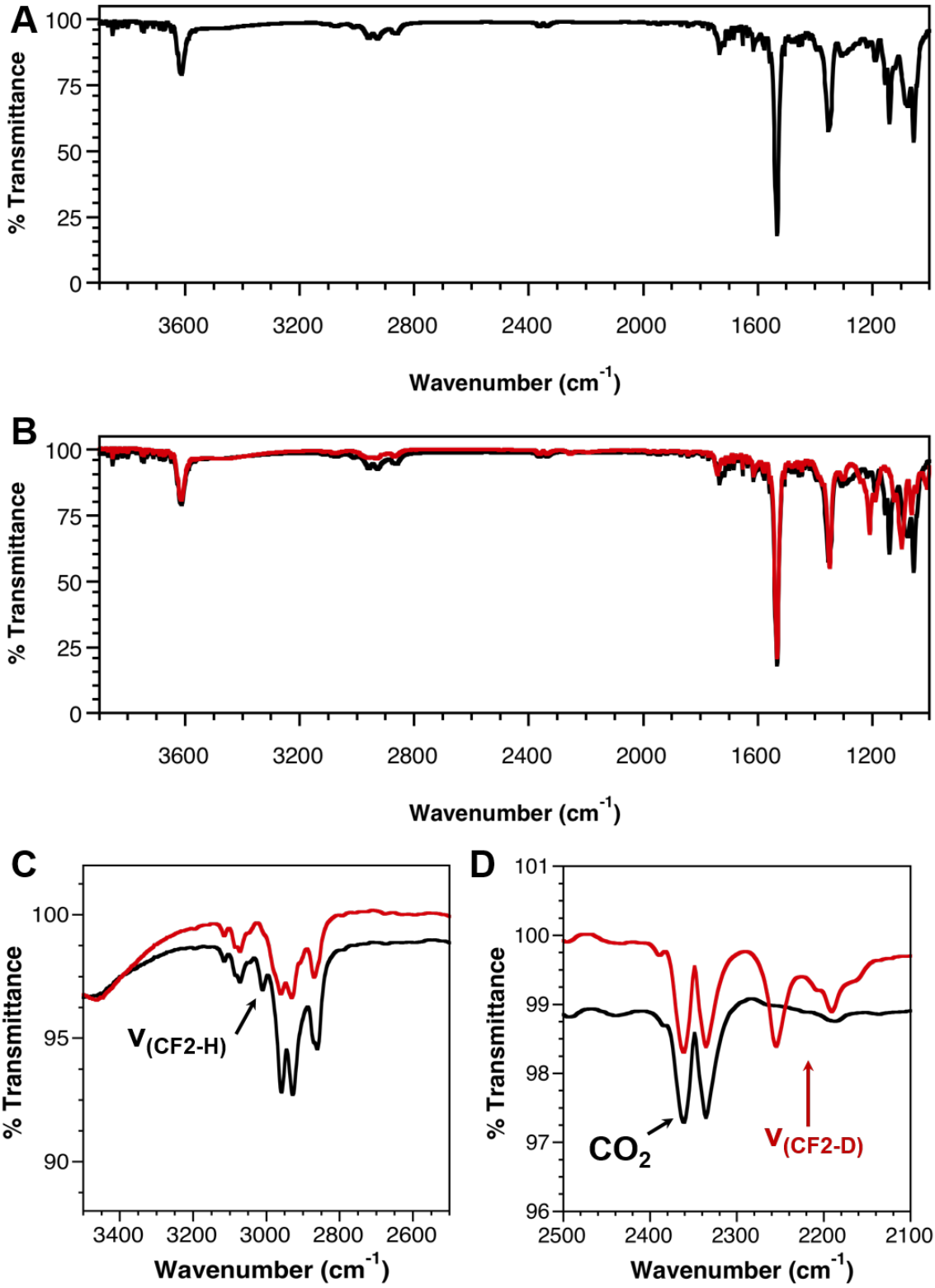


Figure S5. A) IR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethan-1-ol (**3-NO_2**). B) Superimposed IR spectra of **3-NO_2** (black) and **3-NO_2-D** (red). C) and D) Expansion of superimposed IR spectra of **3-NO_2** (black) and **3-NO_2-D** (red).

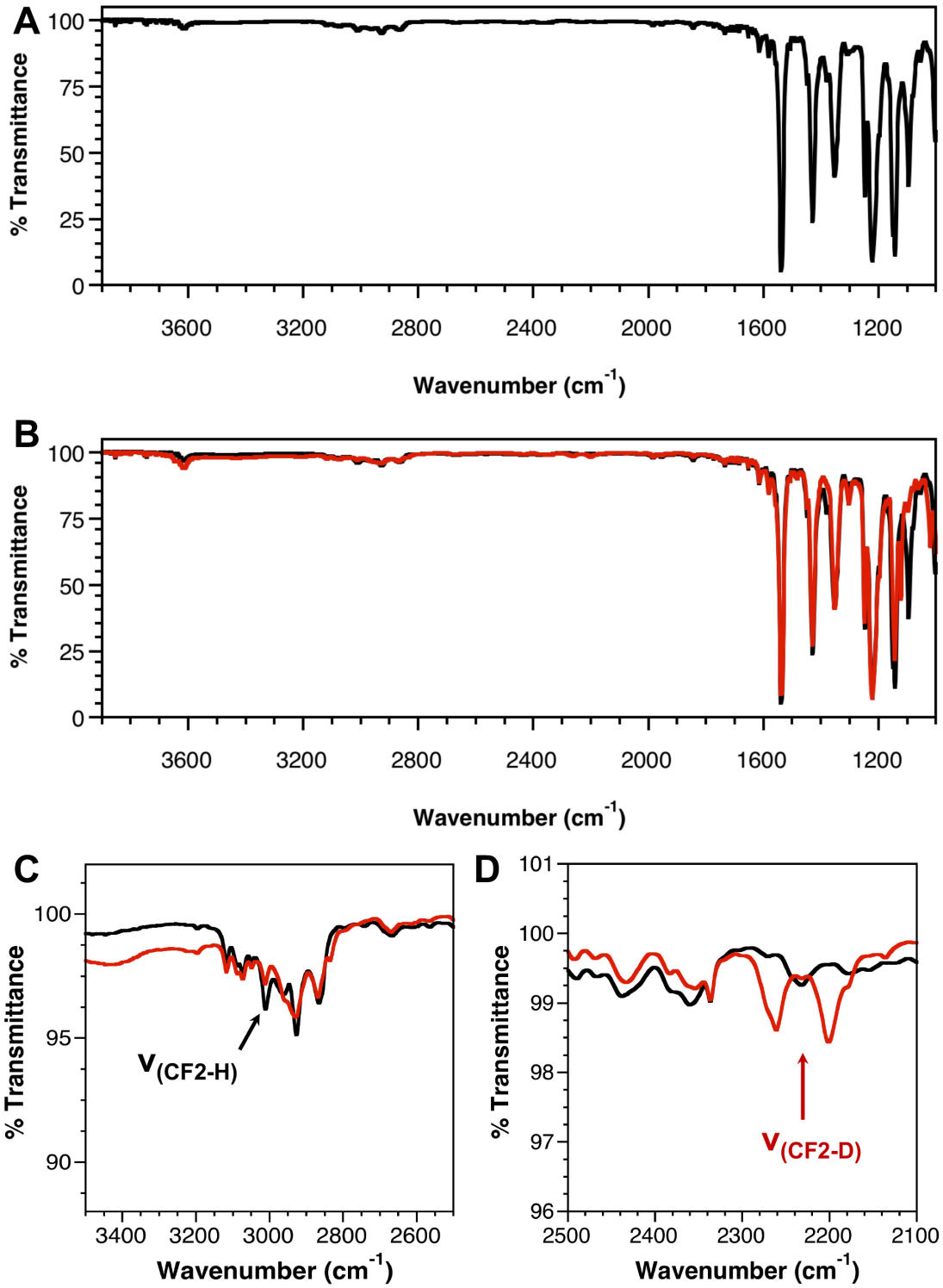


Figure S6. A) IR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethan-1-ol triflate (**4-NO$_2$**). B) Superimposed IR spectra of **4-NO$_2$** (black) and **4-NO$_2$-D** (red). C) and D) Expansion of superimposed IR spectra of **4-NO$_2$** (black) and **4-NO$_2$-D** (red). The IR spectrum of **4-NO$_2$** is complicated in the region from 2800 to 3200 cm^{-1}; we tentatively assign the peak at 3008 cm^{-1} to the CF_2–H stretch. Peaks in the IR spectrum of the deuterated analogue **4-NO$_2$-D** at 2260 and 2200 cm^{-1} were attributed to CF_2–D bond stretches. The two bands are most likely due to Fermi resonance.

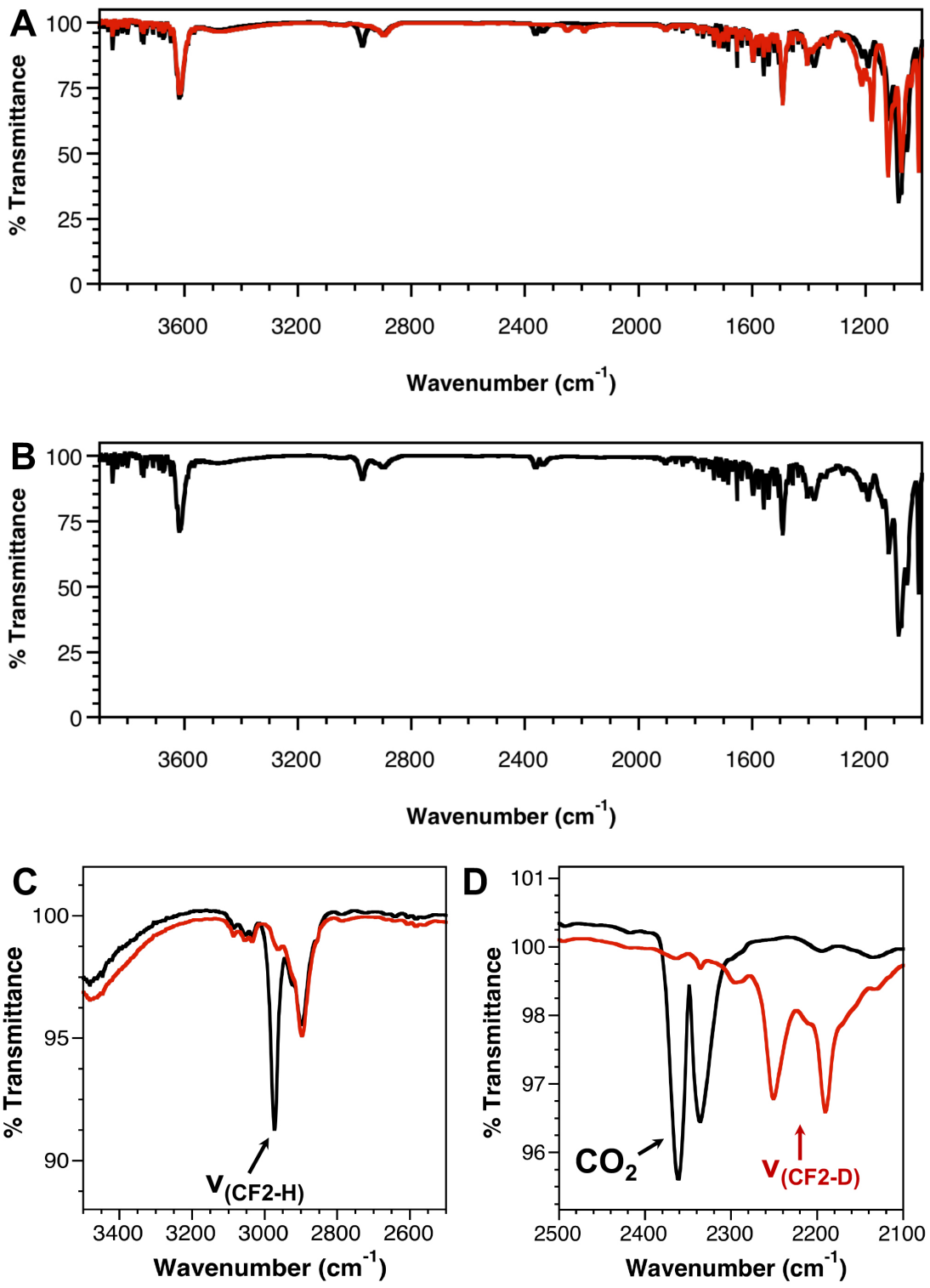


Figure S7. A) IR spectrum of 2,2-difluoro-1-(4-bromophenyl)ethan-1-ol (**3-Br**). B) Superimposed IR spectra of **3-Br** (black) and **3-Br-D** (red). C) and D) Expansion of superimposed IR spectra of **3-Br** (black) and **3-Br-D** (red).

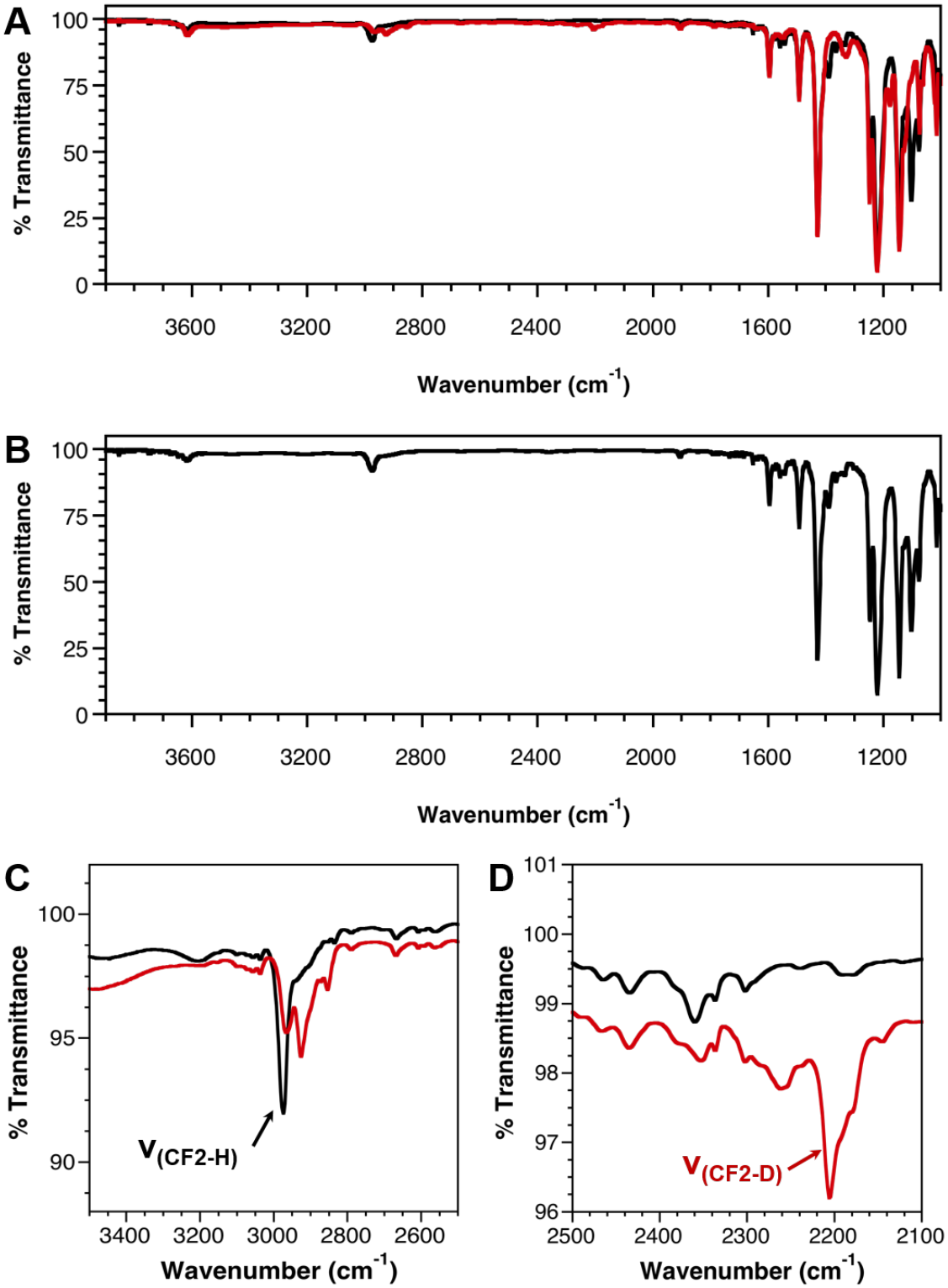


Figure S8. A) IR spectrum of 2,2-difluoro-1-(4-bromophenyl)ethan-1-ol triflate (**4-Br**). B) Superimposed IR spectra of **4-Br** (black) and **4-Br-D** (red). C) and D) Expansion of superimposed IR spectra of **4-Br** (black) and **4-Br-D** (red).

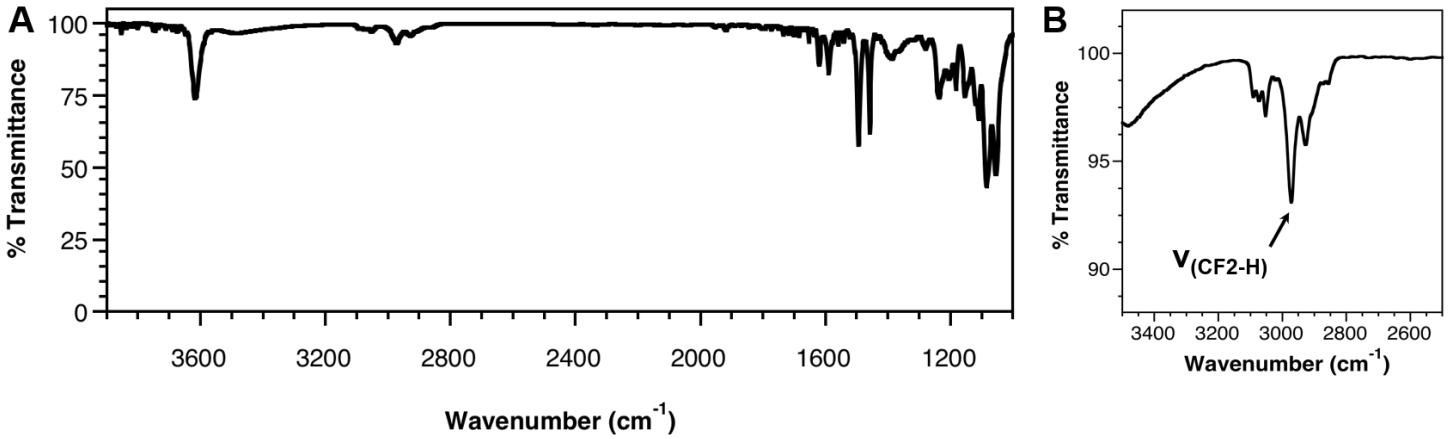


Figure S9. A) IR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**). B) Expansion of IR spectrum of **3-F**.

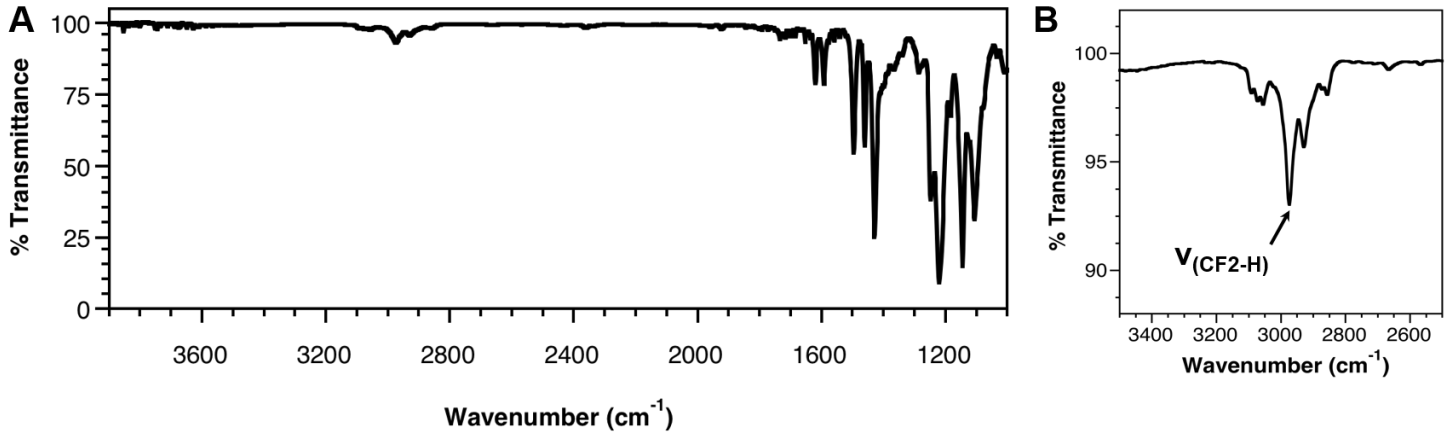


Figure S10. A) IR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol triflate (**4-F**). B) Expansion of IR spectrum of **4-F**.

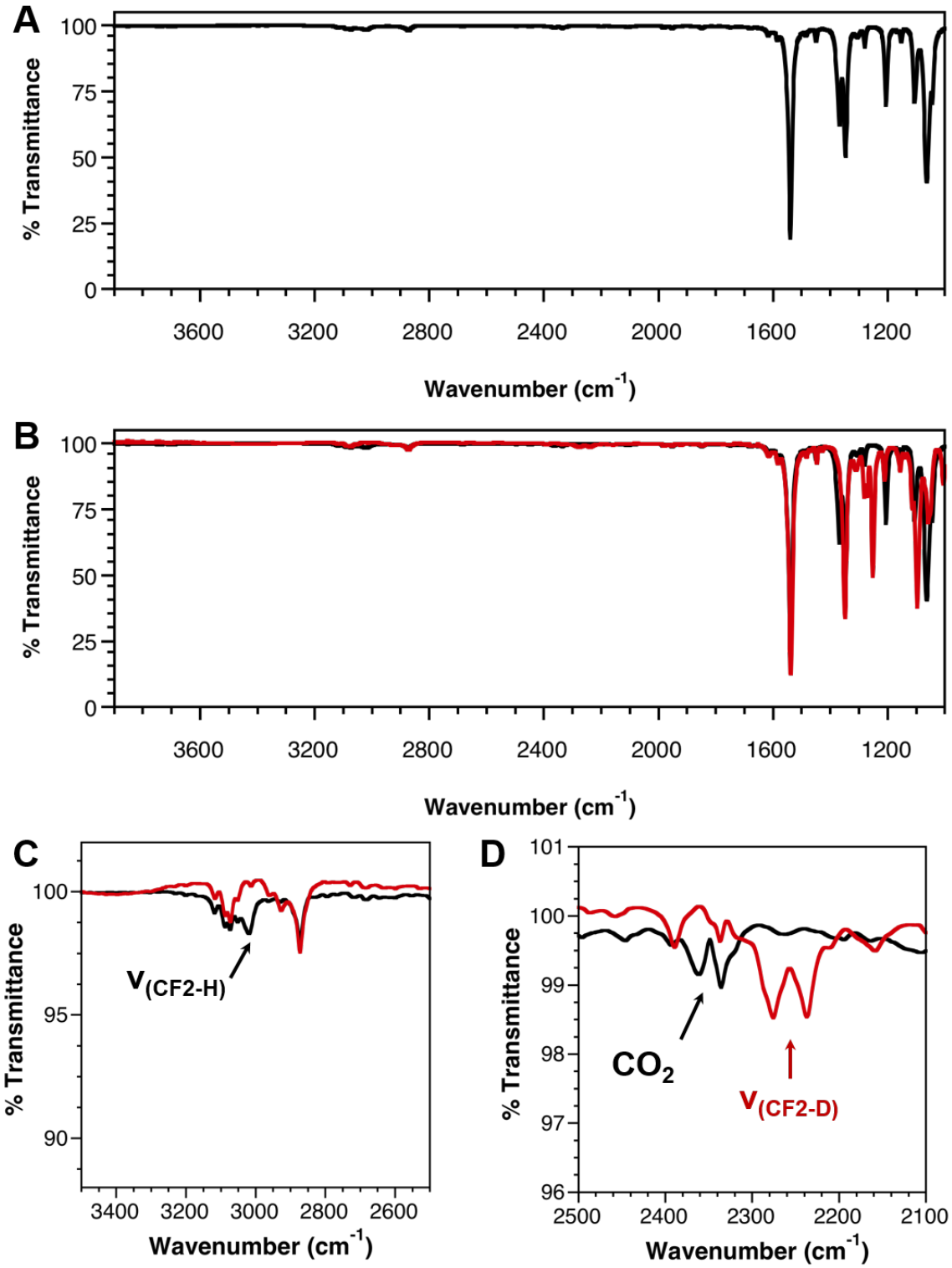


Figure S11. A) IR spectrum of *o*-nitro-α,α-difluorotoluene (**1-CF_2H**). B) Superimposed IR spectra of **1-CF_2H** (black) and **1-CF_2D** (red). C) and D) Expansion of superimposed IR spectra of **1-CF_2H** (black) and **1-CF_2D** (red). Peaks in the IR spectrum of the deuterated analogue **1-CF_2D** at 2276 and 2237 cm^{-1} were attributed to CF_2–D bond stretches. The two bands are probably due to Fermi resonance.

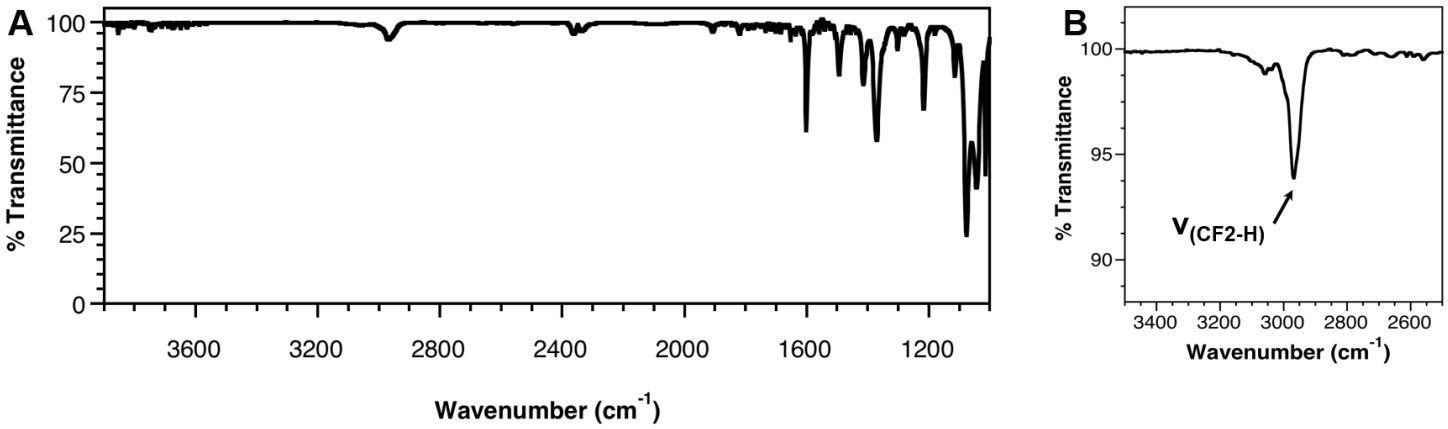


Figure S12. A) IR spectrum of *p*-bromo-α,α-difluorotoluene (**2-CF_2H**). B) Expansion of IR spectrum of **2-CF_2H**.

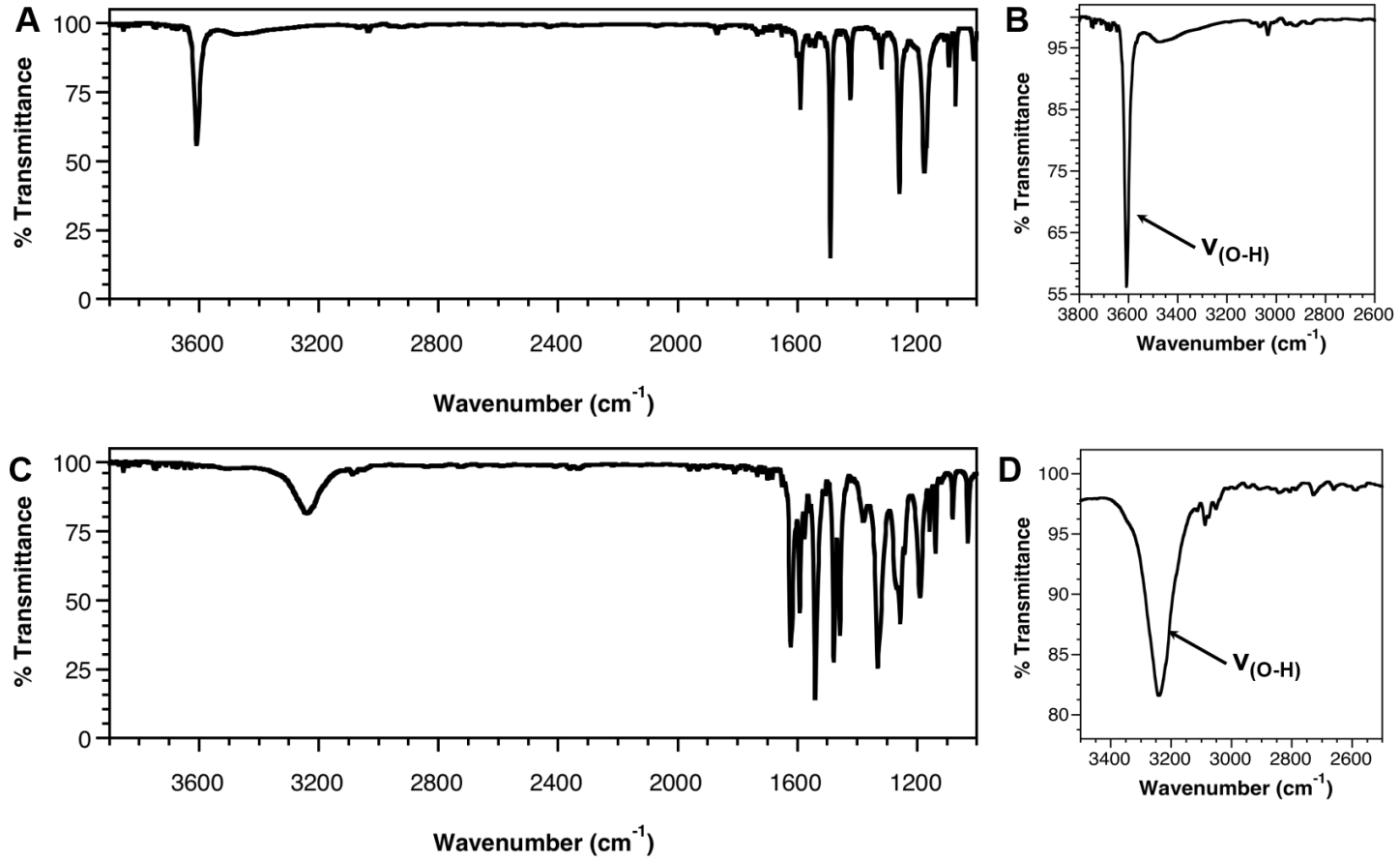


Figure S13. A) IR spectrum of *p*-bromophenol(**2-OH**). B) Expansion of IR spectrum of **2-OH**. C) IR spectrum of *o*-nitrophenol (**1-OH**). D) Expansion of IR spectrum of **1-OH**.

5. Theoretical Calculations

5.1. Potential Energy Surface Calculations and Conformational Distribution

The conformations of **4-NO$_2$** are determined by four critical rotations τ_1-τ_4 (Figure S14). To identify the conformational distribution of **4-NO$_2$**, two model compounds, 1-(2-nitrophenyl)-2,2,2-trifluoroethanol triflate and 1-(2-nitrophenyl)ethanol triflate, were chosen to generate potential energy surfaces (PESs) as a function of the τ_1 and τ_2 rotations. Because of the C_{3v} symmetry of the trifluoromethyl and methyl group, the PESs of these two molecules are independent of τ_3. The rotations τ_1 and τ_2 were scanned from −180° to +180° with an increment of 30° of each step. The conformations generated were optimized at the PCM-B3LYP/6-31+G(d) level in $CHCl_3$ using Gaussian 09.[5] The conformational distribution about τ_1 and τ_2 was obtained as a 13×13 PES with 169 geometry optimizations. For both model compounds, four local minima were identified (Figures S15 and S16). The search of local minima of **4-NO$_2$** was achieved by substituting the CF_3 group with a CF_2H moiety. Further geometry optimization of these structures was performed at the PCM-B3LYP/6-31+G(d,p) level in $CHCl_3$, which led to very small geometric changes.

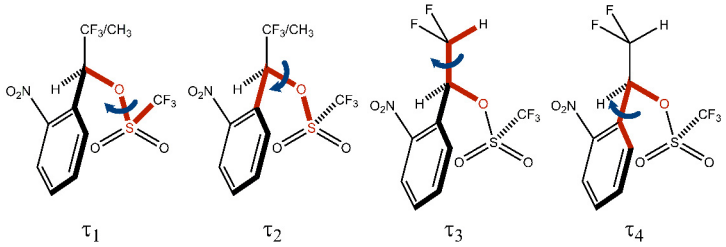


Figure S14. Critical rotations determining the conformations of **4-NO$_2$**.

In addition to the τ_1 and τ_2 rotations, two more rotations, τ_3 and τ_4, were also considered because they govern the formation of intramolecular H-bonding (Figure S14). As such, each local minimum on the PES corresponds to 3×2 = 6 conformers and, overall, 24 conformers were identified for **4-NO$_2$** at the PCM-B3LYP/6-31+G(d,p) level of theory in $CHCl_3$. Similarly, 12 and 24 conformers were found for **4-Br** and **4-F**, respectively.

5.1.1. 1-(2-Nitrophenyl)-2,2,2-trifluoroethanol Triflate

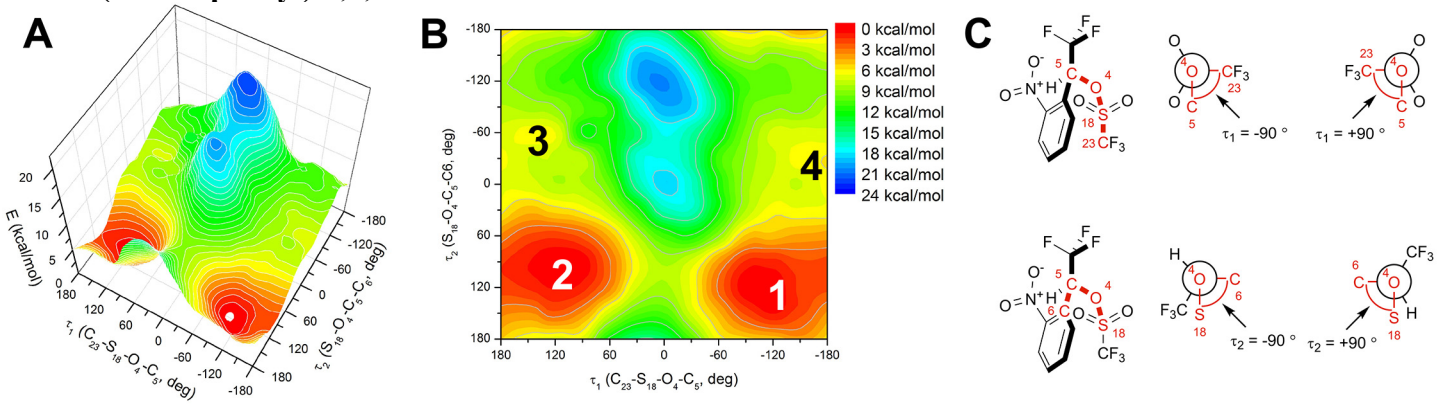


Figure S15. A) 3D-PES of 1-(2-nitrophenyl)-2,2,2-trifluoroethanol triflate. B) Contour map of PES of 1-(2-nitrophenyl)-2,2,2-trifluoroethanol triflate. C) Definition of the value of τ_1 and τ_2.

Table S1. Conformers and energy of 1-(2-nitrophenyl)-2,2,2-trifluoroethanol triflate due to the rotations of τ_1 and τ_2 at the B3LYP/6-31+G(d) level of theory in the gas phase.

Conformer	τ_1	τ_2	Energy (hartree)	Relative Energy (kcal/mol)
1	-180	-180	-1773.954430	5.7
2	-150	-180	-1773.956956	4.1
3	-120	-180	-1773.954207	5.8
4	-90	-180	-1773.954631	5.5
5	-60	-180	-1773.953092	6.5
6	-30	-180	-1773.946659	10.5
7	0	-180	-1773.940325	14.5
8	30	-180	-1773.939514	15.0
9	60	-180	-1773.943704	12.4
10	90	-180	-1773.952119	7.1
11	120	-180	-1773.95194	7.2
12	150	-180	-1773.952763	6.7
13	180	-180	-1773.955271	5.1
14	-180	-150	-1773.951265	7.7
15	-150	-150	-1773.949538	8.7
16	-120	-150	-1773.948832	9.2
17	-90	-150	-1773.950176	8.3
18	-60	-150	-1773.947543	10.0
19	-30	-150	-1773.939266	15.2
20	0	-150	-1773.934136	18.4
21	30	-150	-1773.933474	18.8
22	60	-150	-1773.941371	13.9
23	90	-150	-1773.944964	11.6
24	120	-150	-1773.947716	9.9
25	150	-150	-1773.949063	9.0
26	180	-150	-1773.951559	7.5
27	-180	-120	-1773.948285	9.5
28	-150	-120	-1773.948281	9.5
29	-120	-120	-1773.947202	10.2
30	-90	-120	-1773.946529	10.6
31	-60	-120	-1773.942267	13.3
32	-30	-120	-1773.934818	18.0
33	0	-120	-1773.930970	20.4
34	30	-120	-1773.932517	19.4
35	60	-120	-1773.939452	15.1
36	90	-120	-1773.944915	11.6
37	120	-120	-1773.945780	11.1
38	150	-120	-1773.948464	9.4
39	180	-120	-1773.949243	8.9
40	-180	-90	-1773.950552	8.1
41	-150	-90	-1773.948532	9.4
42	-120	-90	-1773.948787	9.2
43	-90	-90	-1773.947245	10.2
44	-60	-90	-1773.940200	14.6
45	-30	-90	-1773.933626	18.7

46	0	-90	-1773.932493	19.4
47	30	-90	-1773.936722	16.8
48	60	-90	-1773.945055	11.6
49	90	-90	-1773.946855	10.4
50	120	-90	-1773.949172	9.0
51	150	-90	-1773.949787	8.6
52	180	-90	-1773.950439	8.2
53	-180	-60	-1773.951809	7.3
54	-150	-60	-1773.951950	7.2
55	-120	-60	-1773.951877	7.3
56	-90	-60	-1773.948338	9.5
57	-60	-60	-1773.942883	12.9
58	-30	-60	-1773.938209	15.8
59	0	-60	-1773.935795	17.4
60	30	-60	-1773.940390	14.5
61	60	-60	-1773.944141	12.1
62	90	-60	-1773.944141	12.1
63	120	-60	-1773.952768	6.7
64	150	-60	-1773.953185	6.5
65	180	-60	-1773.951953	7.2
66	-180	-30	-1773.954054	5.9
67	-150	-30	-1773.953389	6.3
68	-120	-30	-1773.951283	7.6
69	-90	-30	-1773.949235	8.9
70	-60	-30	-1773.946125	10.9
71	-30	-30	-1773.938765	15.5
72	0	-30	-1773.935972	17.3
73	30	-30	-1773.936845	16.7
74	60	-30	-1773.944938	11.6
75	90	-30	-1773.950917	7.9
76	120	-30	-1773.951231	7.7
77	150	-30	-1773.951500	7.5
78	180	-30	-1773.953025	6.6
79	-180	0	-1773.953195	6.4
80	-150	0	-1773.951407	7.6
81	-120	0	-1773.951797	7.3
82	-90	0	-1773.949738	8.6
83	-60	0	-1773.944600	11.8
84	-30	0	-1773.937035	16.6
85	0	0	-1773.933711	18.7
86	30	0	-1773.938503	15.7
87	60	0	-1773.947402	10.1
88	90	0	-1773.950377	8.2
89	120	0	-1773.950406	8.2
90	150	0	-1773.952055	7.2
91	180	0	-1773.952419	6.9
92	-180	30	-1773.953072	6.5

93	-150	30	-1773.952902	6.6
94	-120	30	-1773.953353	6.3
95	-90	30	-1773.950371	8.2
96	-60	30	-1773.944191	12.1
97	-30	30	-1773.937312	16.4
98	0	30	-1773.937873	16.1
99	30	30	-1773.945210	11.5
100	60	30	-1773.950672	8.0
101	90	30	-1773.953428	6.3
102	120	30	-1773.954511	5.6
103	150	30	-1773.955744	4.8
104	180	30	-1773.953373	6.3
105	-180	60	-1773.957001	4.1
106	-150	60	-1773.956605	4.3
107	-120	60	-1773.955654	4.9
108	-90	60	-1773.955369	5.1
109	-60	60	-1773.949007	9.1
110	-30	60	-1773.944616	11.8
111	0	60	-1773.946157	10.9
112	30	60	-1773.950597	8.1
113	60	60	-1773.955987	4.7
114	90	60	-1773.959452	2.5
115	120	60	-1773.960737	1.7
116	150	60	-1773.960121	2.1
117	180	60	-1773.957721	3.6
118	-180	90	-1773.960310	2.0
119	-150	90	-1773.960079	2.1
120	-120	90	-1773.961526	1.2
121	-90	90	-1773.961307	1.4
122	-60	90	-1773.956995	4.1
123	-30	90	-1773.951909	7.3
124	0	90	-1773.950024	8.4
125	30	90	-1773.953012	6.6
126	60	90	-1773.958747	3.0
127	90	90	-1773.963132	0.2
128	120	90	-1773.963467	0.0
129	150	90	-1773.962203	0.8
130	180	90	-1773.960855	1.6
131	-180	120	-1773.960166	2.1
132	-150	120	-1773.960839	1.6
133	-120	120	-1773.963129	0.2
134	-90	120	-1773.963268	0.1
135	-60	120	-1773.958986	2.8
136	-30	120	-1773.952916	6.6
137	0	120	-1773.949984	8.5
138	30	120	-1773.951588	7.5
139	60	120	-1773.957941	3.5

140	90	120	-1773.961686	1.1
141	120	120	-1773.962409	0.7
142	150	120	-1773.961259	1.4
143	180	120	-1773.960456	1.9
144	-180	150	-1773.957194	3.9
145	-150	150	-1773.960307	2.0
146	-120	150	-1773.962352	0.7
147	-90	150	-1773.960159	2.1
148	-60	150	-1773.956003	4.7
149	-30	150	-1773.951773	7.3
150	0	150	-1773.946634	10.6
151	30	150	-1773.947149	10.2
152	60	150	-1773.951365	7.6
153	90	150	-1773.957210	3.9
154	120	150	-1773.959511	2.5
155	150	150	-1773.957349	3.8
156	180	150	-1773.957919	3.5
157	-180	180	-1773.954430	5.7
158	-150	180	-1773.956956	4.1
159	-120	180	-1773.955252	5.2
160	-90	180	-1773.954631	5.5
161	-60	180	-1773.953092	6.5
162	-30	180	-1773.946659	10.5
163	0	180	-1773.940325	14.5
164	30	180	-1773.939514	15.0
165	60	180	-1773.943704	12.4
166	90	180	-1773.952120	7.1
167	120	180	-1773.951941	7.2
168	150	180	-1773.952763	6.7
169	180	180	-1773.955270	5.1

5.1.2. 1-(2-Nitrophenyl)ethanol Triflate

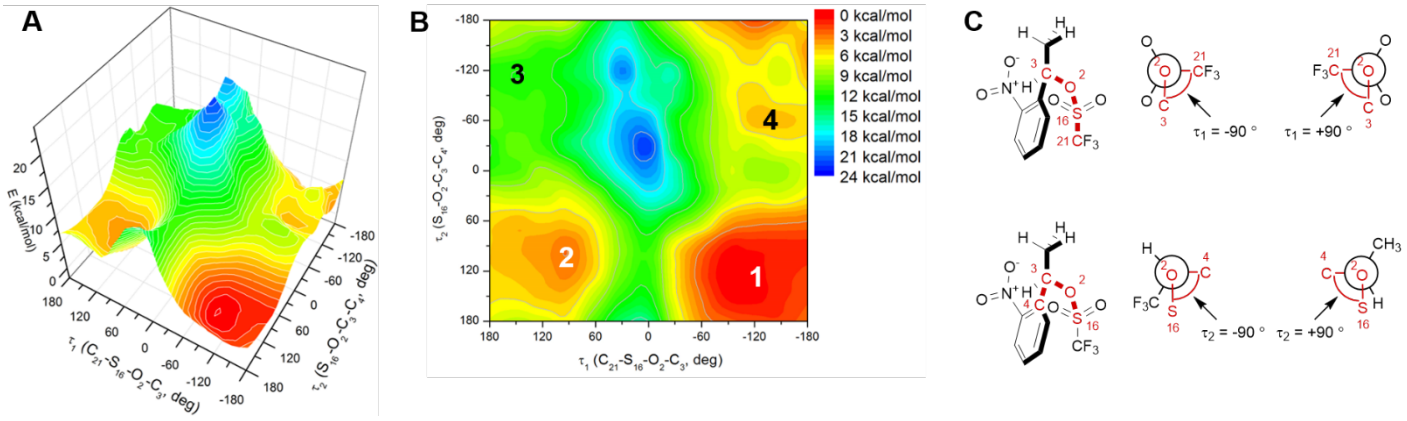


Figure S16. A) 3D-PES of 1-(2-nitrophenyl)ethanol triflate. B) Contour map of PES of 1-(2-nitrophenyl)ethanol triflate. C) Definition of the value of τ_1 and τ_2.

Table S2. Conformers of 1-(2-nitrophenyl)-2,2,2-trifluoroethanol triflate due to the rotations of τ_1 and τ_2 at the B3LYP/6-31+G(d) level of theory in the gas phase.

Conformer	τ_1	τ_2	Energy (hartree)	Relative Energy (kcal/mol)
1	-180	-180	-1476.223423	6.9
2	-150	-180	-1476.228592	3.6
3	-120	-180	-1476.231242	2.0
4	-90	-180	-1476.228125	3.9
5	-60	-180	-1476.226154	5.2
6	-30	-180	-1476.222149	7.7
7	0	-180	-1476.216475	11.2
8	30	-180	-1476.209385	15.7
9	60	-180	-1476.215635	11.8
10	90	-180	-1476.222620	7.4
11	120	-180	-1476.222752	7.3
12	150	-180	-1476.221730	7.9
13	180	-180	-1476.223423	6.9
14	-180	-150	-1476.228121	3.9
15	-150	-150	-1476.224489	6.2
16	-120	-150	-1476.226592	4.9
17	-90	-150	-1476.224795	6.0
18	-60	-150	-1476.222547	7.4
19	-30	-150	-1476.216920	11.0
20	0	-150	-1476.211864	14.1
21	30	-150	-1476.205804	17.9
22	60	-150	-1476.210945	14.7
23	90	-150	-1476.216570	11.2
24	120	-150	-1476.216914	11.0
25	150	-150	-1476.219040	9.6
26	180	-150	-1476.220404	8.8
27	-180	-120	-1476.227336	4.4
28	-150	-120	-1476.222571	7.4
29	-120	-120	-1476.224617	6.1
30	-90	-120	-1476.223705	6.7
31	-60	-120	-1476.219026	9.6
32	-30	-120	-1476.209519	15.6
33	0	-120	-1476.209701	15.5
34	30	-120	-1476.201807	20.4
35	60	-120	-1476.210231	15.2
36	90	-120	-1476.213426	13.2
37	120	-120	-1476.215943	11.6
38	150	-120	-1476.215206	12.0
39	180	-120	-1476.215833	11.6
40	-180	-90	-1476.224712	6.1
41	-150	-90	-1476.224163	6.4
42	-120	-90	-1476.225504	5.6
43	-90	-90	-1476.223796	6.6
44	-60	-90	-1476.217153	10.8
45	-30	-90	-1476.210859	14.8

46	0	-90	-1476.209029	15.9
47	30	-90	-1476.205718	18.0
48	60	-90	-1476.212471	13.8
49	90	-90	-1476.214955	12.2
50	120	-90	-1476.216548	11.2
51	150	-90	-1476.216428	11.3
52	180	-90	-1476.217038	10.9
53	-180	-60	-1476.225950	5.3
54	-150	-60	-1476.226446	5.0
55	-120	-60	-1476.226713	4.8
56	-90	-60	-1476.222529	7.4
57	-60	-60	-1476.218315	10.1
58	-30	-60	-1476.214191	12.7
59	0	-60	-1476.203507	19.4
60	30	-60	-1476.203857	19.2
61	60	-60	-1476.210068	15.3
62	90	-60	-1476.214858	12.3
63	120	-60	-1476.216525	11.2
64	150	-60	-1476.217028	10.9
65	180	-60	-1476.218511	10.0
66	-180	-30	-1476.224080	6.5
67	-150	-30	-1476.224136	6.4
68	-120	-30	-1476.222346	7.6
69	-90	-30	-1476.222265	7.6
70	-60	-30	-1476.218499	10.0
71	-30	-30	-1476.212653	13.6
72	0	-30	-1476.198957	22.2
73	30	-30	-1476.203316	19.5
74	60	-30	-1476.208288	16.4
75	90	-30	-1476.212039	14.0
76	120	-30	-1476.216558	11.2
77	150	-30	-1476.218646	9.9
78	180	-30	-1476.215178	12.1
79	-180	0	-1476.223092	7.1
80	-150	0	-1476.220664	8.6
81	-120	0	-1476.220423	8.8
82	-90	0	-1476.222332	7.6
83	-60	0	-1476.216924	11.0
84	-30	0	-1476.208584	16.2
85	0	0	-1476.202311	20.1
86	30	0	-1476.205689	18.0
87	60	0	-1476.211837	14.2
88	90	0	-1476.218403	10.0
89	120	0	-1476.220485	8.7
90	150	0	-1476.217490	10.6
91	180	0	-1476.216594	11.2
92	-180	30	-1476.224766	6.0

93	-150	30	-1476.222912	7.2
94	-120	30	-1476.223599	6.8
95	-90	30	-1476.221878	7.9
96	-60	30	-1476.215832	11.6
97	-30	30	-1476.209310	15.7
98	0	30	-1476.206566	17.5
99	30	30	-1476.211902	14.1
100	60	30	-1476.219577	9.3
101	90	30	-1476.223294	7.0
102	120	30	-1476.222044	7.7
103	150	30	-1476.221959	7.8
104	180	30	-1476.222544	7.4
105	-180	60	-1476.229664	3.0
106	-150	60	-1476.229111	3.3
107	-120	60	-1476.228866	3.5
108	-90	60	-1476.22738	4.4
109	-60	60	-1476.221304	8.2
110	-30	60	-1476.217344	10.7
111	0	60	-1476.212822	13.5
112	30	60	-1476.217938	10.3
113	60	60	-1476.223658	6.7
114	90	60	-1476.225918	5.3
115	120	60	-1476.225855	5.4
116	150	60	-1476.226690	4.8
117	180	60	-1476.225446	5.6
118	-180	90	-1476.232470	1.2
119	-150	90	-1476.232574	1.1
120	-120	90	-1476.232826	1.0
121	-90	90	-1476.232932	0.9
122	-60	90	-1476.229140	3.3
123	-30	90	-1476.224428	6.3
124	0	90	-1476.216275	11.4
125	30	90	-1476.219579	9.3
126	60	90	-1476.225326	5.7
127	90	90	-1476.229430	3.1
128	120	90	-1476.227935	4.1
129	150	90	-1476.226990	4.6
130	180	90	-1476.225922	5.3
131	-180	120	-1476.231846	1.6
132	-150	120	-1476.232271	1.3
133	-120	120	-1476.233657	0.5
134	-90	120	-1476.234390	0.0
135	-60	120	-1476.230824	2.2
136	-30	120	-1476.224643	6.1
137	0	120	-1476.216189	11.4
138	30	120	-1476.218715	9.8
139	60	120	-1476.225255	5.7

140	90	120	-1476.228893	3.4
141	120	120	-1476.227427	4.4
142	150	120	-1476.226369	5.0
143	180	120	-1476.225991	5.3
144	-180	150	-1476.231198	2.0
145	-150	150	-1476.232365	1.3
146	-120	150	-1476.233684	0.4
147	-90	150	-1476.233592	0.5
148	-60	150	-1476.229738	2.9
149	-30	150	-1476.224196	6.4
150	0	150	-1476.214564	12.4
151	30	150	-1476.216118	11.5
152	60	150	-1476.221571	8.0
153	90	150	-1476.226488	5.0
154	120	150	-1476.226482	5.0
155	150	150	-1476.225184	5.8
156	180	150	-1476.225263	5.7
157	-180	180	-1476.229682	3.0
158	-150	180	-1476.231704	1.7
159	-120	180	-1476.231242	2.0
160	-90	180	-1476.230285	2.6
161	-60	180	-1476.228283	3.8
162	-30	180	-1476.222149	7.7
163	0	180	-1476.210412	15.0
164	30	180	-1476.211251	14.5
165	60	180	-1476.217453	10.6
166	90	180	-1476.224058	6.5
167	120	180	-1476.222752	7.3
168	150	180	-1476.221730	7.9
169	180	180	-1476.223423	6.9

5.1.3. Energy and Population of Conformers

To better estimate the relative energy of each conformer, single point energies were calculated at the PCM-M062X/6-311++G(2d,2p)//B3LYP/6-31+G(d,p) level of theory in $CHCl_3$. The hybrid meta exchange-correlation density functional M06-2X empirically accounts for dispersive interactions and demonstrates high accuracy in main-group thermochemistry.[6] The free energies were calculated by combining single point PCM-M062X/6-311++G(2d,2p)//B3LYP/6-31+G(d,p) calculations with thermal and entropic corrections obtained at the PCM-B3LYP/6-31+G(d,p) level. Frequency analyses confirmed that all structures were true minima on the potential energy surface. The relative populations of the different conformers in 298 K $CHCl_3$ solutions were estimated using Boltzmann statistics.

5.1.3.1. 1-(2-Nitrophenyl)-2,2-difluoroethanol Triflate (4-NO_2)

Table S3. Energy and population of conformers of 1-(2-nitrophenyl)-2,2-difluoroethanol triflate (**4-NO2**).

		PCM-B3LYP/6-31+G(d,p)				PCM-M062X/6-311++G(2d,2p)[a]			
Conformer	Note	Thermal Correction (hartree)	Free Energy (hartree)	Relative Free Energy (kcal/mol)	Pop[b]	Energy (hartree)	Free Energy (hartree)[c]	Relative Free Energy (kcal/mol)	Pop[b]
1-trans-a		0.112272	-1674.612217	0.0	56%	-1674.653592	-1674.541320	0.0	69%
2-trans-a		0.112626	-1674.612069	0.1	39%	-1674.653608	-1674.540982	0.2	30%
3-trans-a		0.112203	-1674.600456	7.4	0%	-1674.642476	-1674.530273	6.9	0%
4-trans-a		0.111510	-1674.600870	7.1	0%	-1674.641174	-1674.529664	7.3	0%
1-trans-b		0.110981	-1674.610702	1.0	1%	-1674.649923	-1674.538942	1.5	0%
2-trans-b		0.111740	-1674.609904	1.5	0%	-1674.650151	-1674.538411	1.8	0%
3-trans-b		0.112625	-1674.599991	7.7	0%	-1674.642145	-1674.529520	7.4	0%
4-trans-b		0.111909	-1674.600377	7.4	0%	-1674.640720	-1674.528811	7.8	0%
1-trans-c		0.111460	-1674.610607	1.0	1%	-1674.649791	-1674.538331	1.9	0%
2-trans-c		0.111278	-1674.610828	0.9	2%	-1674.650151	-1674.538873	1.5	0%
3-trans-c		0.111512	-1674.602392	6.2	0%	-1674.643390	-1674.531878	5.9	0%
4-trans-c		0.111747	-1674.603527	5.5	0%	-1674.643951	-1674.532204	5.7	0%
1-cis-a		0.111385	-1674.602534	6.1	0%	-1674.643048	-1674.531663	6.1	0%
2-cis-a		0.110002	-1674.603595	5.4	0%	-1674.641949	-1674.531947	5.9	0%
3-cis-a	Same as 4-cis-a	0.111241	-1674.602476	6.1	0%	-1674.641833	-1674.530592	6.7	0%
4-cis-a	Same as 3-cis-a	0.111236	-1674.602480	6.1	0%	-1674.641835	-1674.530599	6.7	0%
1-cis-b	Same as 1-cis-c	0.112200	-1674.609211	1.9	0%	-1674.649812	-1674.537612	2.3	0%
2-cis-b	Same as 2-cis-c	0.111122	-1674.610185	1.3	0%	-1674.648737	-1674.537615	2.3	0%
3-cis-b		0.109915	-1674.604159	5.1	0%	-1674.642530	-1674.532615	5.5	0%
4-cis-b		0.111032	-1674.603044	5.8	0%	-1674.642351	-1674.531319	6.3	0%
1-cis-c	Same as 1-cis-b	0.112226	-1674.609186	1.9	0%	-1674.649818	-1674.537592	2.3	0%
2-cis-c	Same as 2-cis-b	0.110843	-1674.610464	1.1	1%	-1674.648745	-1674.537902	2.1	0%
3-cis-c		0.111973	-1674.597897	9.0	0%	-1674.639416	-1674.527443	8.7	0%
4-cis-c		0.111895	-1674.595274	10.6	0%	-1674.637148	-1674.525253	10.1	0%

a. Single point calculation; b. population distribution at 298 K; c. calculated based on single point energy at the PCM-M062X/6-311++G(2d,2p) level with thermal correction at the PCM-B3LYP/6-31+G(d,p) level.

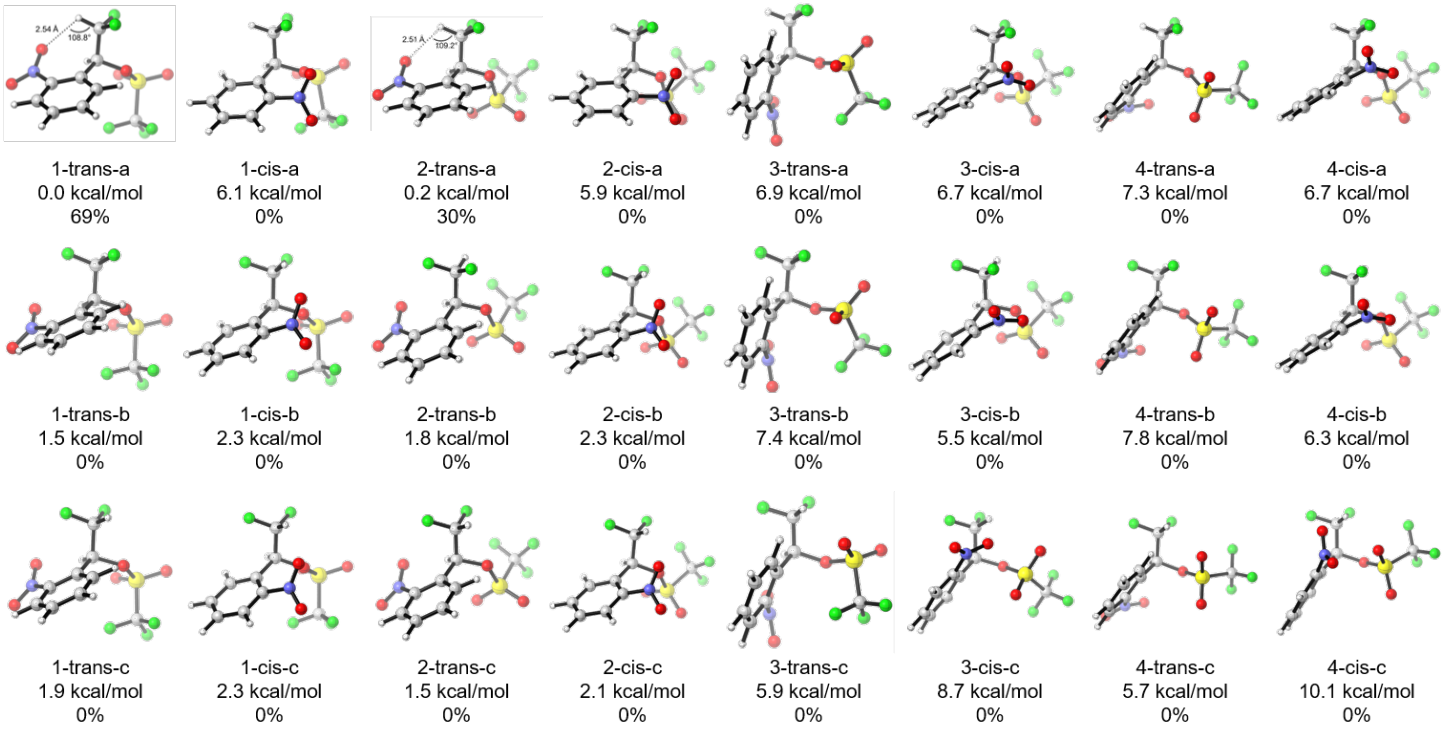


Figure S17. Conformers of 1-(2-nitrophenyl)-2,2-difluoroethanol triflate (**4-NO$_2$**), relative free energies at the PCM-M062X/6-311++G(2d,2p)//PCM-B3LYP/6-31+G(d,p) level of theory, and population distribution.

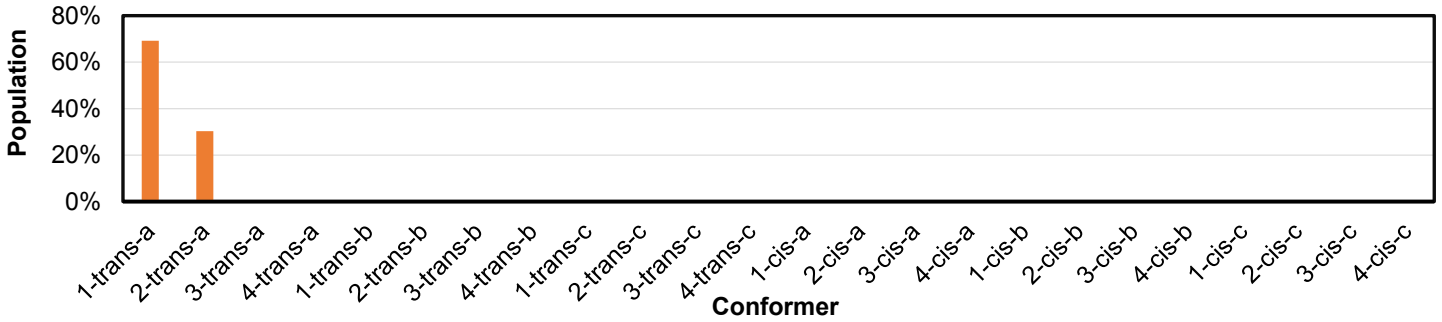


Figure S18. Calculated conformational distribution of 1-(2-nitrophenyl)-2,2-difluoroethanol triflate (**4-NO$_2$**) at the PCM-M062X/6-311++G(2d,2p)//PCM-B3LYP/6-31+G(d,p) level of theory.

5.1.3.2. 1-(4-Bromo)-2,2-difluoroethanol Triflate (4-Br)

Table S4. Energy and population of conformers of 1-(4-bromo)-2,2-difluoroethanol triflate (**4-Br**).

	PCM-B3LYP/6-31+G(d,p)				PCM-M062X/6-311++G(2d,2p)[a]			
Conformer	Thermal Correction (hartree)	Free Energy (hartree)	Relative Free Energy (kcal/mol)	Pop[b]	Energy (hartree)	Free Energy (hartree)[c]	Relative Free Energy (kcal/mol)	Pop[b]
1-a	0.100144	-4041.247341	1.1	1%	-4043.728933	-4043.628789	0.9	3%
2-a	0.100376	-4041.246631	1.6	0%	-4043.728676	-4043.628300	1.2	1%
3-a	0.099897	-4041.238942	6.4	0%	-4043.721209	-4043.621312	5.5	0%
4-a	0.099759	-4041.239247	6.2	0%	-4043.720294	-4043.620535	6.0	0%
1-b	0.100285	-4041.247327	1.2	1%	-4043.729036	-4043.628751	0.9	3%
2-b	0.099899	-4041.247043	1.3	1%	-4043.728057	-4043.628158	1.3	1%
3-b	0.101972	-4041.236209	8.1	0%	-4043.720046	-4043.618074	7.6	0%
4-b	0.099625	-4041.247316	1.2	1%	-4043.728057	-4043.628432	1.1	1%
1-c	0.098969	-4041.249162	0.0	93%	-4043.729120	-4043.630151	0.0	88%
2-c	0.099871	-4041.247833	0.8	4%	-4043.728607	-4043.628736	0.9	3%
3-c	0.101198	-4041.240206	5.6	0%	-4043.723971	-4043.622773	4.6	0%
4-c	0.100355	-4041.241206	5.0	0%	-4043.723145	-4043.622790	4.6	0%

a. Single point calculation; b. population distribution at 298 K; c. calculated based on single point energy at the PCM-M062X/6-311++G(2d,2p) level with thermal correction at the PCM-B3LYP/6-31+G(d,p) level.

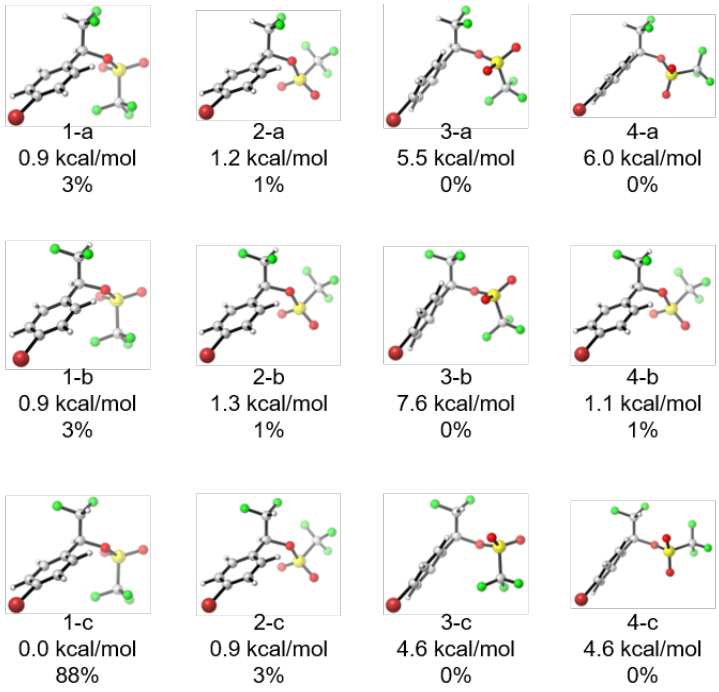


Figure S19. Conformers of 1-(4-bromophenyl)-2,2-difluoroethanol triflate (**4-Br**), relative free energies at the PCM-M062X/6-311++G(2d,2p)//PCM-B3LYP/6-31+G(d,p) level of theory, and population distribution.

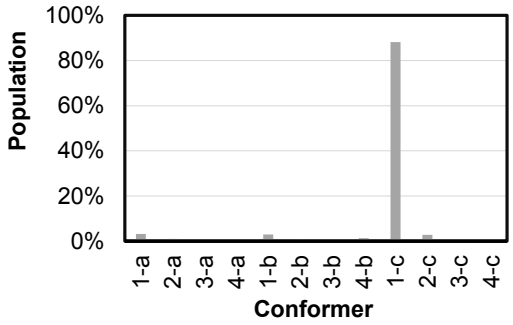


Figure S20. Calculated conformational distribution of 1-(4-bromophenyl)-2,2-difluoroethanol triflate (**4-Br**) at the PCM-M062X/6-311++G(2d,2p)//PCM-B3LYP/6-31+G(d,p) level of theory.

5.1.3.3. 1-(2-Fluoro)-2,2-difluoroethanol Triflate (4-F)

Table S5. Energy and population of conformers of 1-(2-fluoro)-2,2-difluoroethanol triflate (**4-F**).

		PCM-B3LYP/6-31+G(d,p)				PCM-M062X/6-311++G(2d,2p)[a]			
Conformer	Note	Thermal Correction (hartree)	Free Energy (hartree)	Relative Free Energy (kcal/mol)	Pop[b]	Energy (hartree)	Free Energy (hartree)[c]	Relative Free Energy (kcal/mol)	Pop[b]
1-trans-a		0.102401	-1569.356763	0.6	5%	-1569.402655	-1569.300254	0.0	23%
2-trans-a		0.103180	-1569.355643	1.3	0%	-1569.402482	-1569.299302	0.6	2%
3-trans-a		0.103350	-1569.347739	6.2	0%	-1569.396224	-1569.292874	4.6	0%
4-trans-a		0.103021	-1569.347816	6.2	0%	-1569.394612	-1569.291591	5.4	0%
1-trans-b		0.103383	-1569.355759	1.2	0%	-1569.402683	-1569.299300	0.6	2%
2-trans-b		0.102905	-1569.355676	1.3	0%	-1569.401946	-1569.299041	0.8	1%
3-trans-b		0.103322	-1569.347209	6.6	0%	-1569.395286	-1569.291964	5.2	0%
4-trans-b		0.103038	-1569.347214	6.6	0%	-1569.393381	-1569.290343	6.2	0%
1-trans-c		0.101973	-1569.357648	0.0	44%	-1569.402405	-1569.300432	-0.1	35%
2-trans-c		0.102839	-1569.356319	0.9	2%	-1569.402276	-1569.299437	0.5	3%
3-trans-c		0.104101	-1569.348911	5.5	0%	-1569.398239	-1569.294138	3.8	0%
4-trans-c		0.103477	-1569.350042	4.8	0%	-1569.397293	-1569.293816	4.0	0%
1-cis-a		0.103179	-1569.353100	2.9	0%	-1569.399971	-1569.296792	2.2	0%
2-cis-a		0.103959	-1569.351897	3.6	0%	-1569.399175	-1569.295216	3.2	0%
3-cis-a	Same as 4-cis-a	0.104669	-1569.343396	9.0	0%	-1569.394196	-1569.289527	6.7	0%
4-cis-a	Same as 3-cis-a	0.104670	-1569.343395	9.0	0%	-1569.394193	-1569.289523	6.7	0%
1-cis-b		0.103911	-1569.352735	3.1	0%	-1569.400345	-1569.296434	2.4	0%
2-cis-b		0.103598	-1569.352477	3.3	0%	-1569.399127	-1569.295529	3.0	0%
3-cis-b		0.103633	-1569.342092	9.8	0%	-1569.390716	-1569.287083	8.3	0%
4-cis-b		0.104129	-1569.341666	10.0	0%	-1569.391467	-1569.287338	8.1	0%
1-cis-c		0.102027	-1569.357678	0.0	47%	-1569.402423	-1569.300396	-0.1	32%
2-cis-c		0.103335	-1569.355956	1.1	1%	-1569.402161	-1569.298826	0.9	1%
3-cis-c		0.103653	-1569.347467	6.4	0%	-1569.396820	-1569.293167	4.4	0%
4-cis-c		0.103105	-1569.348665	5.7	0%	-1569.395854	-1569.292749	4.7	0%

a. Single point calculation; b. population distribution at 298 K; c. calculated based on single point energy at the PCM-M062X/6-311++G(2d,2p) level with thermal correction at the PCM-B3LYP/6-31+G(d,p) level.

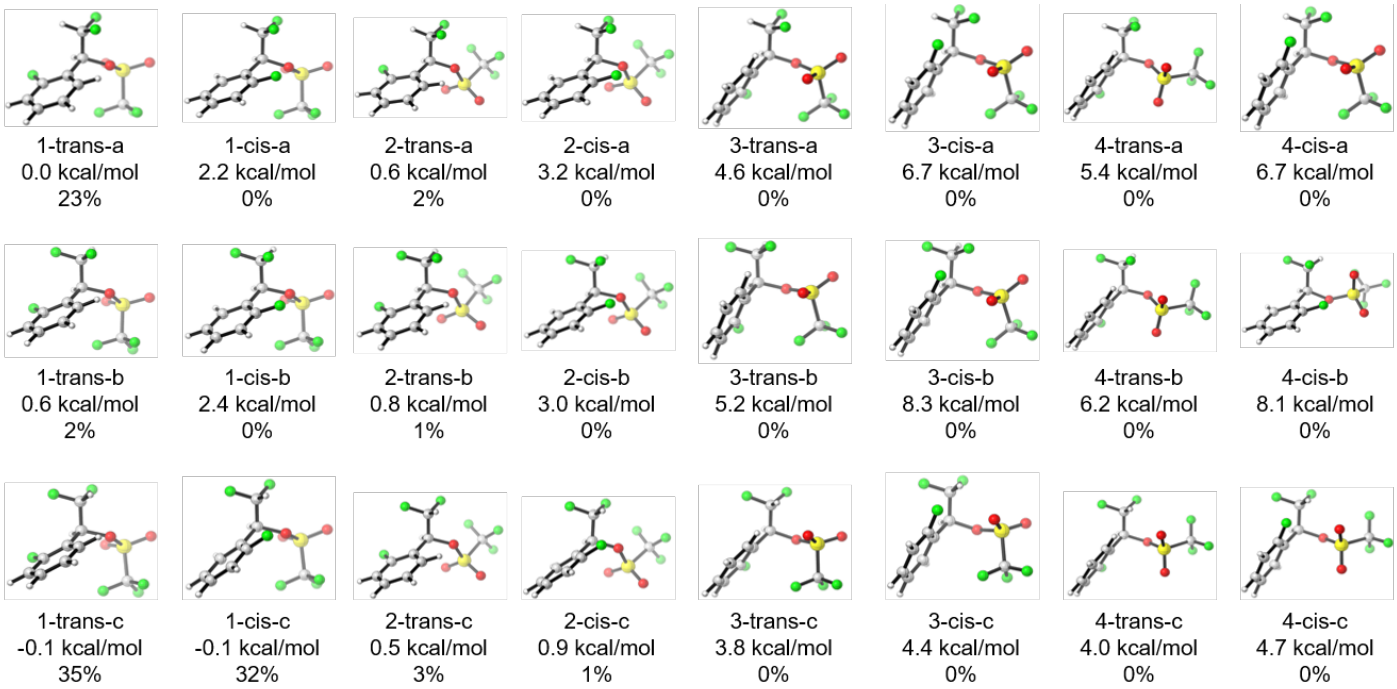


Figure S21. Conformers of 1-(2-fluorophenyl)-2,2-difluoroethanol triflate (**4-F**), relative free energies at the PCM-M062X/6-311++G(2d,2p)//PCM-B3LYP/6-31+G(d,p) level of theory, and population distribution.

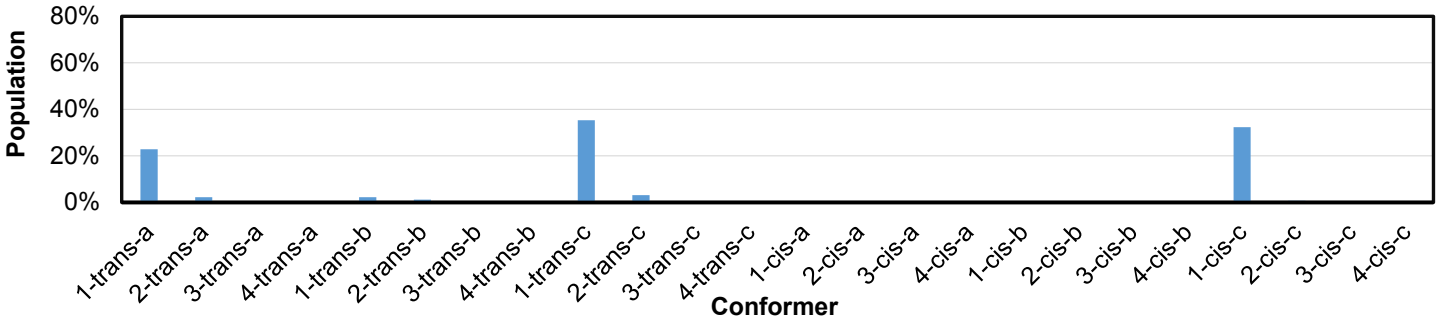


Figure S22. Calculated conformational distribution of 1-(2-fluoro)-2,2-difluoroethanol triflate (**4-F**) at the PCM-M062X/6-311++G(2d,2p)//PCM-B3LYP/6-31+G(d,p) level of theory.

5.1.3.4. α,α-Difluorotoluene

The conformations of α,α-difluorotoluene are determined by the rotation about the Ph–CF_2H bond (Table S6 and Figure S23). The rotations were scanned from 0° to +360° with an increment of 30° of each step. The conformations generated were optimized at the PCM-B3LYP/6-31+G(d) level $CHCl_3$ using Gaussian 09.[5] One local minimum was found, which was further optimized at the PCM-B3LYP/6-31+G(d,p) level in $CHCl_3$.

Table S6. Energy of conformers of α,α-difluorotoluene.

$\varphi_{H\text{-}CF2\text{-}C1\text{-}C2}$ (°)	E (hartree)[a]	E_{rel} (kcal/mol)
0	-470.068923	0.0
30	-470.0683876	0.3
60	-470.0675582	0.9
90	-470.0675213	0.9
120	-470.0675695	0.9
150	-470.0683355	0.4
180	-470.0689228	0.0
210	-470.0683346	0.4
240	-470.0675704	0.9
270	-470.0675216	0.9
300	-470.0675575	0.9
330	-470.0683873	0.3
360	-470.0689255	0.0

a. calculated at the PCM-B3LYP/6-31+G(d) level using "loose" optimization convergence criteria.

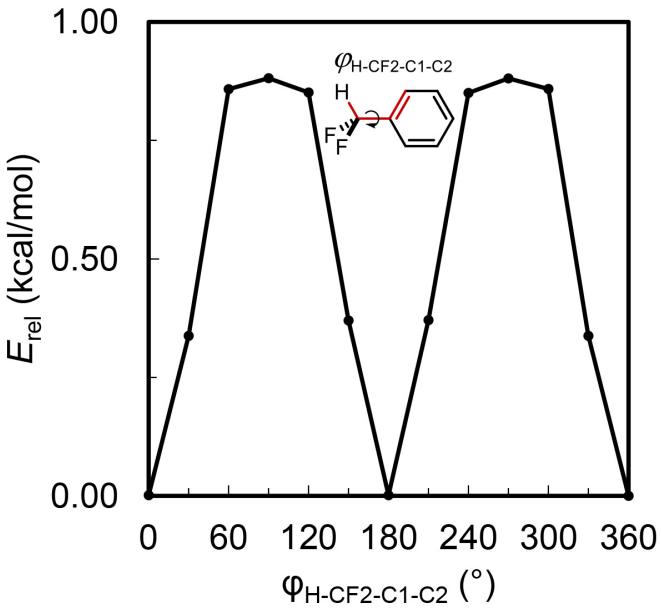


Figure S23. Torsional itinerary for α,α-difluorotoluene.

5.1.3.5. *o*-Nitro-α,α-difluorotoluene (1-CF_2H)

The conformations of **1-CF_2H** are determined by the rotation about the Ar–CF_2H bond (Table S7 and Figure S24). The rotations were scanned from 0° to +360° with an increment of 30° of each step. The generated conformations were optimized at the PCM-B3LYP/6-31+G(d) level $CHCl_3$ using Gaussian 09.[5] Because of the cooperative rotation about the Ar–NO_2 bond, three local minima were found, which were further optimized at the PCM-B3LYP/6-31+G(d,p) level in $CHCl_3$.

Table S7. Energy of conformers of *o*-nitro-α,α-difluorotoluene (**1-CF_2H**).

$\varphi_{H\text{-}CF2\text{-}C1\text{-}C2}$ (°)	E (hartree)[a]	E_{rel} (kcal/mol)
0	-674.571651	0.5
30	-674.571097	0.9
60	-674.572428	0.0
90	-674.569701	1.7
120	-674.565105	4.6
150	-674.568100	2.7
180	-674.567188	3.3
210	-674.568100	2.7
240	-674.564582	5.0
270	-674.569702	1.7
300	-674.572428	0.0
330	-674.572474	0.0
360	-674.571652	0.5

a. calculated at the PCM-B3LYP/6-31+G(d) level using "loose" optimization convergence criteria.

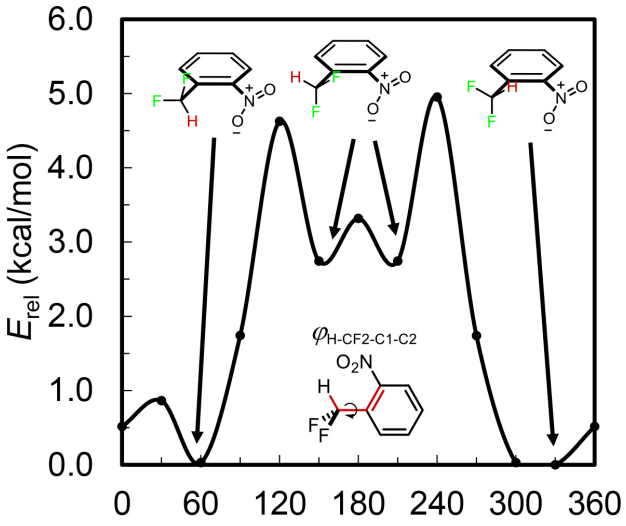


Figure S24. Torsional itinerary for *o*-nitro-α,α-difluorotoluene.

5.1.3.6. Phenol

The conformations of phenol are determined by the rotation about the Ar–OH bond (Table S8 and Figure S25). The rotations were scanned from 0° to +360° with an increment of 30° of each step. The generated conformations were optimized at the PCM-B3LYP/6-31+G(d) level $CHCl_3$ using Gaussian 09.[5] Only one local minimum was found, which was further optimized at the PCM-B3LYP/6-31+G(d,p) level in CHCl3.

Table S8. Energy of conformers of phenol.

$\varphi_{H\text{-}O\text{-}C1\text{-}C2}$ (°)	E (hartree)[a]	E_{rel} (kcal/mol)
0	-307.485201	0.0
30	-307.483831	0.9
60	-307.481003	2.6
90	-307.479432	3.6
120	-307.480710	2.8
150	-307.483626	1.0
180	-307.485212	0.0
210	-307.483642	1.0
240	-307.480708	2.8
270	-307.479434	3.6
300	-307.481003	2.6
330	-307.483823	0.9
360	-307.485221	0.0

a. calculated at the PCM-B3LYP/6-31+G(d) level using “loose” optimization convergence criteria.

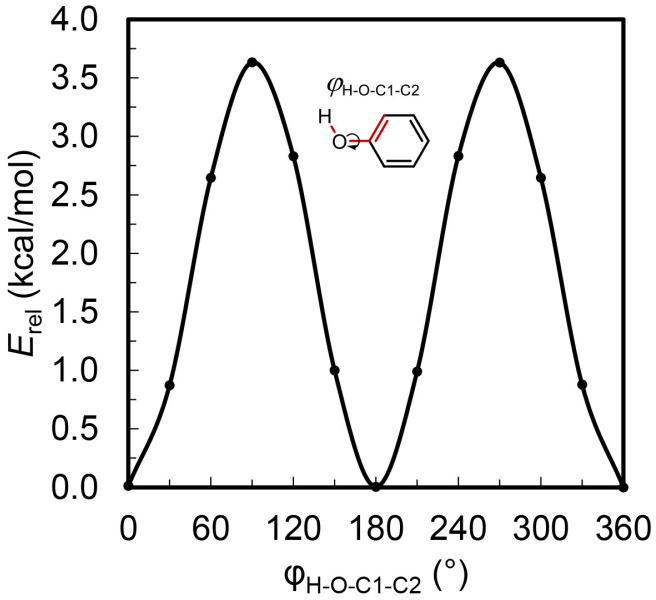


Figure S25. Torsional itinerary for phenol.

5.1.3.7. *o*-Nitrophenol (1-OH)

The conformations of *o*-nitrophenol are determined by the rotation about the Ar–OH bond (Table S9 and Figure S26). The rotations were scanned from 0° to +360° with an increment of 30° of each step. The conformations generated were optimized at the PCM-B3LYP/6-31+G(d) level $CHCl_3$ using Gaussian 09.[5] Two local minima were found, which were further optimized at the PCM-B3LYP/6-31+G(d,p) level in $CHCl_3$.

Table S9. Energy of conformers of *o*-nitrophenol (**1-OH**).

$\varphi_{H\text{-}O\text{-}C1\text{-}C2}$ (°)	E (hartree)[a]	E_{rel} (kcal/mol)
0	-511.991909	8.0
30	-511.990346	8.9
60	-511.986469	11.4
90	-511.984287	12.7
120	-511.991818	8.0
150	-512.000163	2.8
180	-512.004598	0.0
210	-512.000166	2.8
240	-511.991816	8.0
270	-511.986838	11.1
300	-511.986929	11.1
330	-511.989790	9.3
360	-511.992000	7.9

a. calculated at the PCM-B3LYP/6-31+G(d) level using "loose" optimization convergence criteria.

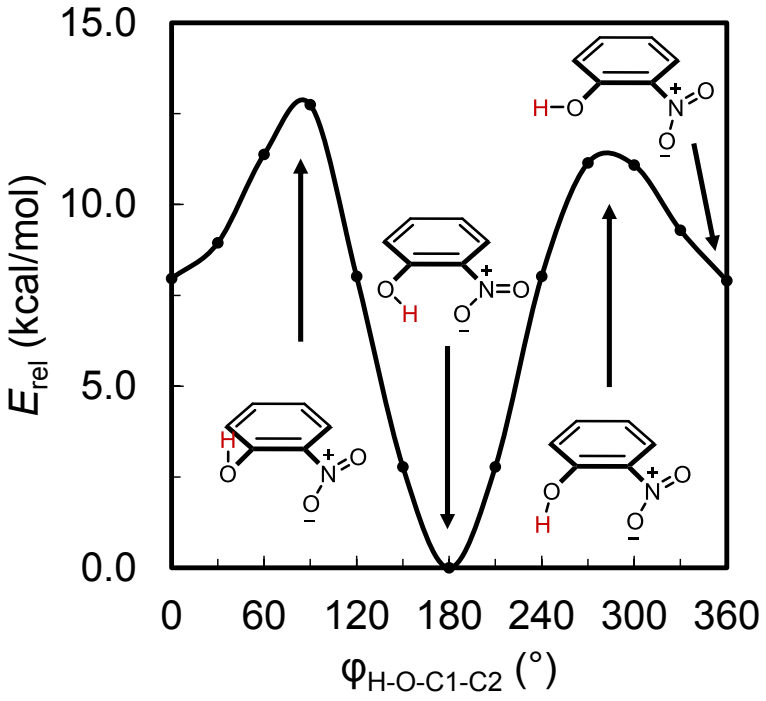


Figure S26. Torsional itinerary for *o*-nitrophenol.

5.1.3.8. Dimerization of *o*-nitro-α,α-difluorotoluenes (1-CF_2H) and *o*-nitrophenol (1-OH)

The possible dimerization of **1-CF_2H** and **1-OH** was investigated by geometry optimization at the PCM-B3LYP/6-31+G(d,p) level of theory in $CHCl_3$ (Table S10). The free energies at the PCM-M062X/6-311++G(2d,2p) level of theory were calculated as a sum of the single point energies at the PCM-M062X/6-311++G(2d,2p)//B3LYP/6-31+G(d,p) level and the thermal and entropic corrections at the PCM-B3LYP/6-31+G(d,p) level. The frequency analysis confirmed that all structures were true minima.

The structure of the dimer of **1-OH** largely resembles that found in X-ray crystallographic studies. Two types of dimers, $(CF_2HNBc)_2$ and $(CF_2HNBc)_2$', were found for **1-CF_2H**. The former, which has an arrangement similar to the crystal structure, is slightly more stable than the latter. As indicated by the relative energies Δ*E*, the dimerization of both **1-CF_2H** and **1-OH** is facilitated by attractive hydrogen bonding interactions, ranging from 1 to 3 kcal/mol for two bondings. Noticeably, the very similar values of Δ*E* of **1-CF_2H** and **1-OH** at both levels of theory suggest that the magnitudes of hydrogen bonding interactions of the NO_2 group with the CF_2H and the OH moieties may be comparable. According to the free energies Δ*G* for the dimerization of **1-CF_2H** and **1-OH**, these processes are unfavorable in $CHCl_3$ at room temperature, likely due to the entropic penalty.

Table S10. Dimerization of *o*-nitro-α,α-difluorotoluenes (**1-CF_2H**) and *o*-nitrophenol (**1-OH**).

	PCM-B3LYP/6-31+G(d,p)				PCM-M062X/6-311++G(2d,2p)[a]			
Conformer /species	Thermal Correction (hartree)	Free Energy (hartree)	Relative Energy Δ*E* (kcal/mol)	Relative Free Energy Δ*G* (kcal/mol)	Energy (hartree)	Free Energy (hartree)[b]	Relative Energy Δ*E* (kcal/mol)	Relative Free Energy Δ*G* (kcal/mol)
PhOH	0.075258	-307.423470	-	-	-307.440639	-307.365381	-	-
1-OH-a	0.074845	-511.941775	0.0	0.0	-511.942316	-511.867471	0.0	0.0
1-OH-b	0.073821	-511.930088	8.0	7.3	-511.931986	-511.858165	6.5	5.8
$(1\text{-OH-a})_2$	0.163048	-1023.871805	-1.0	7.4	-1023.889140	-1023.726092	-2.8	5.6
$PhCF_2H$	0.080359	-469.997675	-	-	-470.012546	-469.932187	-	-
$1\text{-}CF_2H\text{-a}$	0.079415	-674.500788	0.0	0.1	-674.504260	-674.424845	0.0	0.0
$1\text{-}CF_2H\text{-b}$	0.079492	-674.496633	2.6	2.7	-674.499857	-674.420365	2.8	2.8
$1\text{-}CF_2H\text{-c}$	0.079343	-674.500880	0.0	0.0	-674.503649	-674.424306	0.4	0.3
$(1\text{-}CF_2H\text{-a})_2$	0.171262	-1348.991411	-1.4	6.5	-1349.012188	-1348.840926	-2.3	5.5
$(1\text{-}CF_2H\text{-a})_2$'	0.172058	-1348.990048	-1.0	7.3	-1349.012212	-1348.840154	-2.3	6.0

a. Single point calculation; b. calculated based on single point energy at the PCM-M062X/6-311++G(2d,2p) level and thermal correction at the PCM-B3LYP/6-31+G(d,p) level.

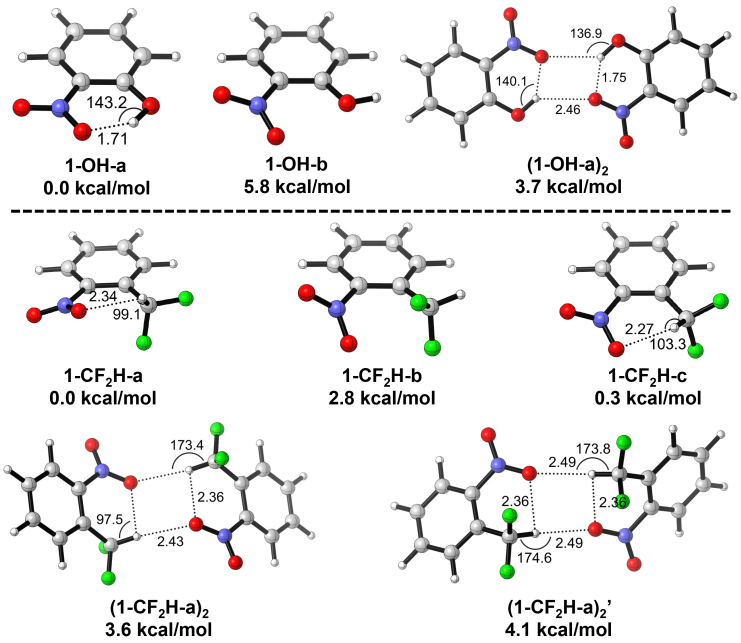


Figure S27. Dimerization of *o*-nitrophenol (**1-OH**) and *o*-nitro-α,α-difluorotoluene (**1-CF_2H**) at the B3LYP/6-31+G(d,p) level. The relative free energy Δ*G* was calculated at the PCM-M062X/6-311++G(2d,2p)//B3LYP/6-31+G(d,p) level in $CHCl_3$. A 1.9 kcal/mol correction was applied to account for the concentration change from the gas phase to 1 M in solution.

We further investigated the solvent effects on the dimerization energies (Table S11). Single point energies were calculated at the PCM-M062X/6-311++G(2d,2p)//B3LYP/6-31+G(d,p) level of theory. As expected, the dimerization energies decrease with the increase in solvent dielectric constants, which facilitates the solvation of monomeric species.

Table S11. Dimerization energies of *o*-nitro-α,α-difluorotoluenes (**1-CF_2H**) and *o*-nitrophenol (**1-OH**) in the gas phase and in different solvents.

	Gas (ε = 0.00)		Pentane (ε = 1.84)		Benzene (ε = 2.27)		$CHCl_3$ (ε = 4.71)		DMF (ε = 37.22)		Water (ε = 78.36)	
	E (hartree)	Δ*E*[a]	*E* (hartree)	Δ*E*[a]	*E* (hartree)	Δ*E*[a]	*E* (hartree)	Δ*E*[a]	*E* (hartree)	Δ*E*[a]	*E* (hartree)	Δ*E*[a]
1-CF_2H-a	-674.497589	0.0	-674.500840	0.0	-674.501786	0.0	-674.504260	0.0	-674.506829	0.0	-674.507052	0.0
1-CF_2H-b	-674.490483	4.5	-674.494995	3.7	-674.496328	3.4	-674.499857	2.8	-674.503592	2.0	-674.503920	2.0
1-CF_2H-c	-674.496578	0.6	-674.500022	0.5	-674.501025	0.5	-674.503649	0.4	-674.506376	0.3	-674.506613	0.3
(1-CF_2H-a)$_2$	-1349.000802	-3.5	-1349.006372	-2.9	-1349.007986	-2.8	-1349.012188	-2.3	-1349.016518	-1.8	-1349.016892	-1.7
(1-CF_2H-a)$_2$'	-1349.000669	-3.4	-1349.006261	-2.9	-1349.007899	-2.7	-1349.012212	-2.3	-1349.016748	-1.9	-1349.017146	-1.9
1-OH-a	-511.937180	0.0	-511.939671	0.0	-511.940401	0.0	-511.942316	0.0	-511.944311	0.0	-511.944485	0.0
1-OH-b	-511.921887	9.6	-511.926769	8.1	-511.928204	7.7	-511.931986	6.5	-511.935944	5.3	-511.936289	5.1
(1-OH-a)$_2$	-1023.880000	-3.5	-1023.884341	-3.1	-1023.885643	-3.0	-1023.889140	-2.8	-1023.892937	-2.7	-1023.893275	-2.7
DMF	-248.479011	-	-248.482500	-	-248.483512	-	-248.486146	-	-248.488846	-	-248.489078	-
Py	-248.248367	-	-248.250232	-	-248.250793	-	-248.252295	-	-248.253906	-	-248.254048	-
BDfTol	-3043.576746	-	-3043.579023	-	-3043.579684	-	-3043.581416	-	-3043.583223	-	-3043.583380	-
BDfTol-DMF	-3292.064576	-5.5	-3292.068842	-4.6	-3292.070025	-4.3	-3292.073026	-3.4	-3292.076036	-2.5	-3292.076293	-2.4
BDfTol-Py	-3291.832107	-4.4	-3291.835185	-3.7	-3291.836045	-3.5	-3291.838244	-2.8	-3291.840471	-2.1	-3291.840662	-2.0

5.2. Simulated NMR Spectra

To validate the conformations identified by NMR studies, the NMR properties of major conformers in $CHCl_3$ were computed at the GIAO-PCM-B3LYP/aug-cc-PVTZ//PCM-B3LYP/6-31+G(d,p) level of theory using Gaussian 09.[5] To obtain scaling factors for achieving accurate computed chemical shifts, we carried out a linear regression analysis of experimental and computational chemical shift values. Similar methods have been exploited to show higher accuracies for ^{1}H NMR and ^{13}C NMR spectroscopy.[7] By correlating the calculated magnetic shielding tensors and experimental NMR chemical shifts of a series of known compounds as references (Table S12), scaling factors for the ^{1}H, ^{19}F NMR, and ^{13}C NMR chemical shifts were obtained with satisfactory R^2 values (Figure S28). On the basis of the scaling factors and the calculated shielding tensors, predicted NMR chemical shifts of individual conformers of **4-NO$_2$**, **4-Br**, and **4-F** were obtained. With these values in hand, we calculated weighted average chemical shifts according to Eq. (S1).

$$\delta = \sum_i P_i \delta_i \qquad \text{Eq. (S1)}$$

Here, P_i is the population (%) of the i^{th} conformer and δ_i is the NMR chemical shift of a specific nucleus of the i^{th} conformer. A comparison of predicted and experimental NMR chemical shifts was achieved by linear regression analysis. Other than the ^{13}C NMR of **4-Br**, the correlations generally have $R^2 > 0.95$, suggesting the validity of NMR assignments and conformational identifications. The low R^2 value of the ^{13}C NMR of **4-Br** mainly arises from the large deviation of the predicted chemical shift of the brominated carbon atom from the experimental value. This result is likely due to the well-known heavy-atom effects, which usually lead to higher errors in calculated ^{13}C NMR chemical shifts.[7] In addition to the major conformers, the chemical shifts of several minor conformers were also calculated. The calculated NMR chemical shifts for the other conformers do not match the experimental data, suggesting that these states are not substantially populated under our experimental conditions.

5.2.1. Establishment of Scaling Factors

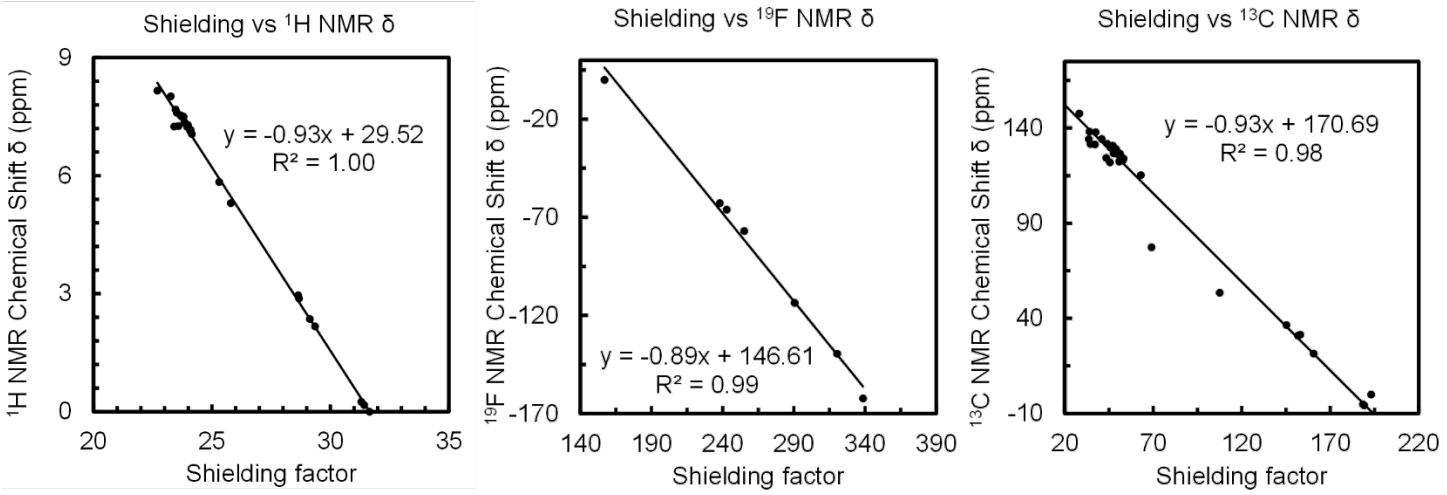
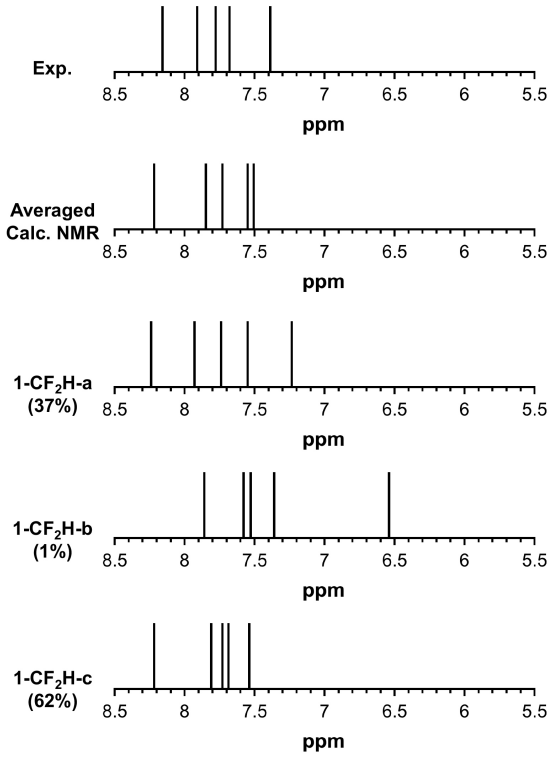


Figure S28. Linear regression analyses of computed shielding tensors and experimental NMR chemical shifts of reference compounds.

Table S12. Experimental chemical shifts and computed shielding tensors of reference compounds.

	^{1}H NMR			^{13}C NMR			^{19}F NMR	
	Atom(s)	δ_{exp} (ppm)	shielding	Atom(s)	δ_{exp} (ppm)	shielding	δ_{exp} (ppm)	shielding
acetone	CH_3	2.17[a]	29.35	*C*O	207.1[a]	-38.44		
				CH_3	30.9[a]	151.69		
PhBr		7.50[b]	23.80		131.4[c]	37.10		
		7.24[b]	23.95		129.9[c]	45.80		
		7.29[b]	23.98		126.7[c]	47.57		
					122.4[c]	50.75		
PhCl			23.87		134.3[c]	33.63		
			23.91		129.6[c]	47.55		
			23.99		128.6[c]	48.84		
					126.6[c]	51.16		
PhF	3,3'	7.34[b]	23.85	1	163.0[c]	9.32	-113.6	290.64
	4	7.14[b]	24.08	3,3'	123.0[c]	47.02		
	2,2'	7.06[b]	24.15	4	124.0[c]	53.23		
				2,2'	115.3[c]	63.05		
benzene		7.36[a]	23.83		128.4[a]	48.57		
C_6F_6					138.15[b]	33.95	-162.25[b]	338.67
$CFCl_3$						25.20	0.0[b]	157.04
CF_3H			24.67			53.63	-77.0	255.12
CH_2Cl_2		5.30[a]	25.79		53.5[a]	107.59		
$CHCl_3$		7.26[a]	23.58		77.4[a]	69.01		
DMF	CO*H*	8.02[a]	23.26	*C*O	162.6[a]	15.10		
	C*H*$_3$(1)	2.88[a]	28.67	*C*H_3(1)	36.5[a]	145.21		
	C*H*$_3$(2)	2.96[a]	28.64	*C*H_3(2)	31.5[a]	153.02		
$PhCF_3$	H2,2'	7.60[d]	23.51	*C*F_3	124.3[d]	43.44	-62.8[d]	238.04
	H3,3',4	7.53[d]	23.69	C4	131.7[d]	44.09		
				C1	130.7[d]	47.24		
				C3	128.7[d]	48.67		
				C2	125.2[d]	51.82		
$PhCH_3$	H2,2',3,3'	7.25[a]	23.40	C1	137.9[a]	37.45		
	H4	7.17[a]	24.09	C2,2'	129.1[a]	49.04		
	CH_3	2.36[a]	29.13	C3,3'	128.3[a]	49.29		
				C4	125.3[a]	51.56		
				CH_3	21.5[a]	160.67		
$PhNO_2$	H2,2'	8.16[e]	22.69	C1	147.7[e]	28.22		
	H4	7.68[e]	23.46	C4	134.3[e]	40.88		
	H3,3'	7.52[e]	23.68	C3,3'	128.9[e]	48.50		
				C2,2'	122.9[e]	52.73		
$TMSCF_2H$	CF_2*H*	5.84[b]	25.3	*C*F_2H	122.1[b]	45.57	-139.6[b]	320.46
	C*H*$_3$	0.17[b]	31.42	*C*H_3	-5.7[b]	189.11		
$(CH_3)_4Si$		0.00[b]	31.65		0.0[b]	193.08		
$TMSCF_3$	CH_3	0.25[f]	31.30	CF_3	131.7[f]	34.52	-66.1	242.83
				CH_3	-5.2[f]	188.48		
$PhCF_2H$	CF_2*H*	6.70[g]	24.72				-110.8[h]	279.07

a. Ref.[8]; b. Determined in $CDCl_3$; c. Ref. [9]; d. Ref. [10]; e. Ref. [11]; f. Ref. [12]; g. Ref. [13]; h. Ref.[14].



Atom	Exp.	Averaged	1-CF_2H-a	1-CF_2H-b	1-CF_2H-c
H1	7.78	7.73	7.74	7.58	7.73
H2	7.68	7.55	7.55	7.53	7.54
H3	8.16	8.22	8.24	7.86	8.22
H4	7.91	7.85	7.93	7.36	7.81
H5	7.39	7.51	7.24	6.54	7.69

Atom	Exp.	Averaged	1-CF_2H-a	1-CF_2H-b	1-CF_2H-c
Fa	-	-115.2	-110.0	-107.3	-118.5
Fb	-	-94.7	-91.5	-84.5	-96.8
(Fa+Fb)/2	-115.5	-105.0	-100.7	-95.9	-107.6

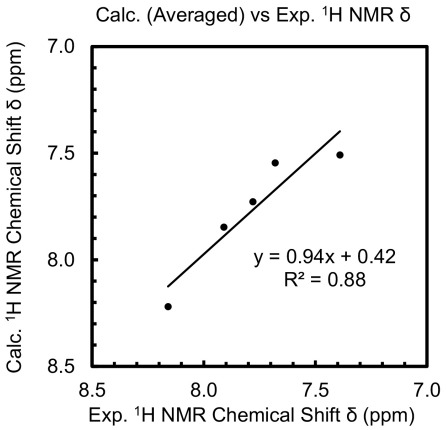
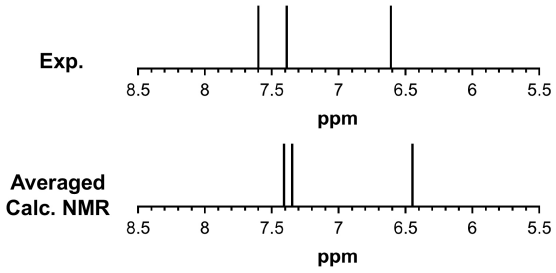
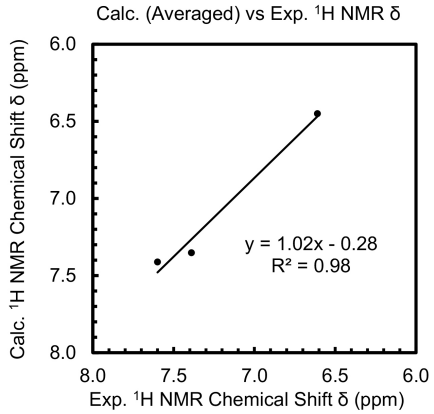


Figure S29. Calculated ^{1}H and ^{19}F NMR chemical shifts of conformers of **1-CF_2H** and their correlation with experimental data.

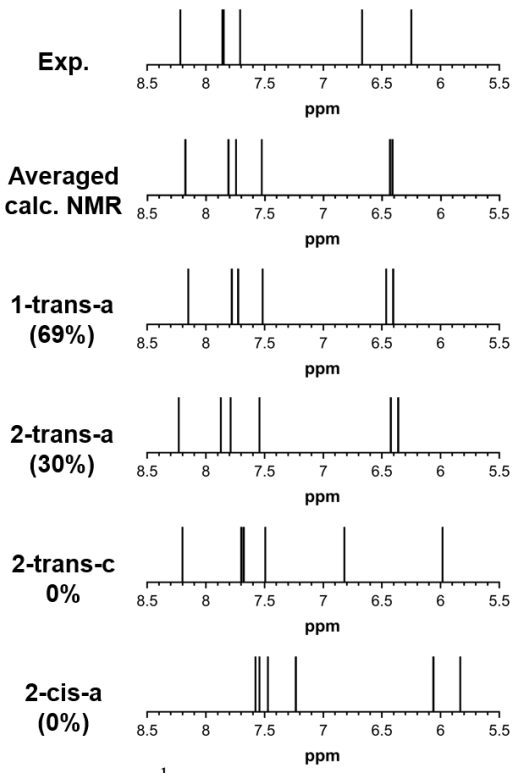


Atom	Exp.	Calculated
H1	-	7.36
H1'	-	7.46
H1 (average)	7.60	7.41
H2	-	7.54
H2'	-	7.17
H2 (average)	7.39	7.35
H3	6.61	6.45



Atom	Exp.	Calculated
Fa	-	-89.2
Fb	-	-89.3
(Fa+Fb)/2	-111.6	-89.2

Figure S30. Calculated ^{1}H and ^{19}F NMR chemical shifts of **2-CF_2H** and their correlation with experimental data.



Atom	Exp.	Averaged	1-trans-a	2-trans-a	2-trans-c	2-cis-a
H3	8.22	8.18	8.15	8.23	8.20	7.58
H4	7.71	7.53	7.52	7.54	7.50	7.47
H5	7.86	7.75	7.73	7.79	7.68	7.54
H6	7.85	7.81	7.78	7.87	7.70	7.23
H2	6.67	6.43	6.46	6.36	6.82	5.83
H1	6.25	6.41	6.41	6.43	5.99	6.06

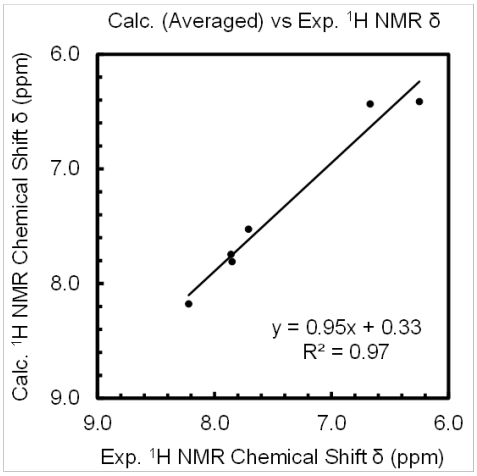
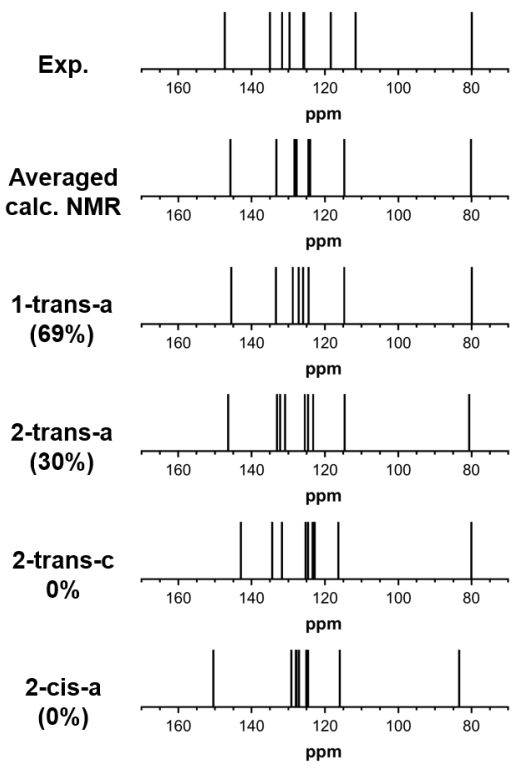


Figure S31. Calculated ^{1}H NMR chemical shifts of conformers of **4-NO$_2$** and their correlation with experimental data.



Atom	Exp.	Averaged	1-trans-a	2-trans-a	2-trans-c	2-cis-a
C8	147.3	145.8	145.5	146.4	142.9	150.5
C5	135.0	133.3	133.3	133.1	134.4	129.2
C4	131.7	127.8	128.8	125.5	131.8	127.1
C6	129.6	128.3	127.2	130.9	123.4	127.8
C7	125.9	127.8	125.9	132.2	122.9	127.9
C3	125.7	124.0	124.4	123.2	125.2	125.1
CF_3	118.4	124.5	124.5	124.6	124.6	124.6
C1	111.7	114.7	114.7	114.6	116.3	116.0
C2	79.9	80.2	79.9	80.7	80.1	83.4

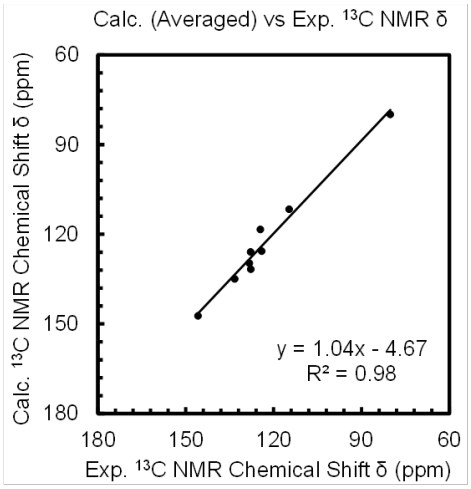
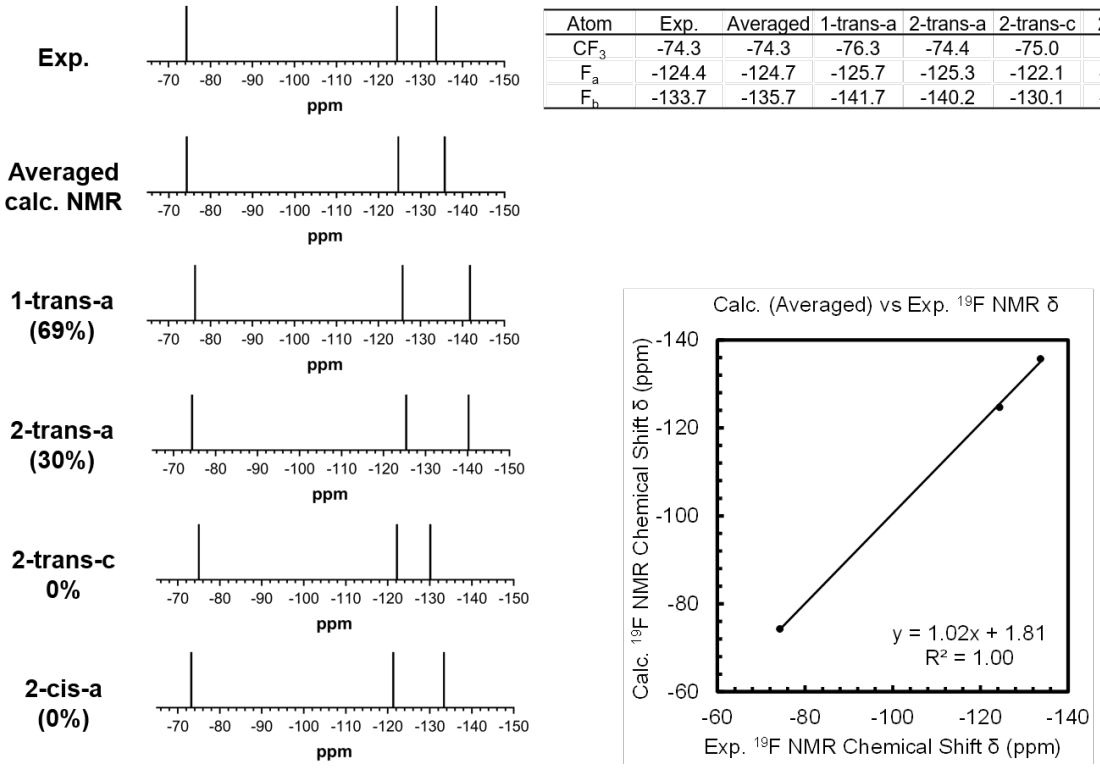
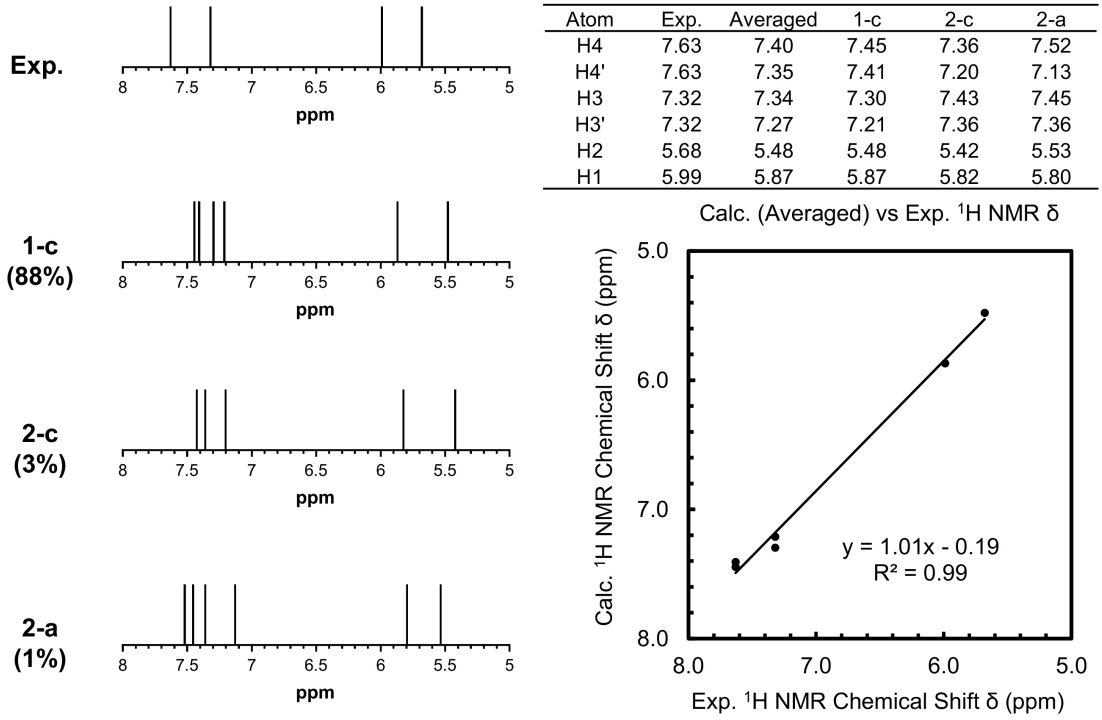


Figure S32. Calculated ^{13}C NMR chemical shifts of conformers of **4-NO$_2$** and their correlation with experimental data.



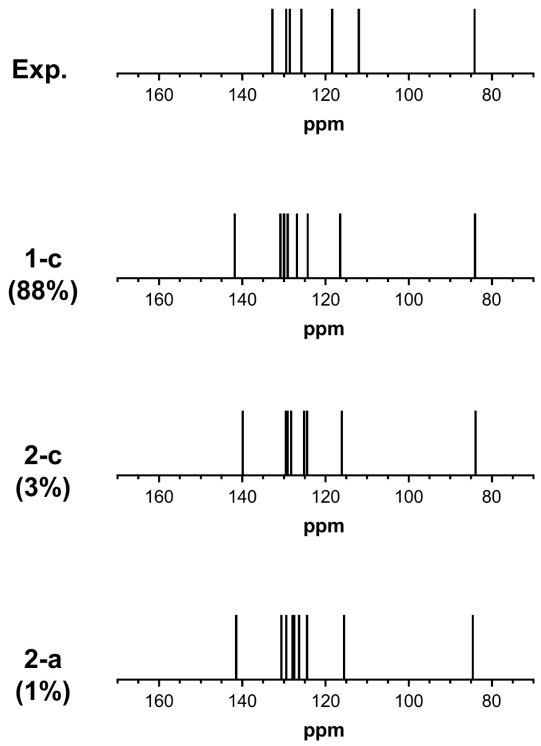
Atom	Exp.	Averaged	1-trans-a	2-trans-a	2-trans-c	2-cis-a
CF_3	-74.3	-74.3	-76.3	-74.4	-75.0	-73.2
F_a	-124.4	-124.7	-125.7	-125.3	-122.1	-121.3
F_b	-133.7	-135.7	-141.7	-140.2	-130.1	-133.3

Figure S33. Calculated ^{19}F NMR chemical shifts of conformers of **4-NO$_2$** and their correlation with experimental data.



Atom	Exp.	Averaged	1-c	2-c	2-a
H4	7.63	7.40	7.45	7.36	7.52
H4'	7.63	7.35	7.41	7.20	7.13
H3	7.32	7.34	7.30	7.43	7.45
H3'	7.32	7.27	7.21	7.36	7.36
H2	5.68	5.48	5.48	5.42	5.53
H1	5.99	5.87	5.87	5.82	5.80

Figure S34. Calculated ^{1}H NMR chemical shifts of conformers of **4-Br** and their correlation with experimental data.



Atom	Exp.	Averaged	1-c	2-c	2-a
C4	132.8	129.6	130.8	125.1	130.6
C4'	132.8	130.0	129.9	128.3	129.4
C3	129.5	128.1	126.9	129.1	127.5
C3'	129.5	130.0	130.1	129.1	126.3
C5	128.6	129.1	129.1	129.5	127.9
C6	125.8	141.8	141.8	139.9	141.4
CF_3	118.4	124.3	124.3	124.4	124.5
C1	112.0	116.4	116.5	116.1	115.5
C2	84.2	84.1	84.1	84.0	84.6

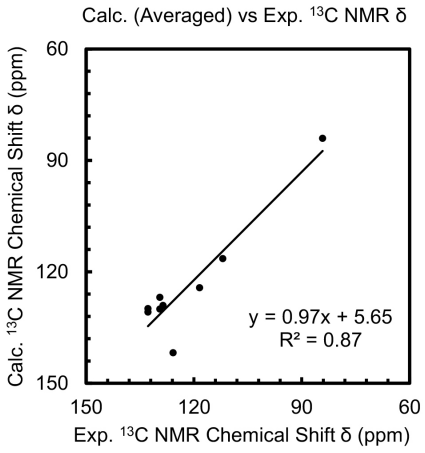
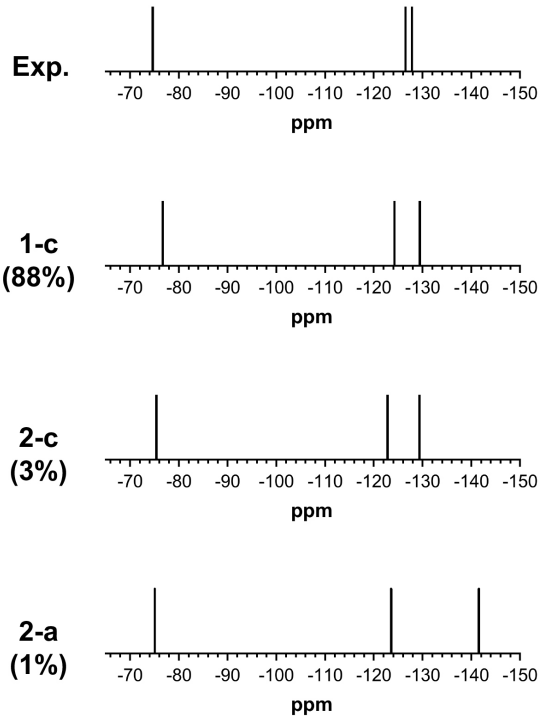


Figure S35. Calculated ^{13}C NMR chemical shifts of conformers of **4-Br** and their correlation with experimental data.



Atom	Exp.	Averaged	1-c	2-c	2-a
CF3	-74.6	-76.7	-76.7	-75.4	-75.0
Fa	-127.8	-129.4	-129.4	-129.3	-141.5
Fb	-126.5	-124.2	-124.2	-122.8	-123.5

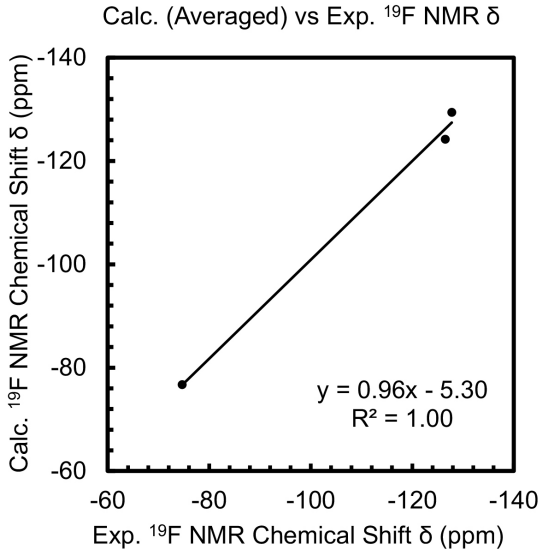
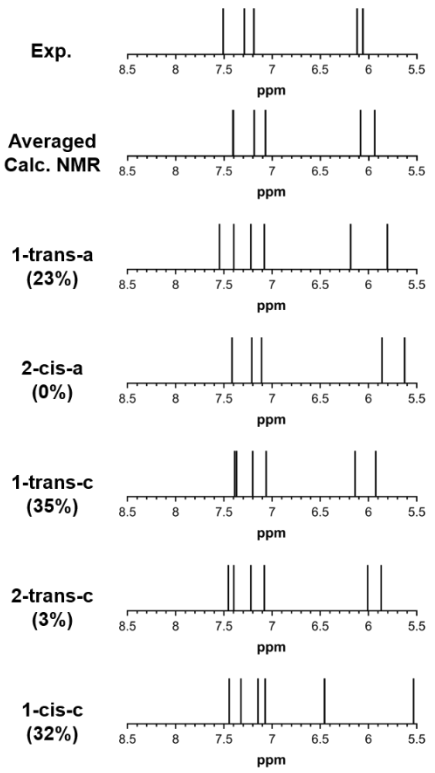


Figure S36. Calculated ^{19}F NMR chemical shifts of conformers of **4-Br** and their correlation with experimental data.



Atom	Exp.	Averaged	1-trans-a	2-cis-a	1-trans-c	2-trans-c	1-cis-c
H3	7.19	7.07	7.08	7.11	7.06	7.08	7.07
H4	7.51	7.40	7.40	7.42	7.37	7.40	7.45
H5	7.29	7.19	7.22	7.11	7.20	7.22	7.15
H6	7.51	7.41	7.55	7.21	7.39	7.45	7.32
H2	6.06	5.94	6.19	5.63	6.14	6.01	5.53
H1	6.12	6.09	5.80	5.86	5.93	5.87	6.46

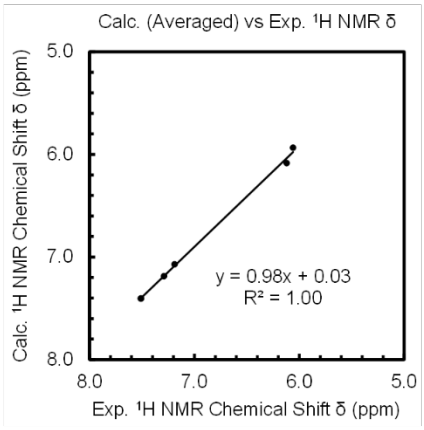
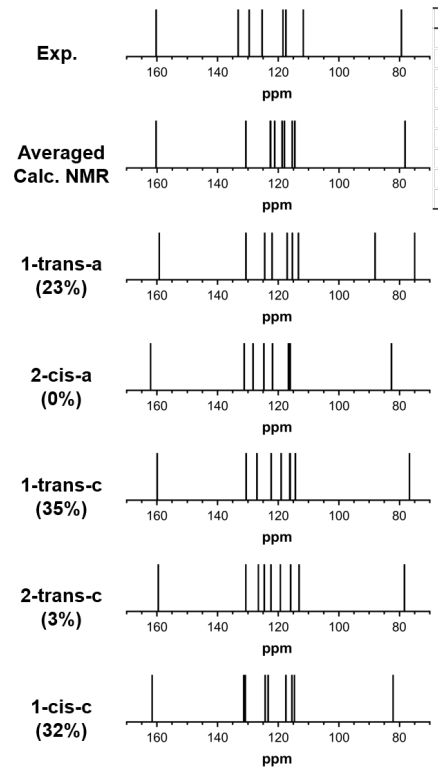


Figure S37. Calculated ^{1}H NMR chemical shifts of conformers of **4-F** and their correlation with experimental data.



Atom	Exp.	Averaged	1-trans-a	2-cis-a	1-trans-c	2-trans-c	1-cis-c
C8	160.3	160.3	159.2	162.1	159.9	159.5	161.6
C5	125.3	122.6	122.0	121.9	122.3	122.4	123.3
C4	133.2	130.7	130.6	131.2	130.6	130.7	130.9
C6	129.6	118.7	88.1	128.3	127.0	126.6	131.4
C7	117.5	118.0	117.0	116.4	119.0	119.3	117.4
C3	117.5	114.5	113.3	116.6	114.4	113.1	115.5
CF_3	118.4	121.2	124.5	124.7	116.2	124.6	124.3
C1	111.7	115.4	115.3	116.0	116.0	115.9	114.7
C2	79.4	78.2	75.0	82.6	76.7	78.4	82.1

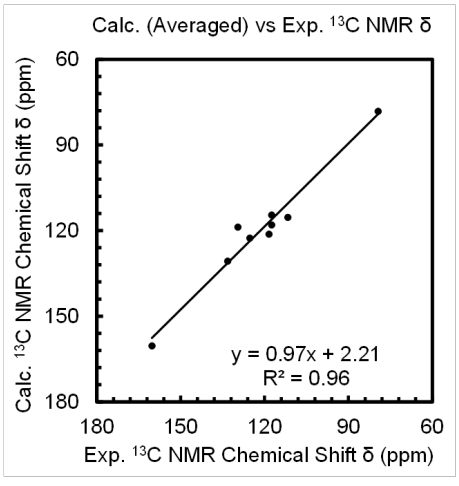
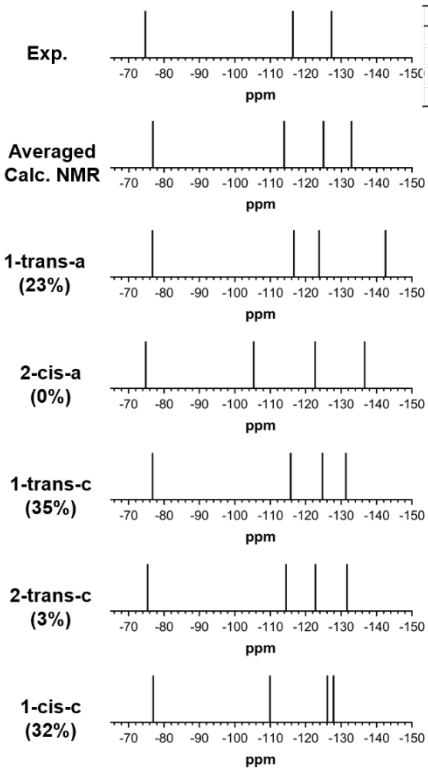


Figure S38. Calculated ^{13}C NMR chemical shifts of conformers of **4-F** and their correlation with experimental data.



Atom	Exp.	Averaged	1-trans-a	2-cis-a	1-trans-c	2-trans-c	1-cis-c
CF_3	-74.7	-76.8	-76.7	-74.8	-76.7	-75.4	-76.9
Fa	-127.3	-132.9	-142.5	-136.6	-131.3	-131.6	-127.8
Fb	-127.3	-125.0	-123.8	-122.6	-124.7	-122.7	-126.1
Fd(Ar)	-116.4	-113.9	-116.6	-105.3	-115.7	-114.4	-109.9

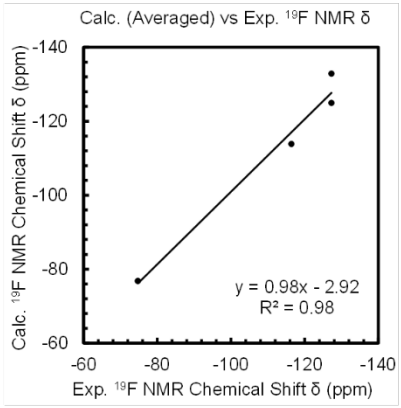
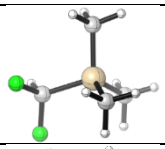
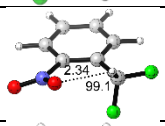
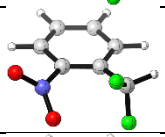
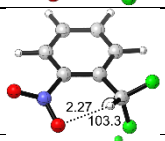
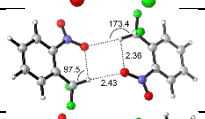
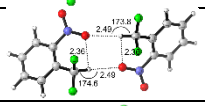
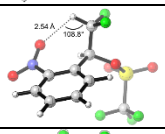
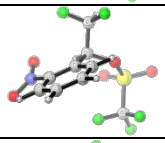
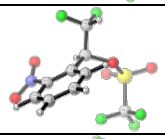
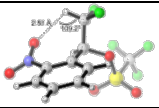


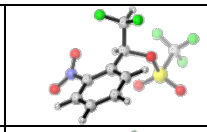
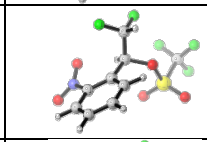
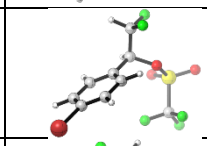
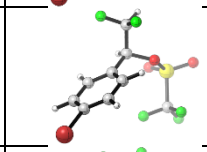
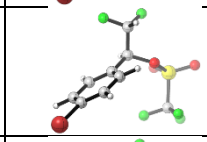
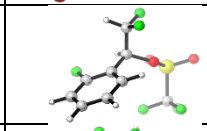
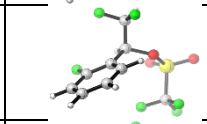
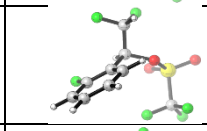
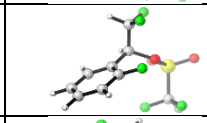
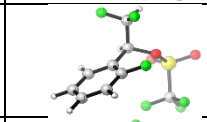
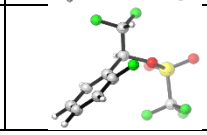
Figure S39. Calculated ^{19}F NMR chemical shifts of conformers of **4-F** and their correlation with experimental data.

5.3. Simulated IR Spectra

IR frequencies were calculated at the PCM-B3LYP/6-31+G(d,p) level of theory using Gaussian 09.[5] The default weighting scheme in Gaussian 09 (SSweight) was used for DFT numerical integration calculations. To account for anharmonic effects, a scaling factor of 0.95 was adopted. Selected experimental and calculated vibrational frequencies of the CF_2–H and CF_2–D bonds are listed in Table S13. The predicted $\nu_{CF2\text{-}H/D}$ values of major conformers are in good agreement with experimental results (< 20 cm^{-1}). For the experimental $\nu_{CF2\text{-}D,}$ which shows two bands due to Fermi resonance, the average value of the two bands is given in brackets.

Table S13. Selected experimental and calculated vibrational frequencies of the CF_2–H and CF_2–D bonds.

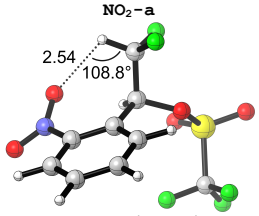
Species	Optimized structure	Calc. $\nu_{CF2\text{-}H}$ (cm^{-1})	Calc. $\nu_{CF2\text{-}D}$ (cm^{-1})	Scaled Calc. $\nu_{CF2\text{-}H}$ (cm^{-1})	Scaled Calc. $\nu_{CF2\text{-}D}$ (cm^{-1})	Scaled Calc. ν_H-ν_D (cm^{-1})	Scaled Calc. ν_H/ν_D (cm^{-1})	Exp. $\nu_{CF2\text{-}H}$ (cm^{-1})	Exp. $\nu_{CF2\text{-}D}$ (cm^{-1})	Exp. ν_H-ν_D (cm^{-1})	Exp. ν_H/ν_D (cm^{-1})
$TMSCF_2H$		3076	2266	2922	2153	770	1.36	2899	2167	735	1.34
1-CF_2H-a (79%)		3186	2348	3026	2231	796	1.36	3013	2237, 2276 [2257]	776	1.33
1-CF_2H-b (0%)		3126	2306	2970	2190	780	1.36	3013	2237, 2276 [2257]	776	1.33
1-CF_2H-c (21%)		3192	2354	3032	2236	796	1.36	3013	2237, 2276 [2257]	776	1.33
($CF_2HNBa)_2$ (0%)		3190	2352	3030	2234	796	1.36	3013	2237, 2276 [2257]	776	1.33
($CF_2HNBa)_2$' (0%)		3195	2355	3035	2237	798	1.36	3013	2237, 2276 [2257]	776	1.33
NO_2-1-trans-a (69%)		3167	2335	3009	2219	790	1.36	3008	2200, 2260 [2230]	813	1.35
NO_2-1-trans-b (0%)		3138	2315	2981	2199	782	1.36	3008	2200, 2260 [2230]	813	1.35
NO_2-1-trans-c (0%)		3130	2309	2974	2193	780	1.36	3008	2200, 2260 [2230]	813	1.35
NO_2-2-trans-a (30%)		3167	2335	3009	2219	790	1.36	3008	2200, 2260 [2230]	813	1.35

NO_2-2-trans-b (0%)		3140	2317	2983	2201	783	1.36	3008	2200, 2260 [2230]	813	1.35
NO_2-2-trans-c (0%)		3129	2308	2972	2192	780	1.36	3008	2200, 2260 [2230]	813	1.35
Br-1-a (3%)		3129	2307	2973	2192	781	1.36	2972	2206	766	1.33
Br-1-b (3%)		3139	2315	2982	2199	783	1.36	2972	2206	766	1.33
Br-1-c (88%)		3141	2316	2984	2200	784	1.36	2972	2206	766	1.33
F-1-trans-a (23%)		3127/ 3132	-	2970/ 2976	-	-	-	2971	-	-	-
F-1-trans-b (2%)		3142/ 3132	-	2985/ 2976	-	-	-	2971	-	-	-
F-1-trans-c (35%)		3133/ 3144	-	2977/ 2987	-	-	-	2971	-	-	-
F-1-cis-a (0%)		3125 /3114	-	2969/ 2959	-	-	-	2971	-	-	-
F-1-cis-b (0%)		3137	-	2980	-	-	-	2971	-	-	-
F-1-cis-c (32%)		3168	-	3010	-	-	-	2971	-	-	-

5.4. Optimized Coordinates of Conformers

5.4.1. Optimized Coordinates of Conformers of 1-(2-Nitrophenyl)-2,2-difluoroethanol Triflate (4-NO_2)

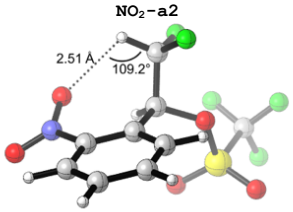
NO_2-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.631691	2.366933	-0.627212
2	9	0	0.656246	2.367800	-1.999715
3	9	0	-0.361543	3.230854	-0.242860
4	8	0	-0.977031	0.591474	-0.683034
5	6	0	0.310336	0.963610	-0.095323
6	6	0	1.344793	-0.078235	-0.488660
7	6	0	2.443398	-0.444523	0.315361
8	6	0	1.200840	-0.750861	-1.708717
9	6	0	3.343574	-1.443150	-0.064426
10	6	0	2.105082	-1.735645	-2.109477
11	1	0	0.360384	-0.506034	-2.346789
12	6	0	3.177853	-2.086121	-1.287139
13	1	0	4.165263	-1.690276	0.595918
14	1	0	1.965638	-2.229339	-3.065578
15	1	0	3.882724	-2.851352	-1.593557
16	8	0	2.272615	1.364317	1.762192
17	1	0	1.586503	2.739771	-0.255647
18	1	0	0.196919	1.046894	0.984400
19	16	0	-2.290896	0.390257	0.251852
20	8	0	-2.031880	0.839056	1.612639
21	8	0	-3.432628	0.830328	-0.527259
22	7	0	2.709529	0.217359	1.598417
23	8	0	3.364398	-0.390750	2.443652
24	6	0	-2.350763	-1.496972	0.294547
25	9	0	-3.393880	-1.867475	1.037979
26	9	0	-2.485482	-1.977337	-0.941182
27	9	0	-1.223609	-1.967275	0.837274

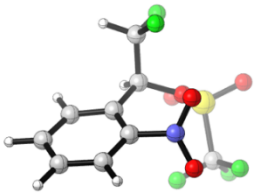
NO_2-a2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.277449	-1.583644	1.482492
2	9	0	0.339814	-0.989699	2.718789
3	9	0	-0.909100	-2.267804	1.424722
4	8	0	-0.820638	0.361043	0.663586
5	6	0	0.309224	-0.522031	0.374933
6	6	0	1.601264	0.282339	0.358687
7	6	0	2.729924	-0.046007	-0.420527
8	6	0	1.685784	1.442782	1.137439
9	6	0	3.878025	0.749816	-0.439300
10	6	0	2.835509	2.234337	1.144748
11	1	0	0.831201	1.735295	1.735245
12	6	0	3.934044	1.891309	0.354251
13	1	0	4.712064	0.456302	-1.064165
14	1	0	2.866356	3.122055	1.767887
15	1	0	4.828583	2.504551	0.354213
16	8	0	2.014408	-2.192970	-0.941572
17	1	0	1.098401	-2.294640	1.389275
18	1	0	0.137534	-1.027721	-0.573397
19	16	0	-1.698149	0.989486	-0.551357
20	8	0	-2.044936	2.345647	-0.166084
21	8	0	-1.101137	0.658248	-1.838356
22	7	0	2.763953	-1.256278	-1.249972
23	8	0	3.542497	-1.291532	-2.201372
24	6	0	-3.267473	-0.048222	-0.371777
25	9	0	-4.157436	0.395869	-1.261971
26	9	0	-2.988772	-1.328495	-0.617105
27	9	0	-3.759560	0.081102	0.858584

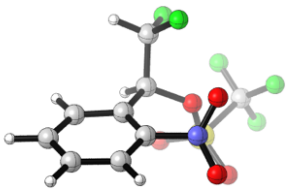
NO_2-a-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.691579	2.581744	0.087975
2	9	0	-1.111334	2.587462	1.383037
3	9	0	0.479984	3.300413	0.036974
4	8	0	0.633560	0.560272	0.355319
5	6	0	-0.412993	1.166715	-0.446379
6	6	0	-1.642811	0.281135	-0.549792
7	6	0	-2.411896	0.443117	-1.712360
8	6	0	-2.067244	-0.703963	0.355751
9	6	0	-3.563713	-0.308336	-1.944903
10	6	0	-3.189487	-1.498230	0.116042
11	6	0	-3.953975	-1.285931	-1.028704
12	1	0	-4.137526	-0.143829	-2.850771
13	1	0	-3.459663	-2.261793	0.836165
14	1	0	-4.838401	-1.888575	-1.205097
15	1	0	-1.438422	3.095175	-0.523699
16	1	0	-0.026888	1.316154	-1.458525
17	16	0	2.151661	0.431457	-0.235418
18	8	0	2.214608	0.952516	-1.595276
19	8	0	3.069034	0.839224	0.810993
20	6	0	2.249026	-1.451871	-0.353263
21	9	0	3.442699	-1.769783	-0.857923
22	9	0	2.110322	-1.992579	0.853349
23	9	0	1.287027	-1.898607	-1.164259
24	1	0	-2.090338	1.164391	-2.458424
25	7	0	-1.368857	-0.978337	1.628999
26	8	0	-1.080923	-2.153698	1.864983
27	8	0	-1.164226	-0.038930	2.391137

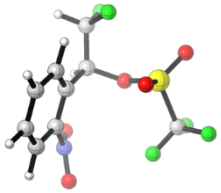
NO_2-a2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.261138	2.235611	0.648438
2	9	0	-0.486311	1.946326	1.959582
3	9	0	1.028177	2.703458	0.553122
4	8	0	0.502275	-0.018415	0.194937
5	6	0	-0.407706	1.011954	-0.270032
6	6	0	-1.834032	0.505745	-0.419780
7	6	0	-2.622216	1.160963	-1.378064
8	6	0	-2.427062	-0.573483	0.254136
9	6	0	-3.942208	0.786035	-1.628166
10	6	0	-3.730491	-0.991963	-0.016588
11	6	0	-4.499289	-0.297240	-0.947493
12	1	0	-4.521297	1.325299	-2.370332
13	1	0	-4.132572	-1.846360	0.515404
14	1	0	-5.519168	-0.609675	-1.144411
15	1	0	-0.940605	3.036420	0.344555
16	1	0	-0.072665	1.350998	-1.254687
17	16	0	1.540272	-0.733135	-0.845120
18	8	0	1.424331	-2.168817	-0.668002
19	8	0	1.468865	-0.092723	-2.153136
20	6	0	3.169605	-0.218690	-0.032427
21	9	0	4.149719	-0.890666	-0.641660
22	9	0	3.361963	1.089005	-0.186146
23	9	0	3.148753	-0.528421	1.261280
24	7	0	-1.730536	-1.346162	1.304438
25	8	0	-1.715028	-2.571453	1.177838
26	8	0	-1.261988	-0.731850	2.258170
27	1	0	-2.185395	1.971772	-1.953865

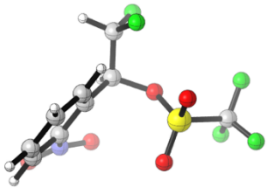
NO_2-a3



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.290841	2.623852	0.872501
2	9	0	-0.267341	3.028823	-0.317711
3	9	0	-0.579000	2.999044	1.861689
4	8	0	-0.823485	0.433975	0.765632
5	6	0	0.474519	1.108008	0.926858
6	6	0	1.582600	0.535048	0.060497
7	6	0	2.107070	-0.762042	0.258184
8	6	0	2.135815	1.280187	-0.988238
9	6	0	3.119481	-1.284574	-0.546475
10	6	0	3.170686	0.780149	-1.782107
11	1	0	1.741913	2.262855	-1.213862
12	6	0	3.665586	-0.503949	-1.563119
13	1	0	3.477763	-2.288809	-0.358168
14	1	0	3.575582	1.395939	-2.578291
15	1	0	4.465545	-0.902485	-2.177588
16	8	0	1.681035	-2.871765	1.120013
17	1	0	0.686628	0.877939	1.969981
18	16	0	-1.693931	0.343249	-0.609188
19	8	0	-2.880151	1.175782	-0.495815
20	8	0	-0.850248	0.361785	-1.795741
21	7	0	1.629333	-1.660575	1.329575
22	8	0	1.230330	-1.165243	2.387640
23	6	0	-2.251750	-1.440028	-0.326244
24	9	0	-2.913654	-1.541487	0.824712
25	9	0	-3.057801	-1.773889	-1.338035
26	9	0	-1.194404	-2.253663	-0.313509
27	1	0	1.230988	3.160963	1.018636

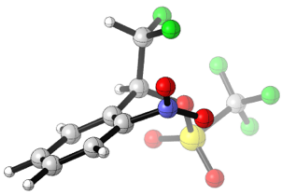
NO_2-a4



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.208506	2.305220	1.180713
2	9	0	-0.420180	2.914525	0.126368
3	9	0	-0.625752	2.438261	2.263193
4	8	0	-0.848070	0.184740	0.665076
5	6	0	0.454067	0.812376	0.937039
6	6	0	1.556836	0.493209	-0.056635
7	6	0	2.477514	-0.562414	0.132099
8	6	0	1.744709	1.296369	-1.190518
9	6	0	3.522756	-0.803885	-0.758109
10	6	0	2.776217	1.051251	-2.100297
11	1	0	1.069042	2.121541	-1.375860
12	6	0	3.666441	0.000275	-1.887017
13	1	0	4.201075	-1.625147	-0.564232
14	1	0	2.877438	1.687095	-2.973460
15	1	0	4.468130	-0.197862	-2.590200
16	8	0	3.431152	-2.010115	1.671678
17	1	0	0.704532	0.399355	1.912545
18	16	0	-1.357581	-0.328767	-0.785591
19	8	0	-1.548013	0.771421	-1.721888
20	8	0	-0.660041	-1.540872	-1.194745
21	7	0	2.387881	-1.487594	1.276069
22	8	0	1.278329	-1.703642	1.770877
23	6	0	-3.057530	-0.834858	-0.130525
24	9	0	-3.736840	-1.341466	-1.164309
25	9	0	-2.933417	-1.760728	0.818126
26	9	0	-3.703258	0.226011	0.350539
27	1	0	1.136972	2.841506	1.394437

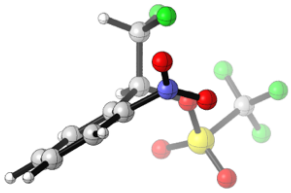
NO_2-a3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.409870	1.343680	1.692765
2	9	0	0.778515	2.373511	0.868958
3	9	0	-0.830482	1.649870	2.189411
4	8	0	-0.632864	0.168592	-0.128103
5	6	0	0.338655	0.007077	0.947345
6	6	0	1.681458	-0.536053	0.486359
7	6	0	2.107454	-1.719586	1.109203
8	6	0	2.588850	0.060057	-0.413583
9	6	0	3.355187	-2.289651	0.849729
10	6	0	3.847415	-0.483603	-0.665724
11	6	0	4.229953	-1.669556	-0.040201
12	1	0	3.636704	-3.212249	1.346154
13	1	0	4.510351	0.019587	-1.359625
14	1	0	5.203089	-2.099444	-0.251925
15	1	0	-0.071124	-0.703947	1.668340
16	16	0	-1.715637	-1.004338	-0.425762
17	8	0	-1.618493	-1.386939	-1.823353
18	8	0	-1.709910	-1.988240	0.652125
19	6	0	-3.284963	0.034938	-0.253831
20	9	0	-3.234518	1.075116	-1.082761
21	9	0	-4.322397	-0.744211	-0.571911
22	9	0	-3.414433	0.459874	1.001930
23	1	0	1.117166	1.295162	2.524836
24	7	0	2.280560	1.279514	-1.190320
25	8	0	3.132570	2.170218	-1.191454
26	8	0	1.230362	1.312416	-1.824607
27	1	0	1.443307	-2.205948	1.816767

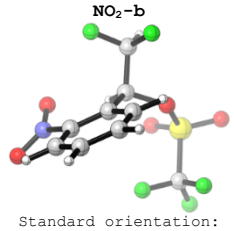
NO_2-a4-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.409629	1.343642	1.692865
2	9	0	0.778668	2.373246	0.868943
3	9	0	-0.830864	1.649980	2.188923
4	8	0	-0.632649	0.168451	-0.128229
5	6	0	0.338646	0.006971	0.947545
6	6	0	1.681423	-0.536104	0.486568
7	6	0	2.107413	-1.719678	1.109356
8	6	0	2.588762	0.060011	-0.413433
9	6	0	3.355081	-2.289804	0.849792
10	6	0	3.847254	-0.483801	-0.665722
11	6	0	4.229775	-1.669773	-0.040262
12	1	0	3.636612	-3.212408	1.346196
13	1	0	4.510154	0.019341	-1.359688
14	1	0	5.202855	-2.099732	-0.252098
15	1	0	-0.071327	-0.704086	1.668396
16	16	0	-1.715571	-1.004152	-0.426162
17	8	0	-1.618608	-1.386060	-1.823950
18	8	0	-1.709925	-1.988528	0.651333
19	6	0	-3.284948	0.034840	-0.253601
20	9	0	-4.322306	-0.744201	-0.572255
21	9	0	-3.414552	0.458938	1.002435
22	9	0	-3.234618	1.075618	-1.081835
23	1	0	1.116633	1.295238	2.525196
24	7	0	2.280771	1.279653	-1.190077
25	8	0	3.133177	2.170009	-1.191187
26	8	0	1.230556	1.313180	-1.824265
27	1	0	1.443256	-2.205969	1.816950

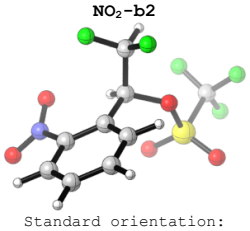
NO_2-b



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.663944	2.542506	-0.026194
2	9	0	-1.894672	2.751693	-0.584323
3	9	0	-0.752229	2.900720	1.296099
4	8	0	0.996922	0.933797	0.534039
5	6	0	-0.291359	1.054805	-0.165985
6	6	0	-1.283210	0.098176	0.466814
7	6	0	-2.173777	-0.729205	-0.248765
8	6	0	-1.303345	-0.007638	1.864845
9	6	0	-3.044236	-1.610224	0.398621
10	6	0	-2.178696	-0.872263	2.521855
11	1	0	-0.614088	0.594389	2.444194
12	6	0	-3.055592	-1.673552	1.788487
13	1	0	-3.706032	-2.226711	-0.196011
14	1	0	-2.172066	-0.916861	3.605933
15	1	0	-3.742753	-2.345706	2.290963
16	8	0	-1.866094	0.273309	-2.333660
17	1	0	0.061751	3.200617	-0.509162
18	1	0	-0.143500	0.860177	-1.225267
19	16	0	2.345987	0.510131	-0.266957
20	8	0	2.150015	0.635212	-1.704948
21	8	0	3.452729	1.127969	0.439529
22	7	0	-2.240825	-0.731360	-1.720929
23	8	0	-2.680230	-1.741421	-2.272758
24	6	0	2.404664	-1.336293	0.130139
25	9	0	3.483418	-1.855142	-0.456369
26	9	0	2.477163	-1.515765	1.447965
27	9	0	1.305979	-1.930093	-0.344411

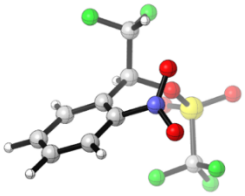
NO_2-b2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.200468	1.653823	-1.519640
2	9	0	-1.279127	1.585691	-2.355379
3	9	0	-0.290570	2.841896	-0.837959
4	8	0	0.908592	0.724195	0.338557
5	6	0	-0.238442	0.464068	-0.542603
6	6	0	-1.512652	0.367485	0.276380
7	6	0	-2.549391	-0.561951	0.047434
8	6	0	-1.671946	1.242075	1.360174
9	6	0	-3.687697	-0.610249	0.856826
10	6	0	-2.810976	1.211950	2.164855
11	1	0	-0.881631	1.949137	1.581128
12	6	0	-3.824639	0.286355	1.911847
13	1	0	-4.452889	-1.345346	0.643319
14	1	0	-2.901243	1.911912	2.989019
15	1	0	-4.714752	0.257266	2.530972
16	8	0	-1.767015	-1.326002	-2.014898
17	1	0	0.712854	1.673392	-2.117768
18	1	0	-0.056386	-0.441032	-1.115805
19	16	0	1.794199	-0.514428	0.910431
20	8	0	2.167463	-0.180873	2.272649
21	8	0	1.195403	-1.788968	0.539203
22	7	0	-2.500799	-1.548315	-1.046345
23	8	0	-3.208105	-2.551875	-0.946331
24	6	0	3.336965	-0.284138	-0.155499
25	9	0	4.212490	-1.238521	0.158977
26	9	0	3.003490	-0.387390	-1.445897
27	9	0	3.873408	0.913370	0.072990

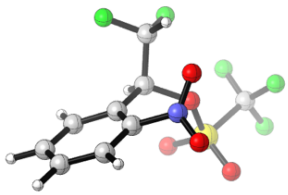
NO_2-b-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.788373	2.494622	0.359820
2	9	0	0.273956	3.360919	0.280665
3	9	0	-1.813668	3.041018	-0.374313
4	8	0	0.699803	0.617069	0.492671
5	6	0	-0.383002	1.173334	-0.314394
6	6	0	-1.494095	0.161218	-0.513923
7	6	0	-2.044889	0.077738	-1.799270
8	6	0	-1.985596	-0.743969	0.445342
9	6	0	-3.052220	-0.838074	-2.110371
10	6	0	-2.960187	-1.693957	0.140366
11	6	0	-3.508504	-1.730515	-1.140503
12	1	0	-3.462036	-0.862401	-3.114597
13	1	0	-3.289890	-2.379208	0.911880
14	1	0	-4.280969	-2.455043	-1.374523
15	1	0	-1.096496	2.407050	1.398667
16	1	0	0.016927	1.443356	-1.294551
17	16	0	2.197835	0.440504	-0.123687
18	8	0	2.278748	1.025601	-1.455479
19	8	0	3.135132	0.752859	0.938231
20	6	0	2.209985	-1.436766	-0.334150
21	9	0	3.400288	-1.794589	-0.817675
22	9	0	2.003130	-2.028242	0.840198
23	9	0	1.251248	-1.794095	-1.193221
24	1	0	-1.670688	0.739582	-2.573946
25	7	0	-1.517650	-0.738237	1.842223
26	8	0	-1.380601	-1.824726	2.403220
27	8	0	-1.327078	0.351621	2.385371

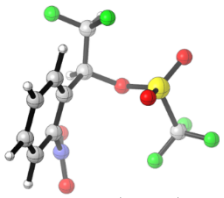
NO_2-b2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.284623	2.054418	0.914345
2	9	0	0.973649	2.602263	0.882321
3	9	0	-1.166252	3.043246	0.549341
4	8	0	0.563322	-0.093963	0.292478
5	6	0	-0.360602	0.947290	-0.149582
6	6	0	-1.744034	0.387488	-0.423193
7	6	0	-2.390725	0.846344	-1.577742
8	6	0	-2.414507	-0.593866	0.331095
9	6	0	-3.651086	0.375869	-1.952140
10	6	0	-3.654746	-1.105105	-0.051057
11	6	0	-4.283937	-0.605970	-1.190154
12	1	0	-4.123531	0.764751	-2.848008
13	1	0	-4.119499	-1.872926	0.555552
14	1	0	-5.256822	-0.989105	-1.478579
15	1	0	-0.505071	1.733620	1.929286
16	1	0	0.020586	1.382288	-1.076705
17	16	0	1.575455	-0.803921	-0.770827
18	8	0	1.492100	-2.238521	-0.564751
19	8	0	1.449482	-0.187072	-2.085440
20	6	0	3.221133	-0.244068	-0.025186
21	9	0	4.197944	-0.880690	-0.675471
22	9	0	3.364291	1.070740	-0.178938
23	9	0	3.263254	-0.557844	1.268085
24	7	0	-1.862817	-1.135484	1.584937
25	8	0	-2.025057	-2.333802	1.809577
26	8	0	-1.306174	-0.354248	2.359714
27	1	0	-1.889835	1.579498	-2.201851

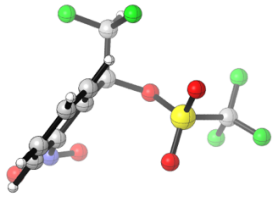
NO_2-b3



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.730870	2.430824	1.052029
2	9	0	2.002380	2.807715	1.401139
3	9	0	0.442283	3.015021	-0.159337
4	8	0	-0.750517	0.511599	0.834216
5	6	0	0.662989	0.902739	0.995402
6	6	0	1.609780	0.163195	0.066464
7	6	0	1.797007	-1.235362	0.148933
8	6	0	2.341080	0.834529	-0.921192
9	6	0	2.651752	-1.924630	-0.711140
10	6	0	3.223157	0.159629	-1.768496
11	1	0	2.218506	1.901349	-1.046390
12	6	0	3.379751	-1.221348	-1.668126
13	1	0	2.748038	-2.998402	-0.610933
14	1	0	3.776532	0.721116	-2.513927
15	1	0	4.058464	-1.752216	-2.326891
16	8	0	0.854899	-3.235789	0.847938
17	1	0	0.839103	0.568236	2.016943
18	16	0	-1.647248	0.732198	-0.511138
19	8	0	-2.522386	1.881667	-0.338410
20	8	0	-0.869063	0.537211	-1.725864
21	7	0	1.111703	-2.072053	1.154753
22	8	0	0.856272	-1.583947	2.259851
23	6	0	-2.702816	-0.812956	-0.238556
24	9	0	-3.325021	-0.746116	0.936948
25	9	0	-3.605205	-0.856304	-1.222101
26	9	0	-1.938126	-1.903309	-0.286294
27	1	0	0.031549	2.830404	1.789180

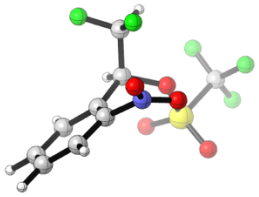
NO_2-b4



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.288870	2.143982	-1.405351
2	9	0	-1.519813	2.636908	-1.763174
3	9	0	0.192502	2.930938	-0.391377
4	8	0	0.901091	0.160252	-0.756407
5	6	0	-0.460201	0.671145	-1.005544
6	6	0	-1.486764	0.357105	0.066451
7	6	0	-2.344135	-0.765135	-0.002970
8	6	0	-1.669569	1.220134	1.156480
9	6	0	-3.327410	-1.009319	0.955135
10	6	0	-2.637862	0.974347	2.132455
11	1	0	-1.044989	2.098150	1.249131
12	6	0	-3.468458	-0.140520	2.034969
13	1	0	-3.958780	-1.882594	0.851459
14	1	0	-2.737837	1.661207	2.966275
15	1	0	-4.220949	-0.338656	2.790583
16	8	0	-3.271717	-2.384041	-1.380353
17	1	0	-0.723417	0.156420	-1.927462
18	16	0	1.516647	-0.188841	0.704316
19	8	0	1.654184	0.999118	1.536561
20	8	0	0.943181	-1.414646	1.242368
21	7	0	-2.250127	-1.763049	-1.083448
22	8	0	-1.155487	-1.941307	-1.626363
23	6	0	3.223144	-0.607836	0.005485
24	9	0	3.989452	-0.969590	1.038285
25	9	0	3.137322	-1.614219	-0.861789
26	9	0	3.752991	0.460739	-0.589595
27	1	0	0.389172	2.246858	-2.255177

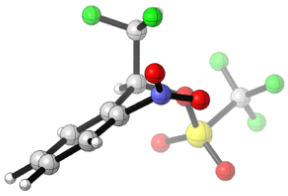
NO_2-b3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.416838	-1.501001	1.579203
2	9	0	-1.161985	-1.320557	2.718643
3	9	0	-1.096597	-2.391014	0.794939
4	8	0	0.763435	-0.327684	-0.124896
5	6	0	-0.256505	-0.130183	0.905555
6	6	0	-1.531395	0.532287	0.415141
7	6	0	-1.886812	1.715918	1.079867
8	6	0	-2.445854	0.056597	-0.549835
9	6	0	-3.070686	2.401329	0.801555
10	6	0	-3.641979	0.718867	-0.823420
11	6	0	-3.952967	1.901455	-0.153975
12	1	0	-3.297191	3.318450	1.334949
13	1	0	-4.312135	0.307412	-1.568462
14	1	0	-4.876826	2.421763	-0.382831
15	1	0	0.171897	0.515739	1.674697
16	16	0	1.826671	0.858352	-0.445331
17	8	0	1.815803	1.122849	-1.872329
18	8	0	1.720869	1.920366	0.549456
19	6	0	3.406320	-0.109225	-0.077078
20	9	0	3.458156	-1.206536	-0.829290
21	9	0	4.447107	0.677946	-0.354513
22	9	0	3.433551	-0.446777	1.215127
23	1	0	0.543927	-1.943282	1.850074
24	7	0	-2.208978	-1.143781	-1.375334
25	8	0	-3.156025	-1.898529	-1.541275
26	8	0	-1.108789	-1.290683	-1.881043
27	1	0	-1.217700	2.108366	1.838667

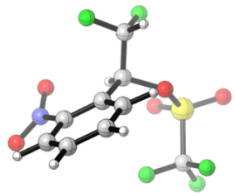
NO_2-b4-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.397017	-1.367244	1.657924
2	9	0	-1.157892	-1.142568	2.778850
3	9	0	-1.041444	-2.322821	0.921533
4	8	0	0.752660	-0.261385	-0.114068
5	6	0	-0.272312	-0.035090	0.904645
6	6	0	-1.564409	0.559125	0.373391
7	6	0	-1.963675	1.764471	0.971256
8	6	0	-2.456876	0.000485	-0.566806
9	6	0	-3.168577	2.392697	0.651106
10	6	0	-3.673400	0.604917	-0.880441
11	6	0	-4.028159	1.811293	-0.278365
12	1	0	-3.429361	3.329134	1.132745
13	1	0	-4.325503	0.129771	-1.603360
14	1	0	-4.968308	2.285903	-0.538170
15	1	0	0.137270	0.667281	1.633581
16	16	0	1.854525	0.892350	-0.422503
17	8	0	1.830749	1.201951	-1.840538
18	8	0	1.808296	1.928301	0.603893
19	6	0	3.397499	-0.151765	-0.110934
20	9	0	4.465871	0.615107	-0.335176
21	9	0	3.407106	-0.571032	1.157379
22	9	0	3.414283	-1.199580	-0.931486
23	1	0	0.573951	-1.763501	1.961939
24	7	0	-2.174607	-1.237320	-1.322154
25	8	0	-3.098553	-2.044401	-1.440371
26	8	0	-1.062366	-1.370766	-1.825669
27	1	0	-1.314255	2.220166	1.711863

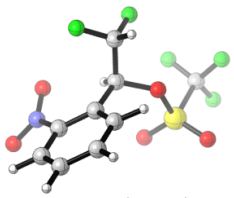
NO_2-c



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.622449	2.394004	-0.880298
2	9	0	-0.242098	3.343952	-0.400905
3	9	0	1.889976	2.780475	-0.539795
4	8	0	-1.004920	0.681056	-0.790101
5	6	0	0.299994	1.043832	-0.219187
6	6	0	1.300717	-0.038916	-0.571343
7	6	0	2.240778	-0.592990	0.320373
8	6	0	1.279390	-0.556181	-1.874244
9	6	0	3.111987	-1.614235	-0.066703
10	6	0	2.157188	-1.562347	-2.278288
11	1	0	0.547182	-0.177744	-2.579225
12	6	0	3.078296	-2.092664	-1.373223
13	1	0	3.811182	-2.011714	0.657950
14	1	0	2.116139	-1.930970	-3.297911
15	1	0	3.765845	-2.874169	-1.677999
16	8	0	2.011210	1.012661	1.994882
17	1	0	0.540919	2.375443	-1.969941
18	1	0	0.196367	1.199601	0.851807
19	16	0	-2.299475	0.439062	0.164038
20	8	0	-2.027606	0.876638	1.525282
21	8	0	-3.459969	0.868581	-0.593871
22	7	0	2.365183	-0.136598	1.715870
23	8	0	2.831759	-0.927671	2.536753
24	6	0	-2.323821	-1.450006	0.178022
25	9	0	-3.347542	-1.851423	0.931769
26	9	0	-2.470661	-1.911473	-1.063708
27	9	0	-1.179451	-1.908459	0.693241

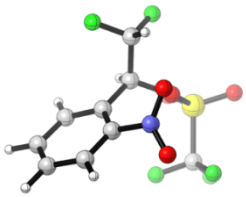
NO_2-c2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.215464	1.695220	-1.505438
2	9	0	-0.908583	2.454224	-1.305157
3	9	0	1.298815	2.515234	-1.353952
4	8	0	-0.856457	-0.286210	-0.855667
5	6	0	0.262990	0.575980	-0.451468
6	6	0	1.557974	-0.213798	-0.493237
7	6	0	2.591794	-0.124468	0.461026
8	6	0	1.743053	-1.117648	-1.548347
9	6	0	3.748781	-0.901968	0.368849
10	6	0	2.902789	-1.884977	-1.661355
11	1	0	0.953662	-1.237614	-2.282381
12	6	0	3.910591	-1.776361	-0.701668
13	1	0	4.509806	-0.804315	1.132458
14	1	0	3.012668	-2.568597	-2.496714
15	1	0	4.815484	-2.369084	-0.780511
16	8	0	1.786625	1.776289	1.545137
17	1	0	0.198911	1.321037	-2.532041
18	1	0	0.064396	1.004598	0.526946
19	16	0	-1.702034	-1.108851	0.262777
20	8	0	-2.097557	-2.363176	-0.351706
21	8	0	-1.045920	-1.030007	1.560234
22	7	0	2.516949	0.783240	1.618958
23	8	0	3.201719	0.511032	2.605770
24	6	0	-3.248639	-0.025366	0.342260
25	9	0	-4.111844	-0.595254	1.184778
26	9	0	-2.920648	1.188268	0.786798
27	9	0	-3.797418	0.069728	-0.867885

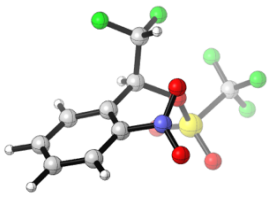
NO_2-c-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.789373	2.494960	0.359689
2	9	0	0.272284	3.362023	0.280899
3	9	0	-1.814879	3.040605	-0.374800
4	8	0	0.700306	0.618900	0.492916
5	6	0	-0.382888	1.173906	-0.314371
6	6	0	-1.493408	0.161091	-0.513804
7	6	0	-2.044119	0.077306	-1.799179
8	6	0	-1.984584	-0.744281	0.445482
9	6	0	-3.051053	-0.838929	-2.110293
10	6	0	-2.958795	-1.694667	0.140473
11	6	0	-3.507051	-1.731492	-1.140406
12	1	0	-3.460816	-0.863437	-3.114536
13	1	0	-3.288247	-2.380037	0.911986
14	1	0	-4.279253	-2.456309	-1.374407
15	1	0	-1.097809	2.407090	1.398426
16	1	0	0.016904	1.444077	-1.294538
17	16	0	2.197866	0.440654	-0.123935
18	8	0	2.278932	1.025463	-1.455836
19	8	0	3.135625	0.752356	0.937759
20	6	0	2.208862	-1.436665	-0.334111
21	9	0	3.399020	-1.795184	-0.817494
22	9	0	2.001652	-2.027774	0.840359
23	9	0	1.250026	-1.793697	-1.193168
24	1	0	-1.670188	0.739240	-2.573907
25	7	0	-1.516754	-0.738408	1.842397
26	8	0	-1.379720	-1.824864	2.403467
27	8	0	-1.326098	0.351474	2.385461

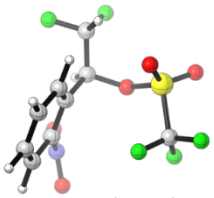
NO_2-c2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.285029	2.057465	0.911056
2	9	0	0.973283	2.605409	0.879092
3	9	0	-1.166316	3.045113	0.542155
4	8	0	0.564469	-0.092117	0.296586
5	6	0	-0.359352	0.947415	-0.149905
6	6	0	-1.742312	0.386833	-0.424332
7	6	0	-2.386953	0.842429	-1.581291
8	6	0	-2.414136	-0.592444	0.331466
9	6	0	-3.646657	0.370892	-1.956628
10	6	0	-3.653670	-1.104766	-0.051436
11	6	0	-4.280858	-0.608810	-1.193047
12	1	0	-4.117435	0.757276	-2.854455
13	1	0	-4.119509	-1.870879	0.556505
14	1	0	-5.253231	-0.992770	-1.482098
15	1	0	-0.506678	1.739510	1.926626
16	1	0	0.023070	1.380170	-1.077566
17	16	0	1.573771	-0.808878	-0.764939
18	8	0	1.491706	-2.242055	-0.548800
19	8	0	1.443537	-0.201054	-2.083329
20	6	0	3.221331	-0.243032	-0.027966
21	9	0	4.196783	-0.881911	-0.678056
22	9	0	3.362228	1.071155	-0.189349
23	9	0	3.268200	-0.549707	1.266828
24	7	0	-1.864527	-1.130325	1.587721
25	8	0	-2.026493	-2.328088	1.815413
26	8	0	-1.309681	-0.346582	2.361264
27	1	0	-1.884960	1.573769	-2.206634

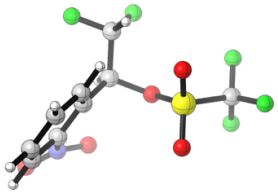
NO_2-c3



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.082433	2.686230	0.101875
2	9	0	0.718719	3.362203	-0.781070
3	9	0	-1.275918	3.362593	0.177836
4	8	0	0.866200	0.614560	-0.879143
5	6	0	-0.387008	1.302320	-0.487300
6	6	0	-1.311397	0.422440	0.328394
7	6	0	-2.068538	-0.619860	-0.250060
8	6	0	-1.423321	0.581290	1.715501
9	6	0	-2.885533	-1.456689	0.508000
10	6	0	-2.259921	-0.230781	2.484800
11	1	0	-0.844714	1.345282	2.219021
12	6	0	-2.993414	-1.251294	1.882500
13	1	0	-3.436988	-2.247729	0.015021
14	1	0	-2.326801	-0.064895	3.554764
15	1	0	-3.643608	-1.888241	2.472354
16	8	0	-2.120140	-2.085890	-2.042074
17	1	0	-0.819012	1.487199	-1.468939
18	16	0	2.074939	0.234156	0.134143
19	8	0	3.319014	0.518350	-0.557695
20	8	0	1.801109	0.719877	1.482292
21	7	0	-2.047774	-0.906411	-1.699639
22	8	0	-1.989855	0.038489	-2.491418
23	6	0	1.909924	-1.650632	0.156457
24	9	0	1.946573	-2.122908	-1.087653
25	9	0	2.936134	-2.138868	0.855879
26	9	0	0.764109	-2.006115	0.739910
27	1	0	0.399204	2.713409	1.078156

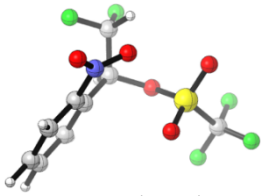
NO_2-c4



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.034811	2.316001	-0.253481
2	9	0	0.894845	2.725251	-1.173968
3	9	0	-1.153672	3.095757	-0.426180
4	8	0	0.776913	0.028196	-0.625596
5	6	0	-0.432420	0.868764	-0.582414
6	6	0	-1.542169	0.296965	0.279485
7	6	0	-2.544548	-0.564302	-0.219410
8	6	0	-1.641417	0.657669	1.630375
9	6	0	-3.584706	-1.035392	0.581282
10	6	0	-2.666040	0.177149	2.448238
11	1	0	-0.903903	1.320657	2.065959
12	6	0	-3.639484	-0.672514	1.925092
13	1	0	-4.330556	-1.688587	0.146332
14	1	0	-2.697924	0.472378	3.491611
15	1	0	-4.438239	-1.051953	2.553028
16	8	0	-3.646402	-1.314053	-2.116683
17	1	0	-0.717569	0.868387	-1.632698
18	16	0	1.553941	-0.485523	0.700419
19	8	0	1.660130	0.584269	1.689948
20	8	0	1.114469	-1.818956	1.081974
21	7	0	-2.557086	-1.025531	-1.619277
22	8	0	-1.481322	-1.114876	-2.217181
23	6	0	3.229117	-0.660882	-0.159442
24	9	0	4.094872	-1.111020	0.752624
25	9	0	3.140631	-1.531157	-1.162431
26	9	0	3.634407	0.522144	-0.615952
27	1	0	0.373555	2.500029	0.739113

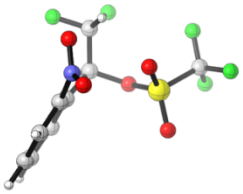
NO_2-c3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.699096	2.233791	-0.699493
2	9	0	-0.045883	3.027616	-1.614626
3	9	0	-2.044684	2.469865	-0.852075
4	8	0	0.982040	0.466146	-0.726773
5	6	0	-0.414916	0.768971	-1.077706
6	6	0	-1.423405	-0.326140	-0.755993
7	6	0	-1.607429	-1.263567	-1.782500
8	6	0	-2.227893	-0.494533	0.391203
9	6	0	-2.514790	-2.319846	-1.677249
10	6	0	-3.158382	-1.527985	0.500950
11	6	0	-3.297350	-2.452137	-0.531957
12	1	0	-2.611951	-3.025571	-2.495508
13	1	0	-3.751074	-1.604510	1.403575
14	1	0	-4.010885	-3.263353	-0.436868
15	1	0	-0.331603	0.784533	-2.166042
16	16	0	1.576440	-0.081565	0.684282
17	8	0	1.927013	1.015052	1.573666
18	8	0	0.867581	-1.262750	1.156586
19	6	0	3.184472	-0.675884	-0.111527
20	9	0	3.830033	0.342271	-0.679526
21	9	0	3.937557	-1.193323	0.863806
22	9	0	2.933146	-1.616394	-1.023457
23	1	0	-0.391250	2.544516	0.294395
24	7	0	-2.118075	0.386125	1.559239
25	8	0	-3.071516	0.458453	2.332162
26	8	0	-1.056723	0.998296	1.720488
27	1	0	-1.025696	-1.161335	-2.693231

NO_2-c4-cis

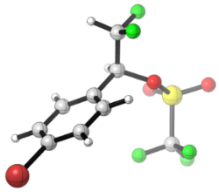


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.020662	2.185922	-0.060294
2	9	0	1.081316	2.780002	-0.636280
3	9	0	-1.057296	3.075174	-0.177264
4	8	0	0.807926	0.081468	-1.051624
5	6	0	-0.373367	0.967393	-0.925743
6	6	0	-1.666939	0.178860	-0.755202
7	6	0	-2.230184	-0.231851	-1.976181
8	6	0	-2.309852	-0.296564	0.410632
9	6	0	-3.354741	-1.052948	-2.051588
10	6	0	-3.422175	-1.138539	0.349769
11	6	0	-3.953124	-1.514451	-0.881368
12	1	0	-3.751880	-1.330693	-3.022146
13	1	0	-3.872149	-1.476015	1.275172
14	1	0	-4.827179	-2.155633	-0.917889
15	1	0	-0.397658	1.372945	-1.938561
16	16	0	1.333787	-0.912065	0.117079
17	8	0	0.890003	-0.444192	1.425196
18	8	0	1.162708	-2.292586	-0.304635
19	6	0	3.170985	-0.502232	-0.062702
20	9	0	3.845139	-1.301957	0.766279
21	9	0	3.565959	-0.719413	-1.316342
22	9	0	3.385450	0.769811	0.266974
23	1	0	0.196176	2.010645	0.988072
24	7	0	-1.921761	0.080804	1.783866
25	8	0	-2.010745	-0.779513	2.656917
26	8	0	-1.587401	1.247936	1.991526
27	1	0	-1.760267	0.095161	-2.898250

5.4.2. Optimized Coordinates of Conformers of 1-(4-Bromophenyl)-2,2-difluoroethanol Triflate (4-Br)

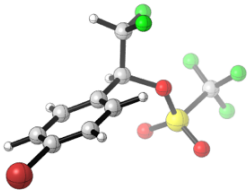
Br-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.278356	2.825465	0.078393
2	9	0	-1.042093	3.045658	-1.254780
3	9	0	-2.587114	3.166138	0.314617
4	8	0	-1.944838	0.587223	-0.433897
5	6	0	-1.053833	1.357281	0.446620
6	6	0	0.374281	0.896743	0.295473
7	6	0	1.133767	0.651084	1.445228
8	6	0	0.957762	0.724567	-0.967815
9	6	0	2.464538	0.241353	1.344796
10	6	0	2.283155	0.308204	-1.080922
11	1	0	0.378879	0.905903	-1.866828
12	6	0	3.022698	0.071913	0.079398
13	1	0	3.048078	0.048252	2.237529
14	1	0	2.731367	0.169447	-2.058065
15	1	0	-0.635038	3.490701	0.659681
16	1	0	-1.388912	1.236443	1.479396
17	16	0	-3.032886	-0.445894	0.175606
18	8	0	-3.108297	-0.320506	1.625996
19	8	0	-4.202489	-0.394747	-0.682613
20	6	0	-2.166000	-2.082837	-0.196035
21	9	0	-2.965212	-3.075614	0.200726
22	9	0	-1.934461	-2.189039	-1.504195
23	9	0	-1.011464	-2.145949	0.470879
24	1	0	0.689655	0.770607	2.429473
25	35	0	4.833776	-0.503891	-0.070937

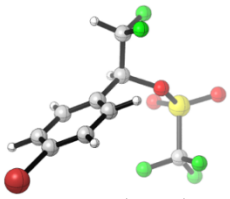
Br-a2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.014708	2.428799	0.230295
2	9	0	-0.788086	2.754698	-1.082516
3	9	0	-2.337229	2.695179	0.486009
4	8	0	-1.578358	0.214410	-0.447302
5	6	0	-0.723057	0.949733	0.493117
6	6	0	0.729114	0.575753	0.318363
7	6	0	1.512697	0.338489	1.453586
8	6	0	1.309070	0.479608	-0.954225
9	6	0	2.865192	0.015496	1.329563
10	6	0	2.656569	0.150019	-1.091110
11	1	0	0.710035	0.651313	-1.841776
12	6	0	3.420632	-0.076478	0.054978
13	1	0	3.467513	-0.172076	2.210832
14	1	0	3.102200	0.069096	-2.075846
15	1	0	-0.401571	3.077149	0.861255
16	1	0	-1.049214	0.735538	1.513677
17	16	0	-2.272456	-1.179740	0.000816
18	8	0	-2.070627	-2.143600	-1.066728
19	8	0	-1.974546	-1.477266	1.396620
20	6	0	-4.081487	-0.643102	-0.088317
21	9	0	-4.840719	-1.712093	0.166053
22	9	0	-4.319055	0.299771	0.823950
23	9	0	-4.359151	-0.175438	-1.304405
24	1	0	1.070909	0.394943	2.444425
25	35	0	5.262906	-0.534213	-0.127591

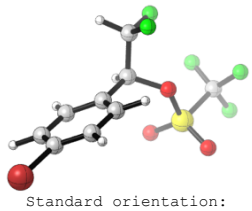
Br-a-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.278118	2.825343	0.078602
2	9	0	-1.041795	3.045691	-1.254544
3	9	0	-2.586882	3.165983	0.314802
4	8	0	-1.944587	0.587174	-0.434037
5	6	0	-1.053635	1.357110	0.446640
6	6	0	0.374458	0.896539	0.295477
7	6	0	1.133942	0.650821	1.445220
8	6	0	0.957958	0.724452	-0.967810
9	6	0	2.464723	0.241116	1.344783
10	6	0	2.283358	0.308119	-1.080938
11	6	0	3.022892	0.071768	0.079377
12	1	0	3.048257	0.047975	2.237508
13	1	0	2.731592	0.169452	-2.058082
14	1	0	-0.634820	3.490511	0.659990
15	1	0	-1.388763	1.236134	1.479385
16	16	0	-3.033101	-0.445579	0.175302
17	8	0	-3.108926	-0.319944	1.625649
18	8	0	-4.202416	-0.394290	-0.683297
19	6	0	-2.166473	-2.082774	-0.195808
20	9	0	-2.965906	-3.075316	0.201115
21	9	0	-1.934807	-2.189353	-1.503917
22	9	0	-1.012028	-2.145911	0.471248
23	1	0	0.689830	0.770293	2.429473
24	1	0	0.379085	0.905855	-1.866819
25	35	0	4.834000	-0.503980	-0.070984

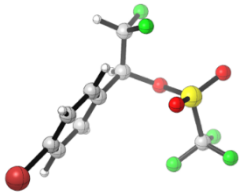
Br-a2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.023063	2.422854	0.228127
2	9	0	-0.777939	2.770184	-1.075661
3	9	0	-2.348832	2.685854	0.469898
4	8	0	-1.580770	0.221748	-0.493197
5	6	0	-0.735215	0.939085	0.469959
6	6	0	0.719167	0.568903	0.305936
7	6	0	1.491437	0.321487	1.446748
8	6	0	1.312345	0.487063	-0.961428
9	6	0	2.845727	0.002482	1.333487
10	6	0	2.661787	0.160794	-1.087744
11	6	0	3.414403	-0.075951	0.063771
12	1	0	3.439333	-0.192572	2.219055
13	1	0	3.117765	0.090817	-2.068583
14	1	0	-0.418595	3.060048	0.878486
15	1	0	-1.071613	0.708188	1.483440
16	16	0	-2.266222	-1.188850	-0.086774
17	8	0	-2.149240	-2.077468	-1.229222
18	8	0	-1.877803	-1.581178	1.262240
19	6	0	-4.070994	-0.635846	-0.010159
20	9	0	-4.823782	-1.712617	0.228848
21	9	0	-4.228560	0.246895	0.977958
22	9	0	-4.430570	-0.085594	-1.168516
23	1	0	1.039416	0.366983	2.433546
24	35	0	5.259629	-0.527758	-0.104219
25	1	0	0.722344	0.667136	-1.853370

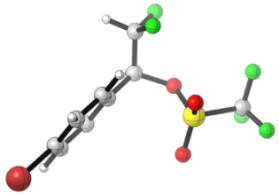
Br-a3



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.440133	2.762408	0.257925
2	9	0	-1.718397	2.598223	-1.078061
3	9	0	-2.599838	3.192204	0.851402
4	8	0	-2.072935	0.438843	0.728467
5	6	0	-0.997726	1.447771	0.897109
6	6	0	0.395611	0.973074	0.563128
7	6	0	1.086766	0.249629	1.546375
8	6	0	1.035707	1.254935	-0.651962
9	6	0	2.386861	-0.201054	1.324449
10	6	0	2.339388	0.817730	-0.883392
11	1	0	0.523638	1.801290	-1.434981
12	6	0	2.999886	0.090454	0.106214
13	1	0	2.912169	-0.761913	2.088848
14	1	0	2.828309	1.037356	-1.825399
15	1	0	-1.064097	1.606233	1.975775
16	16	0	-2.448010	-0.380640	-0.618952
17	8	0	-3.812630	-0.054589	-1.001900
18	8	0	-1.363539	-0.406759	-1.588723
19	6	0	-2.508424	-2.078896	0.203674
20	9	0	-3.414882	-2.088010	1.182024
21	9	0	-2.848540	-2.974425	-0.727922
22	9	0	-1.309452	-2.389828	0.701226
23	1	0	-0.686494	3.546288	0.365064
24	1	0	0.608937	0.033086	2.497794
25	35	0	4.779168	-0.512338	-0.211593

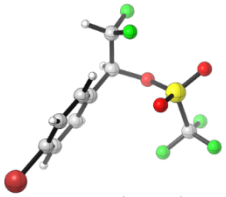
Br-a4



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.220846	2.696766	-0.039335
2	9	0	-1.447994	2.399489	-1.358071
3	9	0	-2.400090	3.192606	0.462770
4	8	0	-1.920334	0.481241	0.637129
5	6	0	-0.810790	1.460034	0.760107
6	6	0	0.577174	0.935205	0.481553
7	6	0	1.359195	0.535006	1.575442
8	6	0	1.120317	0.862055	-0.810721
9	6	0	2.655509	0.057917	1.392411
10	6	0	2.417680	0.389432	-1.005250
11	1	0	0.535758	1.157867	-1.673240
12	6	0	3.170851	-0.010191	0.098325
13	1	0	3.251899	-0.251139	2.242802
14	1	0	2.832854	0.334449	-2.004814
15	1	0	-0.877329	1.743196	1.812706
16	16	0	-1.849689	-0.916710	-0.172194
17	8	0	-1.587750	-0.725367	-1.592578
18	8	0	-1.130842	-1.929210	0.590916
19	6	0	-3.697557	-1.260096	0.026526
20	9	0	-3.944448	-2.433956	-0.563588
21	9	0	-4.021934	-1.335136	1.317645
22	9	0	-4.413426	-0.305349	-0.565384
23	1	0	-0.464629	3.484139	0.018329
24	1	0	0.954261	0.591315	2.581598
25	35	0	4.945584	-0.647469	-0.166306

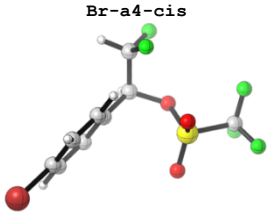
Br-a3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.440411	2.762472	0.257999
2	9	0	-1.718606	2.598429	-1.077990
3	9	0	-2.600155	3.192255	0.851459
4	8	0	-2.073135	0.438865	0.728282
5	6	0	-0.998098	1.447727	0.897102
6	6	0	0.395324	0.973156	0.563146
7	6	0	1.086493	0.249704	1.546369
8	6	0	1.035404	1.255031	-0.651956
9	6	0	2.386596	-0.200962	1.324419
10	6	0	2.339076	0.817832	-0.883411
11	6	0	2.999588	0.090519	0.106165
12	1	0	2.911944	-0.761777	2.088824
13	1	0	2.827989	1.037508	-1.825411
14	1	0	-1.064510	1.606155	1.975777
15	16	0	-2.447916	-0.380916	-0.619132
16	8	0	-3.812633	-0.055299	-1.002039
17	8	0	-1.363441	-0.406687	-1.588894
18	6	0	-2.507698	-2.079078	0.203755
19	9	0	-3.414201	-2.088362	1.182055
20	9	0	-2.847408	-2.974969	-0.727643
21	9	0	-1.308625	-2.389410	0.701414
22	1	0	-0.686753	3.546330	0.365282
23	1	0	0.608674	0.033145	2.497794
24	35	0	4.778942	-0.512087	-0.211577
25	1	0	0.523323	1.801433	-1.434933

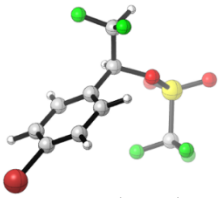
Br-a4-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.221085	2.696658	-0.039332
2	9	0	-1.448334	2.399290	-1.358027
3	9	0	-2.400363	3.192344	0.462857
4	8	0	-1.920137	0.480989	0.637522
5	6	0	-0.810785	1.460079	0.760177
6	6	0	0.577214	0.935348	0.481630
7	6	0	1.359169	0.534882	1.575486
8	6	0	1.120406	0.862437	-0.810628
9	6	0	2.655456	0.057769	1.392414
10	6	0	2.417769	0.389794	-1.005199
11	6	0	3.170854	-0.010086	0.098328
12	1	0	3.251820	-0.251501	2.242745
13	1	0	2.832989	0.334994	-2.004753
14	1	0	-0.877355	1.743379	1.812735
15	16	0	-1.849609	-0.916684	-0.172302
16	8	0	-1.587777	-0.724895	-1.592645
17	8	0	-1.130723	-1.929454	0.590416
18	6	0	-3.697449	-1.260131	0.026519
19	9	0	-3.944431	-2.433767	-0.563997
20	9	0	-4.021631	-1.335651	1.317661
21	9	0	-4.413432	-0.305177	-0.564925
22	1	0	-0.464976	3.484141	0.018245
23	1	0	0.954165	0.590978	2.581621
24	1	0	0.535919	1.158468	-1.673121
25	35	0	4.945563	-0.647443	-0.166327

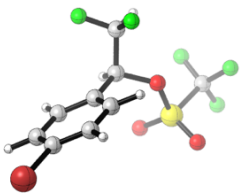
Br-b



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.304652	2.863525	-0.094446
2	9	0	-0.545774	3.664820	0.721946
3	9	0	-0.869014	3.059690	-1.378835
4	8	0	-2.026376	0.646861	-0.518252
5	6	0	-1.103948	1.406953	0.345057
6	6	0	0.301115	0.879526	0.219029
7	6	0	1.062360	0.692188	1.378627
8	6	0	0.862362	0.583044	-1.031154
9	6	0	2.371404	0.214486	1.300565
10	6	0	2.166872	0.100310	-1.121556
11	1	0	0.281718	0.717985	-1.936926
12	6	0	2.907318	-0.078581	0.048085
13	1	0	2.956002	0.066666	2.201243
14	1	0	2.597717	-0.133610	-2.088350
15	1	0	-2.346663	3.184991	-0.033739
16	1	0	-1.453498	1.340109	1.377895
17	16	0	-3.150061	-0.335122	0.114800
18	8	0	-3.305681	-0.084357	1.542213
19	8	0	-4.267367	-0.340268	-0.812277
20	6	0	-2.292650	-2.009540	-0.067890
21	9	0	-3.143349	-2.955398	0.334748
22	9	0	-1.963637	-2.213592	-1.342643
23	9	0	-1.195871	-2.041597	0.691271
24	1	0	0.636319	0.912814	2.353092
25	35	0	4.690357	-0.744047	-0.071422

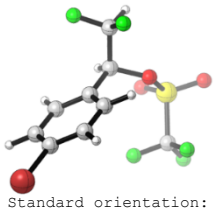
Br-b2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.098017	2.463667	-0.051329
2	9	0	-0.391743	3.302906	0.773418
3	9	0	-0.679074	2.702411	-1.334002
4	8	0	-1.688739	0.224054	-0.492811
5	6	0	-0.799844	1.019120	0.371680
6	6	0	0.636878	0.586542	0.231855
7	6	0	1.420501	0.453172	1.384073
8	6	0	1.204002	0.325372	-1.023232
9	6	0	2.759629	0.071136	1.293239
10	6	0	2.538738	-0.063252	-1.126541
11	1	0	0.604493	0.413062	-1.922448
12	6	0	3.302575	-0.183953	0.035413
13	1	0	3.361941	-0.034731	2.188054
14	1	0	2.974298	-0.270749	-2.097177
15	1	0	-2.158611	2.716430	0.013677
16	1	0	-1.129331	0.915336	1.407951
17	16	0	-2.364519	-1.139633	0.072280
18	8	0	-2.170847	-2.186509	-0.914852
19	8	0	-2.053232	-1.319327	1.484518
20	6	0	-4.172089	-0.605047	-0.041008
21	9	0	-4.935193	-1.615420	0.378426
22	9	0	-4.372312	0.460612	0.740224
23	9	0	-4.480823	-0.300618	-1.300737
24	1	0	0.988421	0.640674	2.362750
25	35	0	5.127763	-0.721177	-0.099571

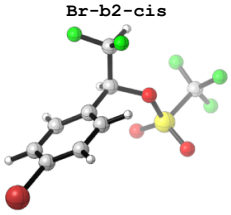
Br-b-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.304314	2.863245	-0.094985
2	9	0	-0.545613	3.664973	0.721152
3	9	0	-0.868631	3.058967	-1.379432
4	8	0	-2.025384	0.646011	-0.517943
5	6	0	-1.103220	1.406948	0.345044
6	6	0	0.301875	0.879737	0.219000
7	6	0	1.063175	0.692349	1.378553
8	6	0	0.863303	0.583316	-1.031098
9	6	0	2.372159	0.214585	1.300623
10	6	0	2.167756	0.100522	-1.121507
11	6	0	2.908224	-0.078432	0.048149
12	1	0	2.956640	0.066614	2.201336
13	1	0	2.598603	-0.133448	-2.088275
14	1	0	-2.346378	3.184566	-0.034461
15	1	0	-1.452605	1.340175	1.377927
16	16	0	-3.150096	-0.334367	0.115741
17	8	0	-3.303892	-0.084012	1.543439
18	8	0	-4.268464	-0.337458	-0.810062
19	6	0	-2.294685	-2.009570	-0.068656
20	9	0	-3.145894	-2.954896	0.334339
21	9	0	-1.967101	-2.213410	-1.343824
22	9	0	-1.197256	-2.043051	0.689409
23	1	0	0.637208	0.912939	2.353065
24	1	0	0.282873	0.718308	-1.937011
25	35	0	4.690913	-0.744716	-0.071241

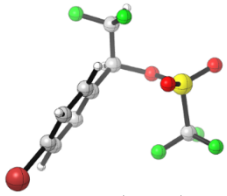
Br-b2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.097336	2.463717	-0.052224
2	9	0	-0.390711	3.303146	0.772030
3	9	0	-0.678209	2.701470	-1.335011
4	8	0	-1.689174	0.224308	-0.492343
5	6	0	-0.799786	1.019279	0.371577
6	6	0	0.636824	0.586208	0.231760
7	6	0	1.421035	0.455233	1.383849
8	6	0	1.203259	0.322725	-1.023135
9	6	0	2.760187	0.073270	1.293025
10	6	0	2.538014	-0.065889	-1.126359
11	6	0	3.302505	-0.184166	0.035407
12	1	0	3.362981	-0.030747	2.187738
13	1	0	2.973082	-0.275232	-2.096824
14	1	0	-2.157825	2.716971	0.012626
15	1	0	-1.129212	0.916131	1.407938
16	16	0	-2.364747	-1.139274	0.073225
17	8	0	-2.170387	-2.186793	-0.913098
18	8	0	-2.054112	-1.317991	1.485741
19	6	0	-4.172302	-0.604943	-0.041243
20	9	0	-4.935491	-1.615395	0.377816
21	9	0	-4.373068	0.460741	0.739822
22	9	0	-4.480384	-0.300597	-1.301145
23	1	0	0.989344	0.644480	2.362356
24	1	0	0.603213	0.408619	-1.922169
25	35	0	5.127717	-0.721283	-0.099520

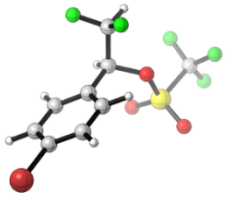
Br-b3



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.628566	2.804798	0.283778
2	9	0	-0.713858	3.780925	0.592569
3	9	0	-1.718858	2.742101	-1.083790
4	8	0	-2.265194	0.508289	0.759365
5	6	0	-1.147153	1.488234	0.900593
6	6	0	0.228546	0.985262	0.549634
7	6	0	0.972836	0.390407	1.580069
8	6	0	0.801575	1.098131	-0.726194
9	6	0	2.256387	-0.100983	1.349577
10	6	0	2.087224	0.616296	-0.968005
11	1	0	0.250365	1.551024	-1.539533
12	6	0	2.799031	0.016820	0.070895
13	1	0	2.822710	-0.558671	2.152317
14	1	0	2.524755	0.706000	-1.955540
15	1	0	-1.190303	1.645426	1.980324
16	16	0	-2.644375	-0.410288	-0.517875
17	8	0	-4.092323	-0.368486	-0.646935
18	8	0	-1.759655	-0.208234	-1.653994
19	6	0	-2.228807	-2.095443	0.226568
20	9	0	-2.902672	-2.273608	1.364387
21	9	0	-2.583142	-3.035211	-0.653957
22	9	0	-0.919093	-2.180896	0.465378
23	1	0	-2.604828	3.105180	0.670211
24	1	0	0.548939	0.306887	2.576916
25	35	0	4.559655	-0.633278	-0.257970

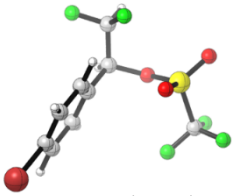
Br-b4



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.096914	2.463638	-0.052668
2	9	0	-0.390838	3.303353	0.771885
3	9	0	-0.677008	2.700897	-1.335230
4	8	0	-1.689195	0.224424	-0.492416
5	6	0	-0.799694	1.019264	0.371551
6	6	0	0.636814	0.585948	0.231882
7	6	0	1.421073	0.455157	1.383944
8	6	0	1.203087	0.321913	-1.022977
9	6	0	2.760208	0.073115	1.293084
10	6	0	2.537815	-0.066735	-1.126239
11	1	0	0.602887	0.407511	-1.921945
12	6	0	3.302423	-0.184668	0.035498
13	1	0	3.363089	-0.030566	2.187778
14	1	0	2.972813	-0.276292	-2.096690
15	1	0	-1.129268	0.916192	1.407862
16	16	0	-2.364916	-1.139092	0.073233
17	8	0	-2.170803	-2.186792	-0.913020
18	8	0	-2.054091	-1.317904	1.485718
19	6	0	-4.172571	-0.604630	-0.041180
20	9	0	-4.935656	-1.615053	0.378104
21	9	0	-4.373331	0.461148	0.739725
22	9	0	-4.480753	-0.300542	-1.301111
23	1	0	-2.157429	2.716915	0.011471
24	1	0	0.989514	0.644726	2.362450
25	35	0	5.127845	-0.721059	-0.099504

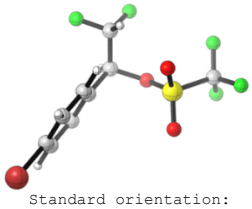
Br-b3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.355774	2.785342	0.104674
2	9	0	-0.520505	3.827815	0.320887
3	9	0	-1.356996	2.545096	-1.220086
4	8	0	-2.046642	0.536420	0.756456
5	6	0	-0.959842	1.511326	0.869861
6	6	0	0.421153	0.939397	0.592889
7	6	0	1.388587	0.813852	1.615690
8	6	0	0.794592	0.494974	-0.680862
9	6	0	2.649821	0.266777	1.381644
10	6	0	2.065395	-0.027579	-0.933852
11	6	0	2.995957	-0.145104	0.096286
12	1	0	3.351080	0.183806	2.203180
13	1	0	2.315306	-0.350789	-1.939632
14	1	0	-1.034562	1.777082	1.923434
15	16	0	-2.437057	-0.316760	-0.586576
16	8	0	-3.574480	0.296713	-1.252089
17	8	0	-1.252948	-0.735445	-1.322468
18	6	0	-3.096278	-1.802171	0.382642
19	9	0	-4.080817	-1.421854	1.192855
20	9	0	-3.561220	-2.678325	-0.511208
21	9	0	-2.114464	-2.360827	1.088168
22	1	0	-2.343254	3.090057	0.382038
23	1	0	1.210800	1.134397	2.620948
24	1	0	0.096016	0.540755	-1.490057
25	35	0	4.733555	-0.866191	-0.233693

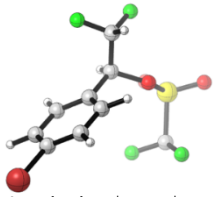
Br-b4-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.097427	2.463535	-0.052296
2	9	0	-0.391131	3.302898	0.772318
3	9	0	-0.677973	2.701573	-1.334928
4	8	0	-1.689040	0.224027	-0.492669
5	6	0	-0.799815	1.019081	0.371393
6	6	0	0.636849	0.586138	0.231650
7	6	0	1.420992	0.455024	1.383790
8	6	0	1.203399	0.322771	-1.023213
9	6	0	2.760151	0.073101	1.293039
10	6	0	2.538184	-0.065775	-1.126378
11	6	0	3.302583	-0.184153	0.035425
12	1	0	3.362882	-0.031004	2.187782
13	1	0	2.973340	-0.274959	-2.096838
14	1	0	-1.129335	0.915817	1.407710
15	16	0	-2.364846	-1.139393	0.072966
16	8	0	-2.170994	-2.186851	-0.913529
17	8	0	-2.053839	-1.318306	1.485371
18	6	0	-4.172338	-0.604731	-0.041016
19	9	0	-4.935581	-1.615069	0.378230
20	9	0	-4.372771	0.460991	0.740084
21	9	0	-4.480652	-0.300354	-1.300850
22	1	0	-2.157954	2.716677	0.012263
23	1	0	0.989255	0.644202	2.362288
24	1	0	0.603439	0.408750	-1.922292
25	35	0	5.127840	-0.721156	-0.099423

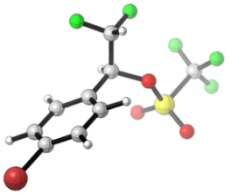
Br-c



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.214580	2.738963	-0.371680
2	9	0	-2.522791	3.119808	-0.209745
3	9	0	-0.445599	3.602075	0.368246
4	8	0	-1.882059	0.476521	-0.653070
5	6	0	-1.019527	1.324631	0.187165
6	6	0	0.402419	0.835867	0.112655
7	6	0	1.140966	0.678979	1.290810
8	6	0	1.006388	0.563281	-1.123022
9	6	0	2.470176	0.256370	1.244218
10	6	0	2.330915	0.133327	-1.182534
11	1	0	0.443697	0.666574	-2.045785
12	6	0	3.049430	-0.013078	0.005280
13	1	0	3.038829	0.133754	2.158808
14	1	0	2.794218	-0.084378	-2.138026
15	1	0	-0.952056	2.848312	-1.426175
16	1	0	-1.394806	1.316315	1.213001
17	16	0	-3.116774	-0.362232	-0.020771
18	8	0	-3.383219	0.057886	1.348289
19	8	0	-4.144715	-0.432109	-1.043365
20	6	0	-2.324059	-2.074105	0.071844
21	9	0	-3.244825	-2.940138	0.498973
22	9	0	-1.886457	-2.441428	-1.132168
23	9	0	-1.302755	-2.046289	0.931631
24	1	0	0.682468	0.884946	2.253507
25	35	0	4.860144	-0.602853	-0.069105

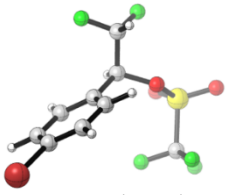
Br-c2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.014141	2.347783	-0.456626
2	9	0	-2.332235	2.686134	-0.281035
3	9	0	-0.263168	3.288969	0.201160
4	8	0	-1.591664	0.064460	-0.582047
5	6	0	-0.740363	0.983506	0.188168
6	6	0	0.706508	0.567146	0.116423
7	6	0	1.491365	0.606515	1.274227
8	6	0	1.285191	0.175214	-1.098465
9	6	0	2.843614	0.265250	1.226679
10	6	0	2.633345	-0.175053	-1.157718
11	1	0	0.684378	0.122519	-2.000987
12	6	0	3.398636	-0.122668	0.008156
13	1	0	3.448257	0.293898	2.125763
14	1	0	3.078098	-0.485520	-2.096158
15	1	0	-0.784549	2.396145	-1.523371
16	1	0	-1.087381	1.020536	1.223278
17	16	0	-2.315778	-1.191965	0.144990
18	8	0	-2.152672	-2.351585	-0.714096
19	8	0	-2.003242	-1.212476	1.567902
20	6	0	-4.112547	-0.634981	-0.032298
21	9	0	-4.895391	-1.613205	0.428767
22	9	0	-4.314752	0.473348	0.680346
23	9	0	-4.392042	-0.404357	-1.314920
24	1	0	1.050874	0.901978	2.221835
25	35	0	5.242058	-0.603873	-0.065269

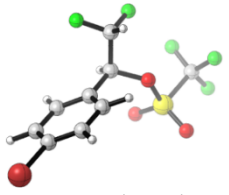
Br-c-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.214902	2.739061	-0.371526
2	9	0	-2.523085	3.119892	-0.209369
3	9	0	-0.445839	3.602088	0.368320
4	8	0	-1.882417	0.476687	-0.653100
5	6	0	-1.019767	1.324715	0.187234
6	6	0	0.402176	0.835959	0.112642
7	6	0	1.140569	0.678674	1.290853
8	6	0	1.006210	0.563754	-1.123077
9	6	0	2.469790	0.256073	1.244259
10	6	0	2.330750	0.133745	-1.182602
11	6	0	3.049056	-0.012990	0.005257
12	1	0	3.038410	0.133207	2.158828
13	1	0	2.794166	-0.083637	-2.138104
14	1	0	-0.952518	2.848447	-1.426058
15	1	0	-1.395017	1.316297	1.213075
16	16	0	-3.116679	-0.362618	-0.020916
17	8	0	-3.383462	0.057405	1.348109
18	8	0	-4.144508	-0.432822	-1.043597
19	6	0	-2.323310	-2.074109	0.071837
20	9	0	-3.243801	-2.940682	0.498495
21	9	0	-1.885014	-2.441177	-1.132011
22	9	0	-1.302394	-2.045914	0.932075
23	1	0	0.681937	0.884419	2.253531
24	1	0	0.443577	0.667381	-2.045837
25	35	0	4.859919	-0.602615	-0.069112

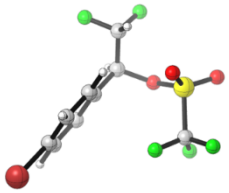
Br-c2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.014042	2.347938	-0.456660
2	9	0	-2.332028	2.686513	-0.280928
3	9	0	-0.262824	3.289125	0.200880
4	8	0	-1.591809	0.064725	-0.581739
5	6	0	-0.740349	0.983725	0.188319
6	6	0	0.706499	0.567272	0.116535
7	6	0	1.491467	0.606835	1.274272
8	6	0	1.285006	0.175049	-1.098337
9	6	0	2.843680	0.265468	1.226642
10	6	0	2.633142	-0.175318	-1.157662
11	6	0	3.398521	-0.122737	0.008124
12	1	0	3.448452	0.294255	2.125633
13	1	0	3.077795	-0.486006	-2.096075
14	1	0	-0.784539	2.396082	-1.523437
15	1	0	-1.087289	1.020948	1.223450
16	16	0	-2.315718	-1.191763	0.145402
17	8	0	-2.151998	-2.351593	-0.713286
18	8	0	-2.003599	-1.211788	1.568412
19	6	0	-4.112576	-0.635301	-0.032654
20	9	0	-4.895323	-1.613495	0.428598
21	9	0	-4.315265	0.473295	0.679456
22	9	0	-4.391769	-0.405267	-1.315450
23	1	0	1.051055	0.902539	2.221831
24	1	0	0.684032	0.122215	-2.000735
25	35	0	5.241943	-0.604049	-0.065390

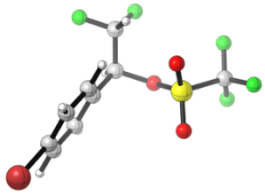
Br-c3



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.766537	2.547873	-0.287485
2	9	0	-3.040290	2.884306	0.094885
3	9	0	-0.987275	3.671503	-0.147839
4	8	0	-2.193887	0.380551	0.835326
5	6	0	-1.212834	1.494843	0.679313
6	6	0	0.196695	1.036515	0.416780
7	6	0	1.008609	0.745624	1.522946
8	6	0	0.726406	0.894251	-0.873846
9	6	0	2.321208	0.309234	1.353401
10	6	0	2.040761	0.466011	-1.057361
11	1	0	0.124556	1.103048	-1.750329
12	6	0	2.823618	0.174243	0.059251
13	1	0	2.941665	0.086859	2.213713
14	1	0	2.445841	0.362847	-2.057274
15	1	0	-1.279021	1.930215	1.678503
16	16	0	-2.696895	-0.602409	-0.342612
17	8	0	-4.110329	-0.851008	-0.117839
18	8	0	-2.177674	-0.185171	-1.640796
19	6	0	-1.812879	-2.201726	0.147416
20	9	0	-2.097162	-2.503786	1.414692
21	9	0	-2.256323	-3.172018	-0.655879
22	9	0	-0.494548	-2.072603	0.003071
23	1	0	-1.792300	2.269072	-1.340457
24	1	0	0.615676	0.860919	2.529076
25	35	0	4.625118	-0.394206	-0.187081

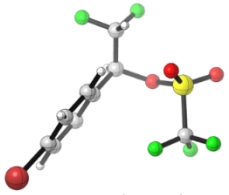
Br-c4



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.318143	2.378994	-0.375303
2	9	0	-2.568205	2.789339	0.014928
3	9	0	-0.493721	3.477965	-0.322211
4	8	0	-1.792320	0.278254	0.813476
5	6	0	-0.788320	1.362075	0.641787
6	6	0	0.612469	0.857984	0.405755
7	6	0	1.415327	0.592102	1.524442
8	6	0	1.140953	0.656107	-0.877528
9	6	0	2.717339	0.119010	1.374263
10	6	0	2.445640	0.191621	-1.041495
11	1	0	0.546596	0.847533	-1.763716
12	6	0	3.219120	-0.075876	0.087411
13	1	0	3.329757	-0.088920	2.243898
14	1	0	2.849105	0.038850	-2.035640
15	1	0	-0.850843	1.839504	1.621622
16	16	0	-1.991673	-0.915803	-0.261157
17	8	0	-1.862934	-0.414720	-1.627093
18	8	0	-1.303699	-2.123360	0.168933
19	6	0	-3.831217	-1.163618	0.096327
20	9	0	-4.247323	-2.190518	-0.649612
21	9	0	-4.015103	-1.443762	1.386003
22	9	0	-4.513914	-0.067904	-0.231304
23	1	0	-1.382352	2.036453	-1.407592
24	1	0	1.022239	0.752728	2.524151
25	35	0	4.996836	-0.722604	-0.132598

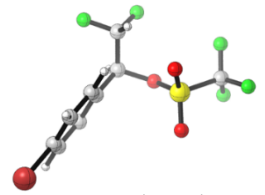
Br-c3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.766323	2.548132	-0.287494
2	9	0	-3.040178	2.884549	0.094832
3	9	0	-0.987055	3.671626	-0.147460
4	8	0	-2.193900	0.380618	0.835129
5	6	0	-1.212848	1.494824	0.679159
6	6	0	0.196711	1.036504	0.416622
7	6	0	1.008617	0.745727	1.522825
8	6	0	0.726434	0.893984	-0.873975
9	6	0	2.321232	0.309316	1.353359
10	6	0	2.040773	0.465702	-1.057415
11	6	0	2.823646	0.174122	0.059247
12	1	0	2.941635	0.087049	2.213736
13	1	0	2.445889	0.362388	-2.057298
14	1	0	-1.278921	1.930190	1.678359
15	16	0	-2.696817	-0.602361	-0.342787
16	8	0	-4.110354	-0.850718	-0.118362
17	8	0	-2.177149	-0.185414	-1.640874
18	6	0	-1.813203	-2.201743	0.147622
19	9	0	-2.097839	-2.503575	1.414894
20	9	0	-2.256529	-3.172090	-0.655620
21	9	0	-0.494785	-2.072726	0.003588
22	1	0	-1.792076	2.269593	-1.340516
23	1	0	0.615730	0.861141	2.528953
24	1	0	0.124505	1.102484	-1.750470
25	35	0	4.625165	-0.394298	-0.187061

Br-c4-cis

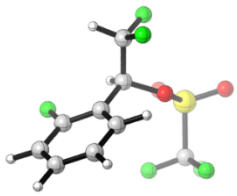


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.318129	2.379431	-0.375059
2	9	0	-2.567851	2.790368	0.015638
3	9	0	-0.493211	3.478003	-0.322643
4	8	0	-1.792765	0.278702	0.813275
5	6	0	-0.788382	1.362402	0.641942
6	6	0	0.612268	0.858102	0.405867
7	6	0	1.414984	0.591709	1.524532
8	6	0	1.140823	0.656521	-0.877439
9	6	0	2.716928	0.118455	1.374312
10	6	0	2.445447	0.191880	-1.041453
11	6	0	3.218773	-0.076146	0.087438
12	1	0	3.329255	-0.089788	2.243937
13	1	0	2.848976	0.039427	-2.035620
14	1	0	-0.850885	1.839595	1.621891
15	16	0	-1.991472	-0.915640	-0.261174
16	8	0	-1.862775	-0.414722	-1.627172
17	8	0	-1.302978	-2.122818	0.169168
18	6	0	-3.830981	-1.164087	0.096168
19	9	0	-4.246638	-2.191266	-0.649635
20	9	0	-4.014960	-1.444057	1.385848
21	9	0	-4.514027	-0.068661	-0.231774
22	1	0	-1.382966	2.036591	-1.407231
23	1	0	1.021825	0.752090	2.524255
24	1	0	0.546585	0.848339	-1.763617
25	35	0	4.996534	-0.722697	-0.132622

5.4.3. Optimized Coordinate of Conformers of 1-(2-Fluorophenyl)-2,2-difluoroethanol Triflate (4-F)

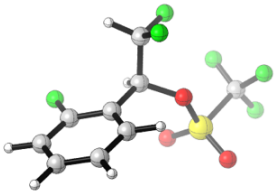
F-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.858959	2.456276	0.026579
2	9	0	1.110787	2.673424	-1.304080
3	9	0	-0.216050	3.240888	0.363690
4	8	0	-0.635605	0.665342	-0.548811
5	6	0	0.522395	0.986169	0.291776
6	6	0	1.654341	0.042096	-0.029013
7	6	0	2.421435	-0.507515	0.999651
8	6	0	1.988223	-0.311821	-1.345718
9	6	0	3.480460	-1.376662	0.775209
10	6	0	3.044643	-1.185268	-1.601994
11	1	0	1.407615	0.095258	-2.166266
12	6	0	3.790454	-1.715451	-0.543278
13	1	0	4.037569	-1.772448	1.617113
14	1	0	3.286359	-1.450950	-2.625716
15	1	0	4.614401	-2.393670	-0.740950
16	1	0	1.726045	2.786797	0.603968
17	1	0	0.237394	0.909655	1.342846
18	16	0	-2.081569	0.336677	0.107843
19	8	0	-2.072972	0.597113	1.541096
20	8	0	-3.090651	0.870898	-0.788144
21	6	0	-2.093469	-1.538069	-0.113226
22	9	0	-3.247550	-2.009706	0.362827
23	9	0	-1.980971	-1.847164	-1.404709
24	9	0	-1.076511	-2.074553	0.566590
25	9	0	2.119728	-0.174758	2.287957

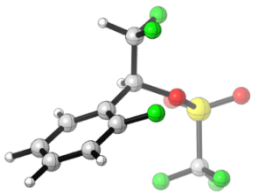
F-a2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.526288	2.171442	-0.131907
2	9	0	0.731069	2.360526	-1.474736
3	9	0	-0.701544	2.706444	0.166685
4	8	0	-0.496553	0.071777	-0.606791
5	6	0	0.544417	0.681039	0.219819
6	6	0	1.884104	0.031196	-0.038957
7	6	0	2.818399	-0.071777	0.992631
8	6	0	2.250562	-0.468129	-1.297041
9	6	0	4.071216	-0.645194	0.828128
10	6	0	3.502603	-1.051674	-1.493086
11	1	0	1.542168	-0.407786	-2.115955
12	6	0	4.411310	-1.139276	-0.433104
13	1	0	4.751564	-0.700149	1.670745
14	1	0	3.767618	-1.438348	-2.471484
15	1	0	5.385562	-1.593038	-0.584094
16	1	0	1.290434	2.725504	0.418796
17	1	0	0.274427	0.590891	1.273972
18	16	0	-1.434808	-1.110007	-0.009324
19	8	0	-1.597534	-2.103080	-1.056118
20	8	0	-1.032281	-1.450162	1.349099
21	6	0	-3.070134	-0.170505	0.105775
22	9	0	-4.015140	-1.034289	0.485254
23	9	0	-2.966183	0.803634	1.010122
24	9	0	-3.384933	0.345826	-1.080914
25	9	0	2.483789	0.419196	2.221824

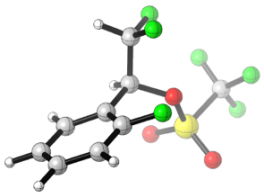
F-a-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.898097	2.437599	-0.329837
2	9	0	-1.296392	2.683774	0.954486
3	9	0	0.205802	3.222056	-0.566672
4	8	0	0.567668	0.658095	0.382285
5	6	0	-0.522384	0.967478	-0.547467
6	6	0	-1.664775	-0.005530	-0.390260
7	6	0	-2.253657	-0.554530	-1.541040
8	6	0	-2.199642	-0.386725	0.845602
9	6	0	-3.334903	-1.432003	-1.454351
10	6	0	-3.267952	-1.266553	0.960463
11	6	0	-3.840662	-1.788510	-0.201334
12	1	0	-3.771483	-1.841500	-2.359069
13	1	0	-3.634175	-1.528539	1.947072
14	1	0	-4.676905	-2.475884	-0.123036
15	1	0	-1.696229	2.750145	-1.008384
16	1	0	-0.138140	0.905840	-1.568621
17	16	0	2.060311	0.341722	-0.163675
18	8	0	2.138244	0.537196	-1.606343
19	8	0	3.001834	0.940302	0.764480
20	6	0	2.100476	-1.520207	0.143780
21	9	0	3.291430	-1.982972	-0.243355
22	9	0	1.919147	-1.775585	1.438307
23	9	0	1.138226	-2.111901	-0.569724
24	1	0	-1.852439	-0.289955	-2.515432
25	9	0	-1.654656	0.100349	1.988018

F-a2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.527929	2.150216	-0.523399
2	9	0	-0.813260	2.609002	0.732736
3	9	0	0.732509	2.597205	-0.838621
4	8	0	0.424045	0.136460	0.370029
5	6	0	-0.560129	0.620655	-0.600690
6	6	0	-1.925163	0.015453	-0.376078
7	6	0	-2.650714	-0.452135	-1.483618
8	6	0	-2.534585	-0.091622	0.879429
9	6	0	-3.930954	-0.987303	-1.339342
10	6	0	-3.802577	-0.631339	1.052273
11	6	0	-4.505776	-1.077474	-0.068740
12	1	0	-4.469743	-1.340651	-2.212070
13	1	0	-4.218851	-0.694660	2.051681
14	1	0	-5.497864	-1.499660	0.055426
15	1	0	-1.237984	2.593912	-1.226165
16	1	0	-0.220080	0.358019	-1.605606
17	16	0	1.401565	-1.101059	-0.003803
18	8	0	1.389333	-2.035258	1.108202
19	8	0	1.194421	-1.522631	-1.384683
20	6	0	3.059047	-0.197115	0.067671
21	9	0	4.027132	-1.103323	-0.096036
22	9	0	3.124416	0.705743	-0.910702
23	9	0	3.202722	0.402772	1.247983
24	1	0	-2.197868	-0.398491	-2.469648
25	9	0	-1.870448	0.330141	1.983954

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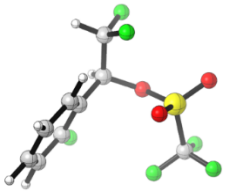

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.769346	2.557768	0.414751
2	9	0	0.285653	2.756906	-0.855998
3	9	0	-0.006498	3.316003	1.253890
4	8	0	-0.744905	0.661952	0.767714
5	6	0	0.671896	1.089957	0.825733
6	6	0	1.663213	0.157071	0.179137
7	6	0	2.072906	-0.976624	0.890009
8	6	0	2.252234	0.370585	-1.077753
9	6	0	3.009083	-1.881016	0.411493
10	6	0	3.201993	-0.517233	-1.582493
11	1	0	1.956349	1.227155	-1.671557
12	6	0	3.577439	-1.642157	-0.841627
13	1	0	3.280579	-2.741787	1.012393
14	1	0	3.642663	-0.333878	-2.556655
15	1	0	4.312916	-2.336118	-1.235936
16	1	0	0.825792	1.071277	1.906382
17	16	0	-1.597197	0.272105	-0.555164
18	8	0	-2.777021	1.120454	-0.604839
19	8	0	-0.760615	0.043965	-1.723531
20	6	0	-2.174372	-1.416895	0.059199
21	9	0	-2.833555	-1.292579	1.211253
22	9	0	-2.987768	-1.934009	-0.866808
23	9	0	-1.124369	-2.223804	0.227445
24	1	0	1.795360	2.930465	0.461317
25	9	0	1.526468	-1.203684	2.117022

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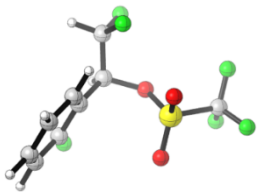
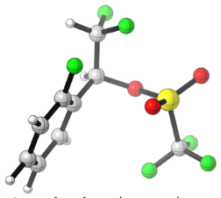


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.531029	2.485906	0.147260
2	9	0	0.086087	2.489992	-1.149195
3	9	0	-0.397872	3.178953	0.885000
4	8	0	-0.682430	0.441932	0.637585
5	6	0	0.658464	1.069191	0.705757
6	6	0	1.796414	0.254640	0.144660
7	6	0	2.496080	-0.604800	1.000707
8	6	0	2.231207	0.323642	-1.190439
9	6	0	3.573105	-1.375900	0.591618
10	6	0	3.312695	-0.440282	-1.629109
11	1	0	1.713241	0.967888	-1.890524
12	6	0	3.981298	-1.288196	-0.741142
13	1	0	4.069846	-2.024995	1.303983
14	1	0	3.629737	-0.374916	-2.664431
15	1	0	4.821151	-1.884799	-1.082694
16	1	0	0.797064	1.179102	1.782576
17	16	0	-1.102809	-0.731036	-0.396245
18	8	0	-0.984178	-0.315777	-1.787552
19	8	0	-0.591865	-2.023159	0.043888
20	6	0	-2.931860	-0.650145	0.074422
21	9	0	-3.564819	-1.576183	-0.652965
22	9	0	-3.092387	-0.916496	1.370383
23	9	0	-3.429914	0.553045	-0.206070
24	1	0	1.480184	3.026202	0.194521
25	9	0	2.100118	-0.691556	2.299815

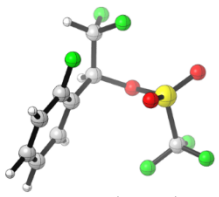
F-a3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.985021	2.378344	0.519800
2	9	0	0.365062	2.649006	-0.668665
3	9	0	0.460934	3.258444	1.441123
4	8	0	-0.759851	0.686828	0.844920
5	6	0	0.690098	0.949922	0.998320
6	6	0	1.590255	-0.171681	0.535361
7	6	0	1.681034	-1.313382	1.352313
8	6	0	2.365494	-0.166612	-0.627307
9	6	0	2.487214	-2.395206	1.006285
10	6	0	3.186944	-1.224894	-0.993545
11	6	0	3.242043	-2.349903	-0.170413
12	1	0	2.533079	-3.264127	1.654112
13	1	0	3.762551	-1.155371	-1.909900
14	1	0	3.878009	-3.184827	-0.446667
15	1	0	0.754503	0.991967	2.087433
16	16	0	-1.520346	0.320688	-0.542432
17	8	0	-2.569591	1.299654	-0.774328
18	8	0	-0.599273	-0.093922	-1.589515
19	6	0	-2.381039	-1.232013	0.100041
20	9	0	-3.156990	-0.932764	1.143165
21	9	0	-3.133447	-1.722514	-0.889391
22	9	0	-1.476518	-2.144118	0.463040
23	1	0	2.052008	2.584942	0.422501
24	1	0	1.100984	-1.347517	2.270252
25	9	0	2.340040	0.920389	-1.441780

F-a4-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.985326	2.378262	0.519719
2	9	0	0.365068	2.649150	-0.668613
3	9	0	0.461704	3.258451	1.441178
4	8	0	-0.759770	0.686844	0.845053
5	6	0	0.690123	0.949836	0.998305
6	6	0	1.590248	-0.171850	0.535358
7	6	0	1.680724	-1.313617	1.352230
8	6	0	2.365641	-0.166862	-0.627225
9	6	0	2.486822	-2.395538	1.006265
10	6	0	3.187014	-1.225200	-0.993400
11	6	0	3.241849	-2.350257	-0.170286
12	1	0	2.532449	-3.264537	1.654007
13	1	0	3.762759	-1.155748	-1.909669
14	1	0	3.877765	-3.185248	-0.446454
15	1	0	0.754659	0.992012	2.087410
16	16	0	-1.520063	0.320618	-0.542540
17	8	0	-2.568810	1.299957	-0.775019
18	8	0	-0.598698	-0.094686	-1.589065
19	6	0	-2.381572	-1.231562	0.100054
20	9	0	-3.134072	-1.721789	-0.889434
21	9	0	-1.477545	-2.144061	0.463308
22	9	0	-3.157509	-0.931818	1.143063
23	1	0	2.052327	2.584600	0.422046
24	1	0	1.100461	-1.347755	2.270032
25	9	0	2.340325	0.920134	-1.441790

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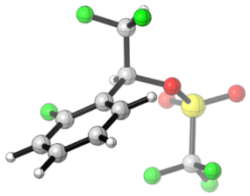
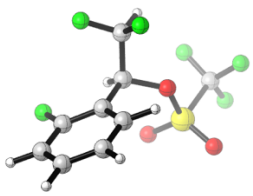


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.062830	2.410040	-0.110091
2	9	0	2.186361	2.634496	0.645001
3	9	0	1.431039	2.497385	-1.427474
4	8	0	-0.686812	0.874739	-0.588941
5	6	0	0.532152	1.009466	0.224794
6	6	0	1.481894	-0.118930	-0.079445
7	6	0	2.161299	-0.760061	0.958026
8	6	0	1.728187	-0.564860	-1.387568
9	6	0	3.055589	-1.801100	0.749222
10	6	0	2.618251	-1.611141	-1.627630
11	1	0	1.209540	-0.092337	-2.214353
12	6	0	3.282740	-2.226457	-0.560983
13	1	0	3.552158	-2.259632	1.597161
14	1	0	2.793958	-1.945121	-2.644803
15	1	0	3.977576	-3.039482	-0.745888
16	1	0	0.335764	3.198700	0.095137
17	1	0	0.258662	1.018927	1.281459
18	16	0	-2.135596	0.642399	0.101790
19	8	0	-2.086776	0.962554	1.522513
20	8	0	-3.118923	1.209296	-0.803097
21	6	0	-2.280621	-1.235969	-0.042177
22	9	0	-3.467452	-1.601733	0.444537
23	9	0	-2.186162	-1.601618	-1.319730
24	9	0	-1.307864	-1.815900	0.665055
25	9	0	1.936083	-0.350195	2.238607

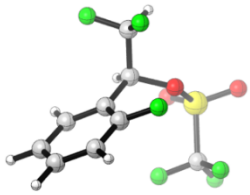
F-b2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.511072	2.172343	-0.208289
2	9	0	1.478379	2.794459	0.539035
3	9	0	0.851606	2.324331	-1.527151
4	8	0	-0.617934	0.140450	-0.617502
5	6	0	0.482566	0.689457	0.186425
6	6	0	1.764194	-0.059765	-0.073690
7	6	0	2.642899	-0.329336	0.977231
8	6	0	2.128319	-0.506336	-1.353221
9	6	0	3.840508	-1.010258	0.807685
10	6	0	3.324274	-1.195261	-1.553525
11	1	0	1.460566	-0.322140	-2.187532
12	6	0	4.179778	-1.445080	-0.475022
13	1	0	4.479863	-1.191561	1.664529
14	1	0	3.587244	-1.537845	-2.548786
15	1	0	5.110943	-1.981132	-0.628531
16	1	0	-0.442768	2.677120	-0.040802
17	1	0	0.217525	0.640236	1.244111
18	16	0	-1.590825	-1.004457	0.001449
19	8	0	-1.789494	-2.017330	-1.019294
20	8	0	-1.204960	-1.323436	1.369347
21	6	0	-3.181838	0.009277	0.086726
22	9	0	-4.146090	-0.762171	0.590004
23	9	0	-2.992740	1.066537	0.882416
24	9	0	-3.525909	0.423042	-1.131914
25	9	0	2.311234	0.091459	2.230667

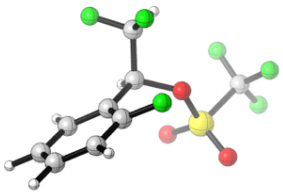
F-b-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.134796	2.391829	-0.043843
2	9	0	-2.116832	2.692009	-0.958700
3	9	0	-1.722218	2.380727	1.189756
4	8	0	0.618003	0.851159	0.459690
5	6	0	-0.551974	1.020099	-0.415851
6	6	0	-1.502201	-0.144340	-0.307487
7	6	0	-2.072301	-0.666150	-1.479572
8	6	0	-1.882316	-0.731099	0.904724
9	6	0	-2.987650	-1.717933	-1.434620
10	6	0	-2.781676	-1.786538	0.976971
11	6	0	-3.340628	-2.278947	-0.204399
12	1	0	-3.415770	-2.100240	-2.355155
13	1	0	-3.031307	-2.204203	1.946199
14	1	0	-4.046550	-3.102126	-0.159526
15	1	0	-0.383395	3.184486	-0.063385
16	1	0	-0.201933	1.111994	-1.446743
17	16	0	2.103687	0.662405	-0.160106
18	8	0	2.111226	0.966741	-1.586107
19	8	0	3.030770	1.267601	0.778795
20	6	0	2.300184	-1.208449	0.009821
21	9	0	3.515457	-1.540643	-0.430353
22	9	0	2.170230	-1.566100	1.285740
23	9	0	1.373345	-1.825031	-0.727496
24	1	0	-1.793067	-0.236056	-2.436992
25	9	0	-1.347405	-0.275092	2.065920

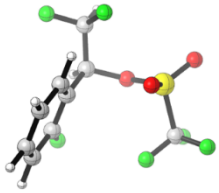
F-b2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.519098	2.163965	-0.133268
2	9	0	-1.348701	2.784282	-1.037275
3	9	0	-1.023257	2.410367	1.112532
4	8	0	0.541760	0.101692	0.397018
5	6	0	-0.506626	0.665014	-0.465274
6	6	0	-1.819912	-0.056776	-0.303286
7	6	0	-2.563219	-0.380758	-1.449455
8	6	0	-2.364117	-0.415897	0.935178
9	6	0	-3.798421	-1.022168	-1.355518
10	6	0	-3.585748	-1.064900	1.056181
11	6	0	-4.308547	-1.364953	-0.100472
12	1	0	-4.353065	-1.259820	-2.257014
13	1	0	-3.952081	-1.323829	2.043543
14	1	0	-5.265120	-1.870888	-0.016909
15	1	0	0.472659	2.616697	-0.200559
16	1	0	-0.179186	0.586452	-1.504846
17	16	0	1.583206	-0.993643	-0.193446
18	8	0	1.639874	-2.116052	0.725674
19	8	0	1.393127	-1.162311	-1.629159
20	6	0	3.171133	-0.002158	0.052124
21	9	0	4.194372	-0.732803	-0.393581
22	9	0	3.098789	1.136564	-0.644270
23	9	0	3.343145	0.273066	1.343660
24	1	0	-2.161976	-0.125426	-2.425798
25	9	0	-1.678048	-0.142556	2.073512

F-b3



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.090810	2.399061	0.643810
2	9	0	2.434564	2.599016	0.832919
3	9	0	0.795321	2.760000	-0.648389
4	8	0	-0.711065	0.792839	0.879634
5	6	0	0.769905	0.927667	0.919865
6	6	0	1.545457	-0.125105	0.173670
7	6	0	1.743063	-1.362652	0.797015
8	6	0	2.132008	0.052854	-1.090166
9	6	0	2.468906	-2.398954	0.229296
10	6	0	2.872687	-0.968393	-1.683893
11	1	0	2.003467	0.991780	-1.613036
12	6	0	3.038757	-2.192558	-1.028689
13	1	0	2.580409	-3.334186	0.766523
14	1	0	3.316314	-0.808756	-2.660929
15	1	0	3.611945	-2.988552	-1.493324
16	1	0	0.931915	0.786893	1.990287
17	16	0	-1.648781	0.647752	-0.435447
18	8	0	-2.691397	1.658059	-0.346984
19	8	0	-0.888455	0.426920	-1.655278
20	6	0	-2.449593	-0.995164	0.038271
21	9	0	-3.070064	-0.884098	1.213158
22	9	0	-3.338702	-1.309072	-0.908159
23	9	0	-1.520353	-1.950105	0.109910
24	1	0	0.540181	3.066550	1.309746
25	9	0	1.193856	-1.562502	2.028765

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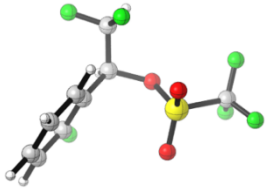
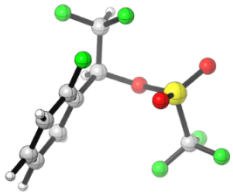


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.620739	2.411434	0.395188
2	9	0	1.855832	2.962353	0.634994
3	9	0	0.344489	2.580343	-0.936822
4	8	0	-0.737947	0.455821	0.712422
5	6	0	0.666985	0.935932	0.804015
6	6	0	1.705769	0.061892	0.152122
7	6	0	2.346736	-0.906857	0.934649
8	6	0	2.102129	0.161381	-1.193400
9	6	0	3.330311	-1.753531	0.447275
10	6	0	3.088971	-0.677572	-1.710144
11	1	0	1.632170	0.893221	-1.837590
12	6	0	3.701121	-1.633045	-0.893525
13	1	0	3.784689	-2.484164	1.106995
14	1	0	3.377840	-0.584809	-2.751635
15	1	0	4.467607	-2.287038	-1.296960
16	1	0	0.826568	0.928274	1.882881
17	16	0	-1.297493	-0.559072	-0.419587
18	8	0	-1.176399	-0.008284	-1.762771
19	8	0	-0.905018	-1.932435	-0.133043
20	6	0	-3.097397	-0.356834	0.121911
21	9	0	-3.833995	-1.148254	-0.663191
22	9	0	-3.248253	-0.725443	1.393778
23	9	0	-3.487432	0.908945	-0.030958
24	1	0	-0.126188	2.968328	0.964874
25	9	0	1.987128	-1.029752	2.242578

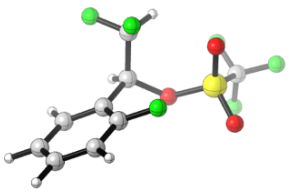
F-b3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.068271	2.256550	-0.834127
2	9	0	-2.426798	2.412085	-0.938449
3	9	0	-0.682363	2.662302	0.414218
4	8	0	0.759330	0.665555	-0.954474
5	6	0	-0.712730	0.788464	-1.113029
6	6	0	-1.519755	-0.341598	-0.519051
7	6	0	-1.610937	-1.519775	-1.284297
8	6	0	-2.197488	-0.334096	0.704919
9	6	0	-2.321776	-2.631899	-0.839831
10	6	0	-2.923408	-1.425149	1.167991
11	6	0	-2.981618	-2.582511	0.391903
12	1	0	-2.368183	-3.525206	-1.453554
13	1	0	-3.427662	-1.351929	2.125262
14	1	0	-3.545816	-3.438715	0.747766
15	1	0	-0.780321	0.685383	-2.198026
16	16	0	1.576213	0.536324	0.443100
17	8	0	2.465255	1.680045	0.574852
18	8	0	0.741165	0.075670	1.540785
19	6	0	2.649773	-0.917974	-0.102550
20	9	0	3.341902	-0.597962	-1.197363
21	9	0	3.495443	-1.198674	0.893034
22	9	0	1.886610	-1.983952	-0.351189
23	1	0	-0.588446	2.920461	-1.556764
24	1	0	-1.107188	-1.557194	-2.246198
25	9	0	-2.171519	0.768841	1.487643

F-b4-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.406028	1.917469	-0.545918
2	9	0	1.137254	3.013906	-0.133843
3	9	0	0.913021	1.549197	-1.756312
4	8	0	-0.512576	-0.104896	0.705614
5	6	0	0.613337	0.842495	0.542540
6	6	0	1.929526	0.112872	0.485332
7	6	0	2.932105	0.434057	1.413231
8	6	0	2.223857	-0.878498	-0.454594
9	6	0	4.174136	-0.201646	1.383547
10	6	0	3.443057	-1.537857	-0.500695
11	6	0	4.427534	-1.188629	0.427246
12	1	0	4.934917	0.066658	2.108808
13	1	0	3.606558	-2.304219	-1.250283
14	1	0	5.387808	-1.693765	0.402630
15	1	0	0.557867	1.390179	1.484596
16	16	0	-1.580005	-0.660501	-0.372885
17	8	0	-1.552933	0.092556	-1.618534
18	8	0	-1.568417	-2.112245	-0.338901
19	6	0	-3.122772	-0.115107	0.567848
20	9	0	-4.194022	-0.486303	-0.137138
21	9	0	-3.160587	-0.685311	1.771858
22	9	0	-3.119186	1.215558	0.702974
23	1	0	-0.631113	2.226936	-0.675019
24	1	0	2.732172	1.194144	2.162708
25	9	0	1.268234	-1.232177	-1.354641

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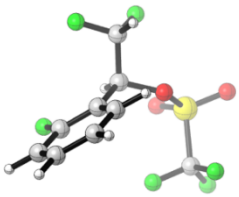

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.941035	2.352749	-0.500053
2	9	0	-0.061196	3.251512	-0.236472
3	9	0	2.058106	2.777722	0.173963
4	8	0	-0.652605	0.596201	-0.717809
5	6	0	0.548410	0.973595	0.042598
6	6	0	1.613888	-0.068591	-0.166300
7	6	0	2.320593	-0.589470	0.919020
8	6	0	1.949150	-0.541384	-1.445192
9	6	0	3.323700	-1.539639	0.782021
10	6	0	2.950108	-1.497544	-1.613383
11	1	0	1.408399	-0.169175	-2.309963
12	6	0	3.637506	-1.994031	-0.500292
13	1	0	3.837191	-1.907476	1.663379
14	1	0	3.192470	-1.855066	-2.608542
15	1	0	4.418445	-2.736899	-0.627448
16	1	0	1.147349	2.371885	-1.572443
17	1	0	0.292485	1.084222	1.097709
18	16	0	-2.099384	0.454995	0.004156
19	8	0	-2.042027	0.922649	1.382044
20	8	0	-3.096262	0.911839	-0.947175
21	6	0	-2.220637	-1.428614	0.059631
22	9	0	-3.374355	-1.757817	0.643342
23	9	0	-2.186337	-1.923354	-1.177536
24	9	0	-1.202731	-1.922913	0.768749
25	9	0	2.015230	-0.149077	2.170846

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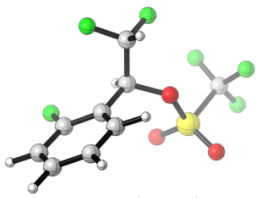
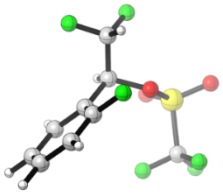


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.526409	2.071240	-0.695260
2	9	0	-0.670626	2.701761	-0.472740
3	9	0	1.503878	2.834704	-0.109529
4	8	0	-0.543186	-0.031086	-0.718847
5	6	0	0.522081	0.696186	-0.016095
6	6	0	1.836814	-0.028057	-0.153637
7	6	0	2.707397	-0.130625	0.932714
8	6	0	2.245778	-0.598689	-1.369060
9	6	0	3.938209	-0.768330	0.856677
10	6	0	3.476772	-1.245727	-1.475202
11	1	0	1.583879	-0.551612	-2.228269
12	6	0	4.321917	-1.328667	-0.363320
13	1	0	4.570088	-0.819762	1.736423
14	1	0	3.774239	-1.686268	-2.420904
15	1	0	5.280284	-1.831911	-0.441914
16	1	0	0.704450	2.036138	-1.772255
17	1	0	0.249909	0.829132	1.032246
18	16	0	-1.476803	-1.096175	0.074728
19	8	0	-1.682634	-2.230673	-0.808121
20	8	0	-1.037511	-1.236087	1.456219
21	6	0	-3.094593	-0.120310	0.092171
22	9	0	-4.028782	-0.877793	0.671352
23	9	0	-2.934123	1.004721	0.789407
24	9	0	-3.463202	0.170353	-1.155125
25	9	0	2.335962	0.417780	2.122312

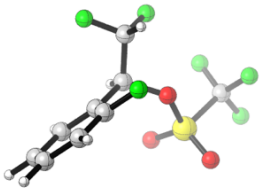
F-c-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.047857	2.353315	0.149621
2	9	0	-0.054336	3.275102	-0.068268
3	9	0	-2.127327	2.731582	-0.610864
4	8	0	0.574750	0.647028	0.517307
5	6	0	-0.573129	0.982294	-0.347072
6	6	0	-1.604938	-0.109674	-0.282327
7	6	0	-1.986848	-0.789832	-1.448146
8	6	0	-2.223233	-0.490347	0.912555
9	6	0	-2.945945	-1.802987	-1.408719
10	6	0	-3.174549	-1.496199	0.985461
11	6	0	-3.536484	-2.156404	-0.192290
12	1	0	-3.227312	-2.315227	-2.322612
13	1	0	-3.615962	-1.747806	1.943464
14	1	0	-4.280197	-2.945902	-0.154169
15	1	0	-1.325932	2.386471	1.203006
16	1	0	-0.218478	1.108301	-1.372401
17	16	0	2.066191	0.475606	-0.092486
18	8	0	2.085822	0.791292	-1.515219
19	8	0	2.997098	1.059247	0.856555
20	6	0	2.233747	-1.398041	0.066661
21	9	0	3.438873	-1.750496	-0.386245
22	9	0	2.110306	-1.759867	1.343104
23	9	0	1.289393	-1.997535	-0.662756
24	1	0	-1.524640	-0.517893	-2.392456
25	9	0	-1.876075	0.155556	2.061844

F-c2-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.547443	2.157172	0.061215
2	9	0	0.674523	2.713789	-0.222452
3	9	0	-1.481936	2.824661	-0.691276
4	8	0	0.457994	0.057366	0.498336
5	6	0	-0.544871	0.688878	-0.381011
6	6	0	-1.872936	-0.009728	-0.272458
7	6	0	-2.464466	-0.579721	-1.409413
8	6	0	-2.566369	-0.124892	0.936187
9	6	0	-3.695292	-1.232724	-1.329017
10	6	0	-3.786912	-0.772223	1.049636
11	6	0	-4.353581	-1.330082	-0.100018
12	1	0	-4.134730	-1.666709	-2.220802
13	1	0	-4.273838	-0.831689	2.016689
14	1	0	-5.308741	-1.840585	-0.029993
15	1	0	-0.763071	2.315591	1.117924
16	1	0	-0.187805	0.651571	-1.412237
17	16	0	1.451856	-1.087680	-0.072758
18	8	0	1.496455	-2.162050	0.903746
19	8	0	1.207665	-1.322539	-1.490631
20	6	0	3.092122	-0.160708	0.071281
21	9	0	4.072718	-1.007621	-0.252566
22	9	0	3.102525	0.875408	-0.767395
23	9	0	3.265438	0.268229	1.321132
24	1	0	-1.948821	-0.510642	-2.362520
25	9	0	-2.018947	0.424123	2.057563

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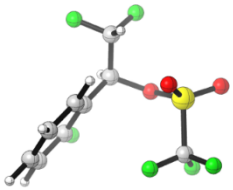
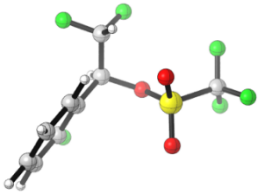


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.745317	2.457984	-0.272258
2	9	0	-0.018903	3.417400	0.340956
3	9	0	2.048308	2.893852	-0.246405
4	8	0	-0.735659	0.818492	0.846014
5	6	0	0.683437	1.168077	0.554410
6	6	0	1.505461	0.023131	0.029461
7	6	0	2.102828	-0.852193	0.943712
8	6	0	1.740373	-0.220213	-1.333984
9	6	0	2.893913	-1.926729	0.566188
10	6	0	2.533316	-1.291462	-1.744674
11	1	0	1.293921	0.422438	-2.083475
12	6	0	3.107344	-2.144163	-0.796846
13	1	0	3.326763	-2.568065	1.325794
14	1	0	2.700314	-1.460543	-2.803074
15	1	0	3.723034	-2.979495	-1.114739
16	1	0	1.013994	1.429941	1.560683
17	16	0	-1.849473	0.439037	-0.261258
18	8	0	-3.099685	1.046479	0.160388
19	8	0	-1.325673	0.596367	-1.613774
20	6	0	-2.039335	-1.411834	0.076885
21	9	0	-2.346303	-1.605521	1.359240
22	9	0	-3.028782	-1.867122	-0.695852
23	9	0	-0.911660	-2.059182	-0.217095
24	1	0	0.422314	2.381763	-1.310022
25	9	0	1.897723	-0.641307	2.273220

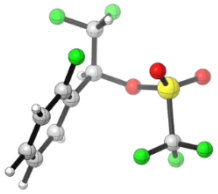
F-c4



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.347112	2.207522	-0.364239
2	9	0	-0.688353	2.911825	0.195408
3	9	0	1.458245	3.016124	-0.326890
4	8	0	-0.609934	0.219928	0.731721
5	6	0	0.644014	0.985048	0.512051
6	6	0	1.800009	0.130616	0.064574
7	6	0	2.589494	-0.501815	1.031695
8	6	0	2.148876	-0.073864	-1.280801
9	6	0	3.675709	-1.305622	0.720511
10	6	0	3.237056	-0.875770	-1.624324
11	1	0	1.563784	0.386540	-2.068947
12	6	0	3.997623	-1.491453	-0.625780
13	1	0	4.246566	-1.768766	1.517523
14	1	0	3.487998	-1.020793	-2.669576
15	1	0	4.843083	-2.118005	-0.891248
16	1	0	0.822936	1.358690	1.521271
17	16	0	-1.258587	-0.742924	-0.397610
18	8	0	-1.129393	-0.149412	-1.726095
19	8	0	-0.912075	-2.135023	-0.155869
20	6	0	-3.043821	-0.502119	0.175890
21	9	0	-3.813890	-1.281943	-0.588052
22	9	0	-3.170248	-0.860654	1.452560
23	9	0	-3.406732	0.770107	0.023352
24	1	0	0.094133	2.005097	-1.404247
25	9	0	2.278054	-0.319368	2.343784

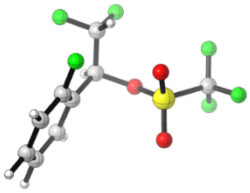
F-c3-cis



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.061346	2.321362	-0.064517
2	9	0	-0.405628	3.369453	-0.663237
3	9	0	-2.408439	2.551414	-0.209082
4	8	0	0.742100	0.873603	-0.932850
5	6	0	-0.736129	1.039660	-0.842336
6	6	0	-1.466552	-0.223603	-0.465591
7	6	0	-1.651503	-1.193712	-1.467904
8	6	0	-1.988232	-0.516450	0.798417
9	6	0	-2.299426	-2.398310	-1.206706
10	6	0	-2.644606	-1.706130	1.087212
11	6	0	-2.795232	-2.655142	0.075898
12	1	0	-2.424180	-3.128263	-1.999348
13	1	0	-3.027136	-1.869268	2.088664
14	1	0	-3.306599	-3.588226	0.289716
15	1	0	-0.950539	1.264865	-1.889449
16	16	0	1.737138	0.587831	0.310942
17	8	0	2.939384	1.370968	0.081056
18	8	0	1.022472	0.607043	1.580451
19	6	0	2.216338	-1.205286	-0.049784
20	9	0	2.680332	-1.310672	-1.295758
21	9	0	3.172659	-1.551761	0.815494
22	9	0	1.164147	-2.008867	0.106274
23	1	0	-0.813187	2.319825	0.994510
24	1	0	-1.271269	-0.991983	-2.465329
25	9	0	-1.877829	0.394935	1.800616

F-c4-cis

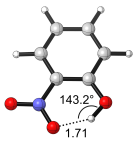


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.426002	2.190905	-0.008818
2	9	0	0.591349	2.914037	-0.584364
3	9	0	-1.573689	2.935902	-0.138245
4	8	0	0.673315	0.175924	-0.878736
5	6	0	-0.619186	0.906422	-0.824794
6	6	0	-1.792284	0.017986	-0.491238
7	6	0	-2.310707	-0.797253	-1.514431
8	6	0	-2.409520	-0.072160	0.760574
9	6	0	-3.374407	-1.665729	-1.284748
10	6	0	-3.476567	-0.923525	1.017375
11	6	0	-3.957896	-1.728792	-0.014759
12	1	0	-3.750353	-2.284979	-2.092079
13	1	0	-3.910508	-0.942951	2.010882
14	1	0	-4.790413	-2.399069	0.173501
15	1	0	-0.701784	1.221413	-1.867433
16	16	0	1.218443	-0.755584	0.331154
17	8	0	0.936208	-0.151058	1.628373
18	8	0	0.932375	-2.158616	0.071113
19	6	0	3.046956	-0.478164	-0.058775
20	9	0	3.752594	-1.224706	0.795210
21	9	0	3.315718	-0.854565	-1.308711
22	9	0	3.361034	0.805798	0.105196
23	1	0	-0.199865	2.061634	1.046852
24	1	0	-1.861023	-0.745837	-2.501880
25	9	0	-1.969076	0.706977	1.784623

5.4.4. Optimized Coordinate of Phenols and α,α-Difluorotoluenes

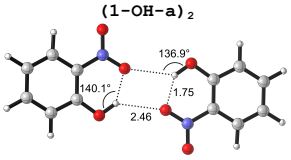
1-OH-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.426635	0.996142	-0.000028
2	6	0	-0.217943	-0.268823	-0.000011
3	6	0	2.557592	-0.163533	-0.000002
4	6	0	0.527134	-1.463328	0.000005
5	6	0	1.908859	-1.413855	0.000003
6	1	0	3.642345	-0.119638	0.000019
7	1	0	-0.005665	-2.405915	0.000012
8	1	0	2.485469	-2.331982	0.000014
9	6	0	1.832415	1.018202	-0.000007
10	1	0	2.323966	1.984954	-0.000011
11	8	0	-0.218291	2.171394	0.000020
12	1	0	-1.184551	1.976217	0.000070
13	7	0	-1.654932	-0.363184	0.000027
14	8	0	-2.192389	-1.470189	-0.000004
15	8	0	-2.324970	0.700022	-0.000022

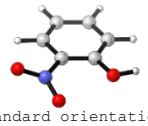
$(1\text{-OH-a})_2$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.234185	-0.891175	0.002319
2	6	0	-3.396113	0.519938	-0.008855
3	6	0	-4.673765	1.105494	0.079473
4	6	0	-5.796076	0.304469	0.177736
5	6	0	-5.647238	-1.096167	0.188604
6	6	0	-4.393956	-1.681746	0.102851
7	7	0	-2.256793	1.394448	-0.109491
8	8	0	-2.059348	-1.529292	-0.074747
9	8	0	-1.116829	0.876333	-0.193313
10	8	0	-2.422101	2.614434	-0.111806
11	1	0	-1.338986	-0.862835	-0.140599
12	1	0	-4.748951	2.185560	0.067974
13	1	0	-6.780488	0.753710	0.245636
14	1	0	-6.524684	-1.730908	0.265284
15	1	0	-4.270514	-2.759238	0.110896
16	6	0	3.234659	0.891258	0.002545
17	6	0	3.395969	-0.519925	-0.008783
18	6	0	4.673378	-1.106049	0.079278
19	6	0	5.796051	-0.305519	0.177440
20	6	0	5.647825	1.095180	0.188467
21	6	0	4.394785	1.681317	0.102969
22	7	0	2.256245	-1.393914	-0.109319
23	8	0	2.060073	1.529863	-0.074302
24	8	0	1.116488	-0.875265	-0.192789
25	8	0	2.420997	-2.613970	-0.111880
26	1	0	1.339469	0.863654	-0.140113
27	1	0	4.748093	-2.186147	0.067665
28	1	0	6.780280	-0.755194	0.245143
29	1	0	6.525559	1.729531	0.265070
30	1	0	4.271817	2.758863	0.111129

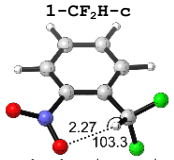
1-OH-b



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.456065	0.981808	-0.044582
2	6	0	0.241575	-0.245361	0.013809
3	6	0	-2.540655	-0.272530	0.028659
4	6	0	-0.450795	-1.463698	0.067692
5	6	0	-1.838077	-1.483997	0.085133
6	1	0	-3.626111	-0.270216	0.037013
7	1	0	0.125028	-2.379926	0.105051
8	1	0	-2.367340	-2.428486	0.142781
9	6	0	-1.859929	0.937910	-0.041099
10	1	0	-2.411228	1.872709	-0.095728
11	8	0	0.210473	2.154782	-0.135273
12	1	0	-0.422102	2.882075	-0.233486
13	7	0	1.699392	-0.306709	0.016241
14	8	0	2.229612	-1.369908	-0.334620
15	8	0	2.338627	0.683377	0.379019

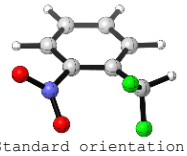
$1\text{-}CF_2H\text{-}c$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.453191	0.395541	-0.073297
2	6	0	-0.580380	1.787537	-0.007157
3	6	0	1.977488	0.679948	0.079041
4	6	0	0.537747	2.613791	0.118191
5	1	0	-1.570218	2.224362	-0.065023
6	6	0	1.819272	2.060854	0.159518
7	1	0	2.958963	0.224060	0.106562
8	1	0	0.404449	3.689008	0.177619
9	1	0	2.692485	2.697380	0.253799
10	6	0	-1.715422	-0.431495	-0.209044
11	1	0	-1.604857	-1.368333	-0.748378
12	9	0	-2.685625	0.310007	-0.855065
13	9	0	-2.228078	-0.712355	1.042587
14	6	0	0.849379	-0.136987	-0.022975
15	7	0	1.094072	-1.586898	-0.065322
16	8	0	2.210073	-1.975710	-0.413873
17	8	0	0.174257	-2.343314	0.261288

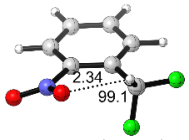
1-CF_2H-b



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.196519	-0.779350	0.078052
2	6	0	1.324128	-1.606321	0.109677
3	6	0	1.698749	1.144266	-0.107408
4	6	0	2.616246	-1.084953	0.003350
5	1	0	1.187461	-2.677078	0.226904
6	6	0	2.804044	0.292703	-0.103296
7	1	0	1.819199	2.218482	-0.179588
8	1	0	3.469360	-1.755038	0.019089
9	1	0	3.802724	0.709591	-0.177735
10	6	0	-1.142922	-1.457960	0.241726
11	1	0	-1.030177	-2.468176	0.640976
12	9	0	-1.813950	-1.569092	-0.956701
13	9	0	-1.962692	-0.764317	1.104355
14	6	0	0.416093	0.604988	-0.035412
15	7	0	-0.696041	1.570114	-0.103444
16	8	0	-1.676398	1.276868	-0.783599
17	8	0	-0.556559	2.635866	0.501778

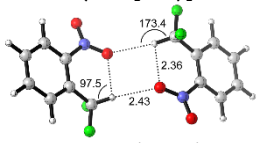
1-CF_2H-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.390594	0.523505	-0.128643
2	6	0	-0.249814	1.913245	-0.080609
3	6	0	2.048390	0.339780	0.048243
4	6	0	1.008908	2.513493	0.017978
5	1	0	-1.138652	2.530307	-0.117098
6	6	0	2.159648	1.728493	0.082985
7	1	0	2.923917	-0.295190	0.097116
8	1	0	1.082812	3.595696	0.047042
9	1	0	3.139320	2.187822	0.159020
10	6	0	-1.782748	-0.076096	-0.191223
11	1	0	-1.958703	-0.742019	-1.032650
12	9	0	-2.727153	0.925903	-0.245258
13	9	0	-2.036413	-0.779241	0.972339
14	6	0	0.787949	-0.246938	-0.066291
15	7	0	0.757978	-1.717352	-0.138411
16	8	0	1.715642	-2.337756	0.325146
17	8	0	-0.212253	-2.255743	-0.678012

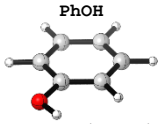
(1-CF_2H-a)$_2$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.255536	-0.645629	0.094955
2	1	0	1.133597	-1.255882	0.212683
3	7	0	2.198915	1.545465	0.745876
4	9	0	2.033459	-1.325222	2.010087
5	8	0	1.076863	1.031195	0.772841
6	6	0	4.350655	-1.290736	-0.486581
7	1	0	4.341778	-2.370811	-0.560139
8	8	0	2.438079	2.685622	1.145003
9	9	0	2.360174	-2.819202	0.421997
10	6	0	5.448915	-0.571337	-0.966869
11	1	0	6.279503	-1.104539	-1.417798
12	6	0	5.479148	0.819069	-0.864149
13	1	0	6.327635	1.383414	-1.235774
14	6	0	4.405882	1.488715	-0.280170
15	1	0	4.399997	2.567321	-0.187710
16	6	0	3.308869	0.760676	0.181957
17	6	0	2.109517	-1.480691	0.636343
18	6	0	-3.256028	0.645409	-0.095036
19	1	0	-1.133834	1.255947	-0.207766
20	7	0	-2.197972	-1.545376	-0.744917
21	9	0	-2.030120	1.327111	-2.007000
22	8	0	-1.076025	-1.030784	-0.769983
23	6	0	-4.352346	1.290109	0.484703
24	1	0	-4.343614	2.370132	0.559001
25	8	0	-2.436114	-2.685630	-1.144371
26	9	0	-2.360178	2.819296	-0.418011
27	6	0	-5.451601	0.570397	0.962223
28	1	0	-6.283132	1.103299	1.411766
29	6	0	-5.481604	-0.819943	0.858546
30	1	0	-6.330850	-1.384534	1.228060
31	6	0	-4.407104	-1.489196	0.276407
32	1	0	-4.400974	-2.567745	0.183337
33	6	0	-3.309138	-0.760860	-0.183005
34	6	0	-2.108891	1.480964	-0.633313

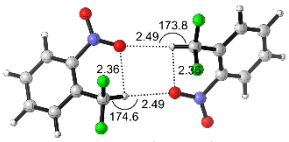
PhOH



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.940166	-0.024539	-0.000083
2	6	0	-0.265758	1.202317	-0.000018
3	6	0	1.174990	-1.191844	0.000077
4	6	0	1.132236	1.221689	-0.000029
5	1	0	-0.827680	2.133302	0.000050
6	6	0	1.860546	0.028555	0.000012
7	1	0	1.728447	-2.126558	0.000190
8	1	0	1.649587	2.176833	-0.000090
9	1	0	2.945816	0.048796	0.000062
10	6	0	-0.220575	-1.225282	-0.000054
11	1	0	-0.760644	-2.166752	-0.000164
12	8	0	-2.310091	-0.112798	-0.000030
13	1	0	-2.702435	0.771397	0.000756

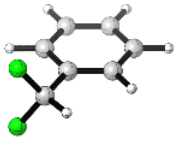
(1-CF_2H-a)$_2$′



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.324716	-0.477123	0.151883
2	6	0	-4.435038	-1.317399	0.029868
3	6	0	-4.432543	1.089036	-1.377590
4	6	0	-5.520023	-0.976851	-0.783226
5	1	0	-4.449270	-2.247960	0.583018
6	6	0	-5.521591	0.226753	-1.487461
7	1	0	-4.404553	2.029723	-1.912737
8	1	0	-6.363306	-1.655599	-0.858894
9	1	0	-6.360193	0.496848	-2.120196
10	6	0	-2.194522	-0.877118	1.083070
11	1	0	-1.216009	-0.956578	0.615690
12	9	0	-2.476786	-2.091773	1.670052
13	9	0	-2.108099	0.035210	2.119881
14	6	0	-3.348676	0.730299	-0.575485
15	7	0	-2.219685	1.674314	-0.547922
16	8	0	-2.436564	2.847166	-0.855361
17	8	0	-1.105649	1.240537	-0.241771
18	1	0	1.218325	0.970392	0.598647
19	6	0	2.194143	0.887633	1.071101
20	6	0	3.326760	0.478082	0.147118
21	6	0	3.349088	-0.734013	-0.572328
22	6	0	4.440782	1.313317	0.024486
23	6	0	4.434866	-1.102292	-1.367420
24	6	0	5.527727	0.963398	-0.782019
25	1	0	4.456405	2.247193	0.571998
26	6	0	5.527603	-0.244782	-1.478399
27	1	0	4.405528	-2.046390	-1.896481
28	1	0	6.373922	1.638403	-0.858613
29	1	0	6.367785	-0.522124	-2.105884
30	7	0	2.216082	-1.673090	-0.543496
31	8	0	2.430750	-2.850146	-0.835946
32	8	0	1.101345	-1.231189	-0.251778
33	9	0	2.479964	2.102931	1.654924
34	9	0	2.097629	-0.020487	2.110767

$PhCF_2H$

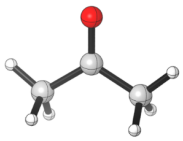


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.168399	0.190391	-0.000343
2	6	0	0.348842	-1.113408	0.000275
3	6	0	2.081871	1.086983	-0.000451
4	6	0	1.729153	-1.310944	0.000596
5	1	0	-0.325546	-1.964132	0.000450
6	6	0	2.596782	-0.211341	0.000220
7	1	0	2.752349	1.940862	-0.000861
8	1	0	2.130124	-2.319950	0.001153
9	1	0	3.671230	-0.369103	0.000416
10	6	0	-1.648939	0.419797	-0.000485
11	1	0	-1.937176	1.473039	-0.001699
12	9	0	-2.244873	-0.173990	1.103078
13	9	0	-2.245150	-0.176756	-1.102369
14	6	0	0.697910	1.288218	-0.000616
15	1	0	0.295909	2.297826	-0.001015

5.4.5. Optimized Coordinates of Reference Compounds for the Development of NMR Scaling Factors

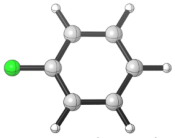
Acetone



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	1.403044	0.000000
2	6	0	0.000000	0.178530	0.000000
3	6	0	1.290559	-0.613074	0.002066
4	1	0	1.283900	-1.359031	0.804561
5	1	0	1.383440	-1.163454	-0.942094
6	1	0	2.146802	0.053166	0.118481
7	6	0	-1.290559	-0.613075	-0.002066
8	1	0	-1.383440	-1.163453	0.942096
9	1	0	-2.146802	0.053164	-0.118484
10	1	0	-1.283898	-1.359036	-0.804558

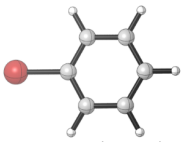
Fluorobenzene



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.261175	-1.221033	-0.000095
2	6	0	-0.924103	-0.000248	-0.000219
3	6	0	1.137679	-1.210990	0.000117
4	6	0	-0.261400	1.221028	-0.000017
5	6	0	1.837783	0.000111	-0.000033
6	1	0	1.676980	-2.153319	0.000138
7	6	0	1.137292	1.211194	0.000030
8	1	0	-0.827527	2.146288	-0.000010
9	1	0	2.923213	0.000336	0.000028
10	1	0	1.676533	2.153558	0.000096
11	9	0	-2.290983	-0.000061	0.000125
12	1	0	-0.826807	-2.146684	-0.000079

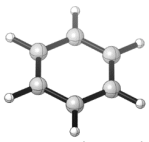
Bromobenzene



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.781818	-1.216532	0.000044
2	6	0	-0.099489	-0.000078	-0.000067
3	6	0	-2.179858	-1.207699	-0.000044
4	6	0	-0.781675	1.216623	-0.000018
5	6	0	-2.883133	0.000034	0.000029
6	1	0	-2.715719	-2.152262	-0.000025
7	6	0	-2.179643	1.207710	0.000010
8	1	0	-0.235958	2.153707	0.000041
9	1	0	-3.968600	0.000231	0.000022
10	1	0	-2.715525	2.152283	0.000027
11	1	0	-0.236086	-2.153658	0.000065
12	35	0	1.808731	-0.000019	0.000004

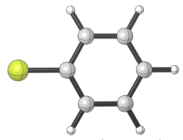
Benzene



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.272201	0.583285	0.000102
2	6	0	-0.130941	1.392519	0.000022
3	6	0	-1.141041	-0.809831	-0.000203
4	6	0	1.141350	0.809531	-0.000086
5	6	0	0.130679	-1.392424	0.000113
6	1	0	-2.026811	-1.439108	-0.000053
7	6	0	1.272316	-0.583193	0.000004
8	1	0	2.026154	1.439887	0.000064
9	1	0	0.231880	-2.474156	0.000140
10	1	0	2.259386	-1.037000	0.000011
11	1	0	-2.259720	1.036247	0.000189
12	1	0	-0.231862	2.474808	-0.000064

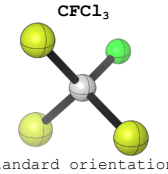
Chlorobenzene



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.178225	-1.218224	0.000073
2	6	0	0.501887	-0.000142	0.000114
3	6	0	-1.576496	-1.209434	-0.000093
4	6	0	-0.178077	1.218328	-0.000005
5	6	0	-2.277624	0.000039	0.000028
6	1	0	-2.113733	-2.153055	-0.000093
7	6	0	-1.576229	1.209493	-0.000012
8	1	0	0.372378	2.152829	0.000023
9	1	0	-3.363181	0.000264	-0.000020
10	1	0	-2.113509	2.153101	-0.000050
11	1	0	0.372128	-2.152880	0.000077
12	17	0	2.267912	-0.000037	-0.000033

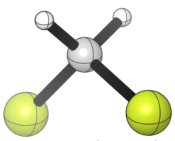
$CFCl_3$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000036	-0.000112	0.240019
2	9	0	-0.000019	-0.000118	1.592915
3	17	0	0.324979	1.666242	-0.309284
4	17	0	-1.605788	-0.551701	-0.309368
5	17	0	1.280832	-1.114438	-0.309369

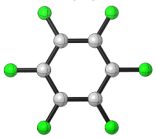
CH_2Cl_2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.775444
2	1	0	0.901391	0.000000	1.381436
3	17	0	0.000000	1.495044	-0.218104
4	17	0	0.000000	-1.495044	-0.218104
5	1	0	-0.901391	0.000000	1.381436

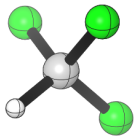
C_6F_6



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.451685	1.317955	0.000012
2	6	0	1.367109	0.267756	0.000003
3	6	0	-0.915530	1.049981	-0.000021
4	6	0	0.915458	-1.050063	0.000124
5	6	0	-1.367207	-0.267758	-0.000026
6	6	0	-0.451686	-1.317944	0.000010
7	9	0	2.681704	0.524959	-0.000150
8	9	0	0.886319	2.585467	0.000033
9	9	0	-1.796131	2.059624	0.000051
10	9	0	-2.681925	-0.525149	-0.000039
11	9	0	-0.886244	-2.585323	-0.000067
12	9	0	1.796390	-2.059529	0.000102

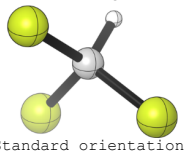
CF_3H



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000246	0.000034	0.348905
2	1	0	-0.000297	0.000092	1.439053
3	9	0	0.684083	-1.060652	-0.130783
4	9	0	0.577002	1.122426	-0.130814
5	9	0	-1.260888	-0.061807	-0.130901

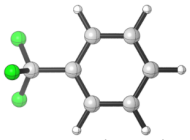
$CHCl_3$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000117	-0.000188	0.459451
2	1	0	0.000156	-0.000194	1.544704
3	17	0	1.518666	-0.774715	-0.084364
4	17	0	-1.430498	-0.927442	-0.084341
5	17	0	-0.088219	1.702236	-0.084319

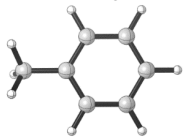
$PhCF_3$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.843231	-0.004851	0.012326
2	6	0	2.139577	-1.213578	0.001750
3	6	0	2.150199	1.208837	0.001837
4	6	0	0.744193	-1.211660	-0.019049
5	6	0	0.753712	1.219163	-0.018743
6	1	0	2.693921	2.148272	0.007642
7	6	0	0.054599	0.007239	-0.031074
8	1	0	0.197280	-2.148627	-0.030277
9	1	0	0.214394	2.159859	-0.029899
10	1	0	3.928923	-0.009557	0.026863
11	1	0	2.675719	-2.157356	0.007427
12	6	0	-1.448396	0.003939	-0.004965
13	9	0	-1.979214	-1.004321	-0.746259
14	9	0	-1.984709	1.159595	-0.472132
15	9	0	-1.939735	-0.160509	1.259030

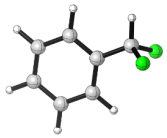
$PhCH_3$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.908561	-0.000083	0.009136
2	6	0	-1.202972	1.207135	0.002120
3	6	0	-1.202768	-1.207245	0.002119
4	6	0	0.195214	1.204169	-0.009623
5	6	0	0.195359	-1.204088	-0.009621
6	1	0	-1.739629	-2.151960	0.002143
7	6	0	0.916701	0.000116	-0.012468
8	1	0	0.733918	2.148858	-0.018793
9	1	0	0.734208	-2.148699	-0.018801
10	1	0	-2.994745	-0.000174	0.015426
11	1	0	-1.739948	2.151787	0.002146
12	6	0	2.428500	0.000053	0.009952
13	1	0	2.835595	0.889472	-0.480717
14	1	0	2.806069	-0.006269	1.040338
15	1	0	2.835700	-0.883364	-0.491432

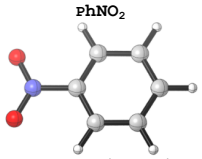
$PhCF_2H$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.168399	0.190391	-0.000343
2	6	0	0.348842	-1.113408	0.000275
3	6	0	2.081871	1.086983	-0.000451
4	6	0	1.729153	-1.310944	0.000596
5	1	0	-0.325546	-1.964132	0.000450
6	6	0	2.596782	-0.211341	0.000220
7	1	0	2.752349	1.940862	-0.000861
8	1	0	2.130124	-2.319950	0.001153
9	1	0	3.671230	-0.369103	0.000416
10	6	0	-1.648939	0.419797	-0.000485
11	1	0	-1.937176	1.473039	-0.001699
12	9	0	-2.244873	-0.173990	1.103078
13	9	0	-2.245150	-0.176756	-1.102369
14	6	0	0.697910	1.288218	-0.000616
15	1	0	0.295909	2.297826	-0.001015

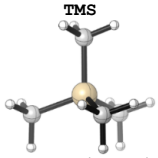
$PhNO_2$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.518838	0.000018	-0.000043
2	6	0	1.823065	-1.214167	-0.000041
3	6	0	1.822905	1.214198	0.000030
4	6	0	0.428664	-1.223744	0.000026
5	6	0	0.428538	1.223766	0.000031
6	1	0	2.364611	2.154290	0.000054
7	6	0	-0.244269	-0.000057	0.000038
8	1	0	-0.131142	-2.150366	0.000009
9	1	0	-0.131408	2.150302	0.000085
10	1	0	3.604387	0.000090	-0.000061
11	1	0	2.364725	-2.154207	-0.000074
12	7	0	-1.713231	-0.000033	0.000090
13	8	0	-2.296639	-1.087967	0.000000
14	8	0	-2.296486	1.087972	-0.000112

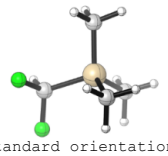
TMS



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.074561	-0.008740	-0.056406
2	6	0	-0.041286	1.540565	-0.772702
3	1	0	-0.287783	2.278494	-0.038127
4	1	0	0.937849	1.734287	-1.158276
5	1	0	-0.753067	1.579952	-1.570647
6	6	0	1.508741	0.157434	1.052259
7	1	0	2.368216	0.290596	0.428985
8	1	0	1.403497	1.002571	1.699999
9	1	0	1.627775	-0.729214	1.639275
10	6	0	0.480816	-1.414307	-0.850427
11	1	0	0.578408	-2.209573	-0.141252
12	1	0	-0.219912	-1.696254	-1.608309
13	1	0	1.432039	-1.218044	-1.299377
14	6	0	-1.860842	-0.274032	0.652410
15	1	0	-2.118185	0.547673	1.287608
16	1	0	-2.560007	-0.332964	-0.155424
17	1	0	-1.889551	-1.183126	1.215991

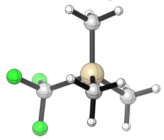
$TMSCF_2H$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.074561	-0.008740	-0.056406
2	6	0	-0.041286	1.540565	-0.772702
3	1	0	-0.287783	2.278494	-0.038127
4	1	0	0.937849	1.734287	-1.158276
5	1	0	-0.753067	1.579952	-1.570647
6	6	0	1.508741	0.157434	1.052259
7	1	0	2.368216	0.290596	0.428985
8	1	0	1.403497	1.002571	1.699999
9	1	0	1.627775	-0.729214	1.639275
10	6	0	0.480816	-1.414307	-0.850427
11	1	0	0.578408	-2.209573	-0.141252
12	1	0	-0.219912	-1.696254	-1.608309
13	1	0	1.432039	-1.218044	-1.299377
14	6	0	-1.860842	-0.274032	0.652410
15	1	0	-2.118185	0.547673	1.287608
16	1	0	-2.560007	-0.332964	-0.155424
17	1	0	-1.889551	-1.183126	1.215991

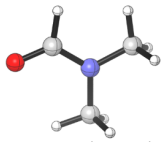
$TMSCF_3$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.090958	0.000334	-0.000615
2	9	0	1.629650	0.985425	0.787267
3	9	0	1.630583	0.189939	-1.247221
4	9	0	1.629541	-1.174558	0.458769
5	14	0	-0.867601	0.000120	-0.000288
6	6	0	-1.381713	-0.275546	1.787324
7	1	0	-1.007696	0.521583	2.438272
8	1	0	-2.475011	-0.286863	1.864204
9	1	0	-1.008471	-1.232434	2.166960
10	6	0	-1.384252	-1.410451	-1.131040
11	1	0	-2.477653	-1.473280	-1.174025
12	1	0	-1.016235	-1.260247	-2.151348
13	1	0	-1.006722	-2.372014	-0.767836
14	6	0	-1.385603	1.684945	-0.654528
15	1	0	-1.012302	1.851727	-1.670347
16	1	0	-2.479116	1.754024	-0.682784
17	1	0	-1.014673	2.492878	-0.015239

DMF



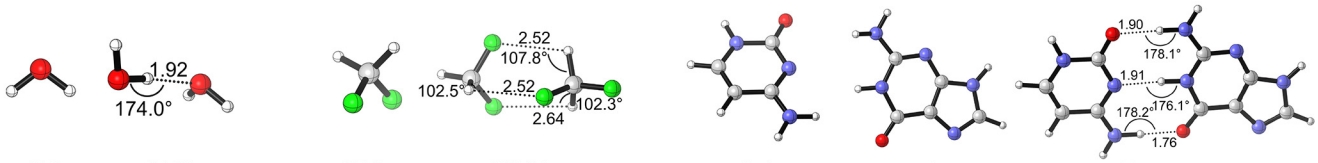
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.962552	-0.092520	0.000010
2	6	0	-0.431898	1.434010	-0.000004
3	1	0	0.575335	1.849184	-0.000550
4	1	0	-0.970035	1.780028	-0.889887
5	1	0	-0.969110	1.780115	0.890403
6	6	0	-1.589895	-0.768843	0.000005
7	1	0	-2.182521	-0.527308	-0.889825
8	1	0	-1.379007	-1.840395	-0.000111
9	1	0	-2.182428	-0.527481	0.889945
10	7	0	-0.340437	-0.020391	0.000005
11	6	0	0.859453	-0.646152	-0.000011
12	1	0	0.764450	-1.745332	-0.000032

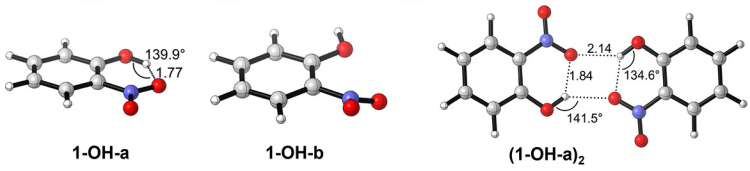
5.5. Partitioning Analysis

5.5.1. Structural Optimization at the M06-2X/6-31+G(d,p) Level of Theory in the Gas Phase

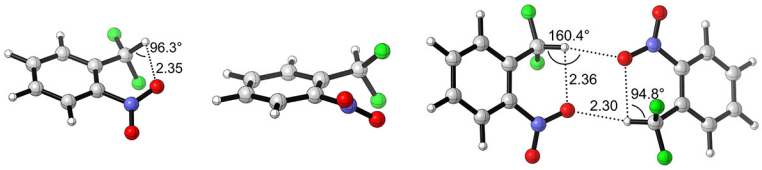
The charge density and the energy partitioning analyses were performed on M06-2X/aug-cc-pVTZ wavefunctions, where geometries had been optimized at the M06-2X/6-31+G(d,p) level of theory. All these calculations were performed in vacuum (no PCM). Selected details of the QTAIM charge density analysis are shown in Table S16. IR frequencies were calculated at the M06-2X/6-31+G(d,p) level of theory using Gaussian 09.[5] The default weighting scheme in Gaussian 09 (SSweight) was used for DFT numerical integration calculations (Figure S41).



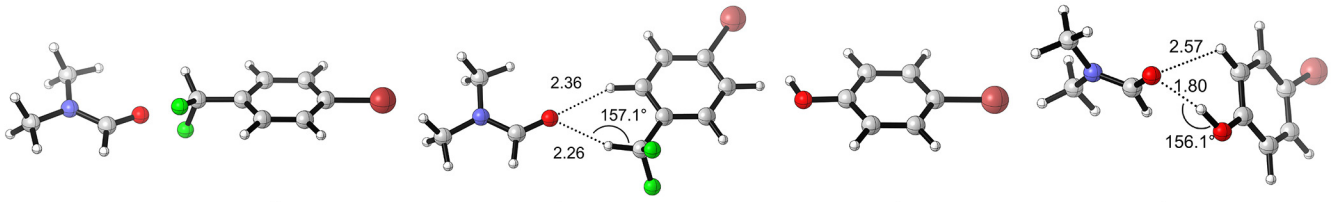
	H_2O	$(H_2O)_2$	CH_2F_2	$(CH_2F_2)_2$	cytosine	guanine	GC base pair
ΔE	0.0	−5.2	0.0	−3.8	-	-	−27.6
$\Delta(E+ZPE)$	0.0	−2.6	0.0	−2.7	-	-	−26.5
ΔH	0.0	−3.3	0.0	−2.4	-	-	−26.5
ΔG	0.0	+4.3	0.0	+7.1	-	-	−15.4



	1-OH-a	**1-OH-b**	**(1-OH-a)$_2$**
ΔE	0.0	+9.9	−3.5
$\Delta(E+ZPE)$	0.0	+9.9	−2.9
ΔH	0.0	+10.0	−2.1
ΔG	0.0	+9.5	+6.7



	1-CF_2H-a	**1-CF_2H-b**	**(1-CF_2H-a)$_2$**
ΔE	0.0	+4.3	−3.1
$\Delta(E+ZPE)$	0.0	+4.2	−2.5
ΔH	0.0	+4.2	−1.7
ΔG	0.0	+4.2	+7.4



	DMF	**2-CF_2H**	**2-CF_2H**···DMF	**2-OH**	**2-OH**···DMF
ΔE	-	-	−5.5	-	−11.2
$\Delta(E+ZPE)$	-	-	−4.8	-	−9.9
ΔH	-	-	−4.0	-	−9.5
ΔG	-	-	+3.8	-	+0.2

Figure S40. Calculated molecules and their complexes in the gas phase and calculated relative energies (Δ*E*), relative energies with zero point energy correction (Δ(*E*+*ZPE)*), enthalpies (Δ*H*), and Gibbs free energies (Δ*G*). All energies are in kcal/mol.

Table S14. Energies of calculated structures at the M06-2X/6-31+G(d,p) level of theory in the gas phase.

	M062X/6-31+G(d,p)										
	E (hartree)	ΔE (kcal/mol)	E+ZPE (hartree)	Δ(E+ZPE) (kcal/mol)	H (hartree)	ΔH (kcal/mol)	G (hartree)	ΔG (kcal/mol)	ZPE correction (hartree)	Thermal Correction to Enthalpy (hartree)	Thermal Correction to Gibbs Free Energy (hartree)
H_2O	-76.394964	-	-76.373332	-	-76.369551	-	-76.391623	-	0.021632	0.025412	0.003341
$(H_2O)_2$	-152.800557	-6.7	-152.753186	-4.1	-152.746778	-4.8	-152.778749	2.8	0.047371	0.053779	0.021807
CF_2H_2	-238.907037	-	-238.873640	-	-238.869582	-	-238.898221	-	0.033397	0.037455	0.008816
$(CF_2H_2)_2$	-477.820057	-3.8	-477.751565	-2.7	-477.742964	-2.4	-477.785057	7.1	0.068491	0.077093	0.034999
cytosine	-394.796685	-	-394.697148	-	-394.689424	-	-394.728079	-	0.099537	0.107260	0.068605
guanine	-542.379877	-	-542.261493	-	-542.252378	-	-542.294465	-	0.118385	0.127500	0.085412
GC base pair	-937.222093	-28.6	-937.002407	-27.5	-936.985441	-27.4	-937.048553	-16.3	0.219686	0.236652	0.173540
1-OH-a	-511.798919	-	-511.690160	-	-511.681610	-	-511.722899	-	0.108759	0.117309	0.076020
1-OH-b	-511.788395	6.6	-511.679637	6.6	-511.670810	6.8	-511.712937	6.3	0.108759	0.117586	0.075458
(**1-OH-a**)$_2$	-1023.604525	-4.2	-1023.385992	-3.6	-1023.367645	-2.8	-1023.436303	6.0	0.218533	0.236880	0.168222
1-CF_2H-a	-674.306390	-	-674.188037	-	-674.177633	-	-674.223819	-	0.118353	0.128756	0.082571
1-CF_2H-b	-674.299204	4.5	-674.181013	4.4	-674.170562	4.4	-674.216700	4.5	0.118191	0.128642	0.082504
(1-CF_2H-a)$_2$	-1348.621675	-5.6	-1348.383934	-4.9	-1348.362066	-4.3	-1348.437428	6.4	0.237741	0.259609	0.184246
DMF	-248.408991	-	-248.305475	-	-248.298435	-	-248.334713	-	0.103517	0.110556	0.074278
2-CF_2H	-3041.082490	-	-3040.977051	-	-3040.967656	-	-3041.013085	-	0.105439	0.114834	0.069405
2-CF_2H···DMF	-3289.501570	-6.3	-3289.291533	-5.7	-3289.273821	-4.9	-3289.343067	3.0	0.210037	0.227748	0.158503
2-OH	-2878.555905	-	-2878.459688	-	-2878.452066	-	-2878.491757	-	0.096217	0.103839	0.064148
2-OH···DMF	-3126.984208	-12.1	-3126.782463	-10.9	-3126.767169	-10.5	-3126.827648	-0.7	0.201745	0.217039	0.156560

Table S15. Single point energies of calculated structures at the M062X/aug-cc-PVTZ level of theory with thermal or zero point energy corrections obtained at the M06-2X/6-31+G(d,p) level of theory in the gas phase.

	M062X/aug-cc-PVTZ							
	E (hartree)	ΔE (kcal/mol)	E+ZPE (hartree)	Δ(E+ZPE) (kcal/mol)	E + Thermal Correction to Enthalpy (hartree)	ΔH (kcal/mol)	E+ Thermal Correction to Gibbs Free Energy (hartree)	ΔG (kcal/mol)
H_2O	-76.43009222	0.0	-76.408460	0.0	-76.404680	0.0	-76.426751	0.0
$(H_2O)_2$	-152.8684207	-5.2	-152.821050	-2.6	-152.814642	-3.3	-152.846614	4.3
CF_2H_2	-239.0024858	0.0	-238.969089	0.0	-238.965031	0.0	-238.993670	0.0
$(CF_2H_2)_2$	-478.01102	-3.8	-477.942529	-2.7	-477.933927	-2.4	-477.976021	7.1
cytosine	-394.9360551	-	-394.836518	-	-394.828795	-	-394.867450	-
guanine	-542.5674374	-	-542.449052	-	-542.439937	-	-542.482025	-
GC base pair	-937.5475562	-27.6	-937.327870	-26.5	-937.310904	-26.5	-937.374016	-15.4
1-OH-a	-511.9766334	0.0	-511.867874	0.0	-511.859324	0.0	-511.900613	0.0
1-OH-b	-511.9608978	9.9	-511.852139	9.9	-511.843312	10.0	-511.885440	9.5
(**1-OH-a**)$_2$	-1023.958827	-3.5	-1023.740294	-2.9	-1023.721947	-2.1	-1023.790605	6.7
1-CF_2H-a	-674.5503432	0.0	-674.4319902	0.0	-674.4215872	0.0	-674.4677722	0.0
1-CF_2H-b	-674.543547	4.3	-674.425356	4.2	-674.414905	4.2	-674.461043	4.2
(1-CF_2H-a)$_2$	-1349.105606	-3.1	-1348.867925	-2.5	-1348.845823	-1.7	-1348.923732	7.4
DMF	-248.4969778	-	-248.393461	-	-248.386422	-	-248.422700	-
2-CF_2H	-3043.687451	-	-3043.582012	-	-3043.572617	-	-3043.618046	-
2-CF_2H···DMF	-3292.193126	-5.5	-3291.983089	-4.8	-3291.965378	-4.0	-3292.034623	3.8
2-OH	-2881.101586	-	-2881.005369	-	-2880.997747	-	-2881.037438	-
2-OH···DMF	-3129.616373	-11.2	-3129.414628	-9.9	-3129.399334	-9.5	-3129.459813	0.2

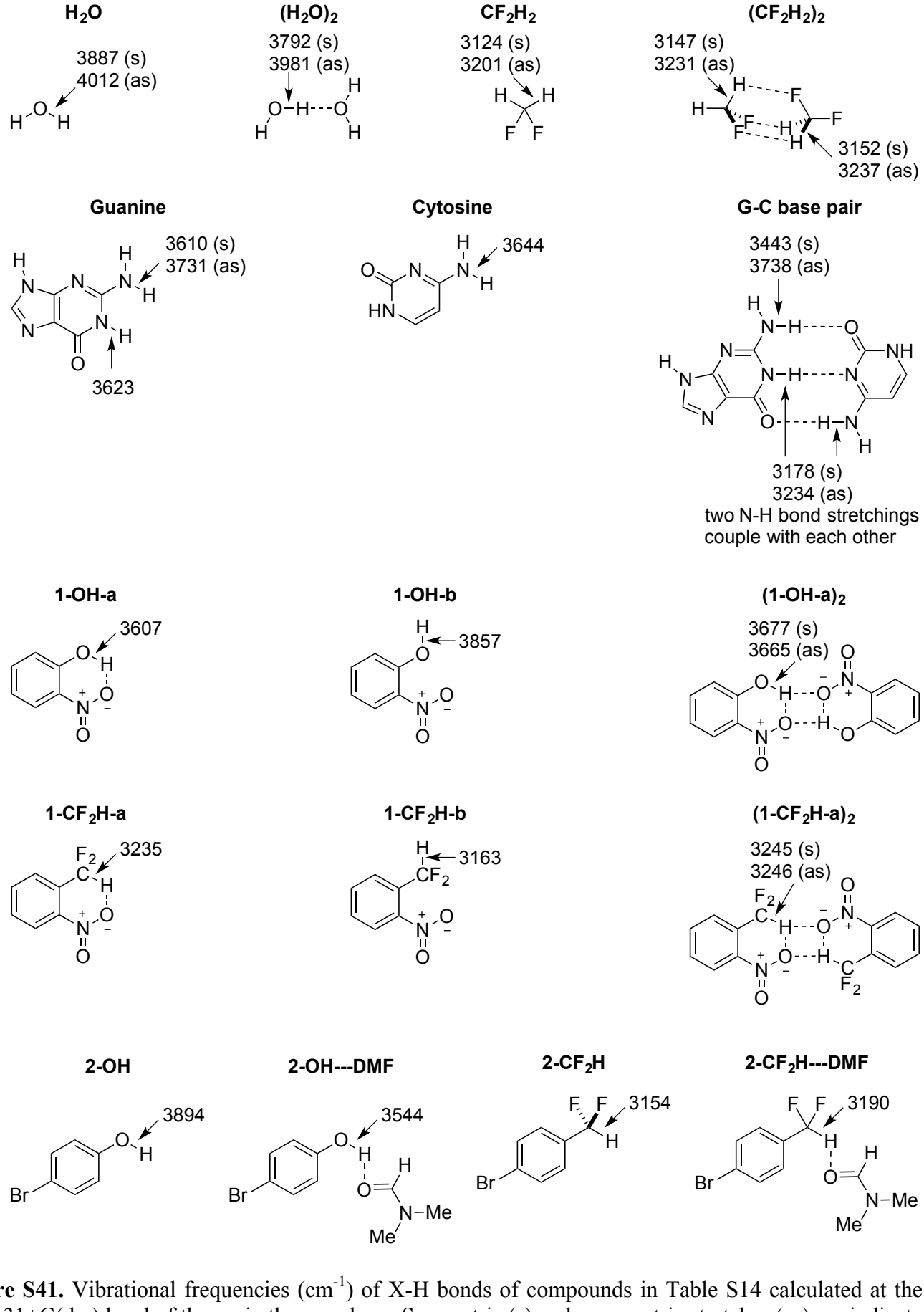
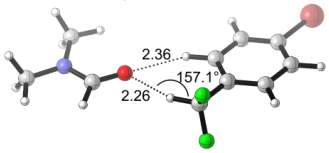


Figure S41. Vibrational frequencies (cm^{-1}) of X-H bonds of compounds in Table S14 calculated at the M06-2X/6-31+G(d,p) level of theory in the gas phase. Symmetric (s) and asymmetric stretches (as) are indicated.

5.5.2. Optimized Coordinates of Molecules and Complexes for Partitioning Analysis

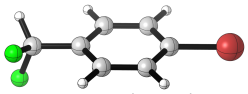
$BrC_6H_4CF_2H$-DMF-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.443053	1.334277	0.012062
2	6	0	-1.710898	1.917465	0.037305
3	6	0	-1.436518	-0.863107	-0.031747
4	6	0	-2.845283	1.115807	0.028447
5	1	0	-1.806813	2.998772	0.065167
6	6	0	-2.692029	-0.269308	-0.006164
7	1	0	-1.344709	-1.943139	-0.058563
8	1	0	-3.837263	1.553133	0.049113
9	6	0	0.778782	2.202886	0.020731
10	1	0	1.711029	1.634601	0.019830
11	9	0	0.765673	3.027082	1.116807
12	9	0	0.772337	3.038490	-1.067201
13	6	0	-0.303250	-0.049904	-0.022005
14	1	0	0.691081	-0.488786	-0.040650
15	6	0	4.251254	-0.139708	-0.088391
16	1	0	4.780551	0.817983	-0.232672
17	35	0	-4.233212	-1.360455	-0.017270
18	8	0	3.031492	-0.198986	-0.015348
19	7	0	5.090456	-1.194562	-0.005768
20	6	0	4.574791	-2.537084	0.186432
21	1	0	4.984137	-2.968705	1.105866
22	1	0	3.489320	-2.483708	0.259997
23	1	0	4.854961	-3.174113	-0.659209
24	6	0	6.527158	-1.040202	-0.103342
25	1	0	6.917616	-1.612973	-0.951505
26	1	0	6.775796	0.013088	-0.248452
27	1	0	7.013795	-1.393307	0.812275

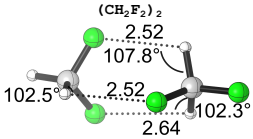
$BrC_6H_4CF_2H$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.707167	0.137039	-0.169344
2	6	0	1.074635	-1.084701	0.050638
3	6	0	-0.435143	1.248320	-0.255229
4	6	0	-0.313918	-1.147168	0.118223
5	1	0	1.666508	-1.987186	0.160850
6	6	0	-1.053813	0.021214	-0.035870
7	1	0	-1.030893	2.146282	-0.373779
8	1	0	-0.817817	-2.092239	0.286392
9	6	0	3.205423	0.229978	-0.215804
10	1	0	3.574196	0.964523	-0.937831
11	9	0	3.758039	-0.976964	-0.520243
12	9	0	3.693137	0.583178	1.012745
13	6	0	0.953164	1.298387	-0.325456
14	1	0	1.447821	2.250424	-0.499671
15	35	0	-2.935014	-0.055890	0.055102

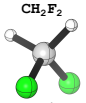
$(CH_2F_2)_2$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.374207	0.014124	-0.338723
2	9	0	0.911679	-0.131721	0.940190
3	9	0	2.757542	0.053840	-0.232102
4	1	0	1.064147	-0.891075	-0.941327
5	1	0	0.992151	0.991805	-0.754580
6	1	0	-1.578022	-0.083114	1.322010
7	6	0	-1.968479	-0.002880	0.311604
8	1	0	-3.053837	0.019535	0.247593
9	9	0	-1.474228	1.124869	-0.262811
10	9	0	-1.512638	-1.058612	-0.413165

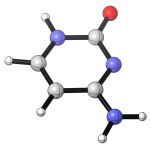
CH_2F_2



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000029	0.506148	-0.000070
2	9	0	1.100811	-0.291190	-0.000090
3	9	0	-1.100839	-0.291163	0.000120
4	1	0	0.000088	1.102378	0.914500
5	1	0	-0.000002	1.101908	-0.914340

Cytosine



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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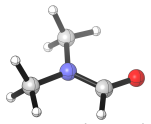
3	6	0	-0.201481	1.709074	0.000657
4	6	0	-1.183024	-0.525664	0.000076
5	7	0	0.082235	-1.051074	0.000787
6	1	0	-0.397579	2.775895	0.000946
7	1	0	1.929075	1.812966	-0.005045
8	1	0	-2.221926	1.253403	0.001888
9	7	0	-1.278786	0.890182	0.001114
10	8	0	-2.213348	-1.171921	0.000272
11	7	0	2.348952	-0.839672	-0.015822
12	1	0	3.195258	-0.303622	0.066194
13	1	0	2.389136	-1.845768	0.038000

DMF



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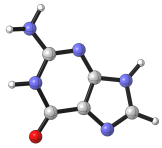
1	6	0	0.862024	-0.648892	-0.000133
2	1	0	0.762796	-1.749802	-0.000271
3	8	0	1.945222	-0.094105	0.000232
4	7	0	-0.343203	-0.022002	-0.000599
5	6	0	-0.417652	1.425268	0.000043
6	1	0	-0.950119	1.778009	0.890570
7	1	0	0.597345	1.821902	0.000590
8	1	0	-0.949502	1.778869	-0.890504
9	6	0	-1.589507	-0.754909	0.000222
10	1	0	-2.182801	-0.510579	-0.888343
11	1	0	-1.385495	-1.827915	-0.001176
12	1	0	-2.180771	-0.512430	0.890682

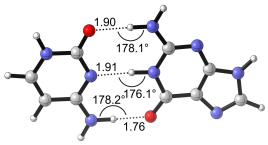
Guanine



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.854404	0.501101	0.009141
2	6	0	-0.530446	-0.848684	-0.000906
3	6	0	1.665829	-0.568088	-0.002467
4	6	0	0.216478	1.466278	0.003247
5	6	0	-2.708640	-0.525140	0.000805
6	1	0	2.269372	1.408825	-0.084300
7	1	0	-3.759440	-0.777663	-0.001258
8	1	0	-1.855151	-2.499426	-0.012731
9	8	0	0.195511	2.678556	-0.003411
10	7	0	1.473345	0.787110	-0.005238
11	1	0	3.064245	-1.994598	0.091595
12	7	0	2.967641	-1.001099	-0.064527
13	1	0	3.673973	-0.435220	0.382633
14	7	0	0.694432	-1.439140	0.007315
15	7	0	-2.218465	0.682484	0.008938
16	7	0	-1.729810	-1.498380	-0.004712

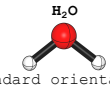
GC base pair



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.836830	-0.738423	-0.000037
2	6	0	3.303211	0.573644	0.000134
3	6	0	1.302136	1.525431	-0.000051
4	6	0	1.420484	-0.941296	-0.000210
5	6	0	4.951068	-0.895066	0.000195
6	1	0	5.969514	-1.257070	0.000288
7	1	0	5.316388	1.226807	0.000518
8	8	0	0.791183	-2.002180	-0.000356
9	7	0	0.730659	0.277849	-0.000195
10	1	0	0.865028	3.489743	0.000308
11	7	0	0.453853	2.571401	0.000062
12	1	0	-0.560288	2.460965	-0.000165
13	7	0	2.605125	1.728905	0.000147
14	7	0	3.882762	-1.638560	0.000013
15	7	0	4.664176	0.457542	0.000334
16	1	0	-0.298939	0.197505	-0.000270
17	6	0	-2.769539	-1.277390	-0.000115
18	6	0	-4.206934	-1.424932	0.000380
19	1	0	-4.840454	1.788829	0.000452
20	1	0	-4.676848	-2.398991	0.000634
21	7	0	-2.184167	-0.079990	-0.000418
22	7	0	-4.318380	0.923416	0.000236
23	6	0	-2.922728	1.057826	-0.000237
24	6	0	-4.936360	-0.286555	0.000566
25	1	0	-6.020492	-0.277540	0.001083
26	7	0	-1.984176	-2.352863	-0.000146
27	1	0	-0.956350	-2.243435	-0.000352
28	1	0	-2.385665	-3.275926	0.000270
29	8	0	-2.444916	2.191654	-0.000487

H_2O



Standard orientation:

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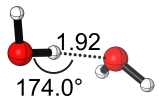
1	8	0	0.000000	0.000000	0.115575
2	1	0	0.000000	-0.768770	-0.462300
3	1	0	0.000000	0.768770	-0.462300

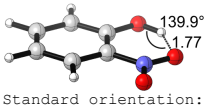
$(H_2O)_2$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.505055	0.029816	-0.116075
2	8	0	1.367203	-0.020421	0.097571
3	1	0	-1.902984	-0.190687	0.730192
4	1	0	-0.546390	-0.018337	0.015399
5	1	0	1.794786	-0.689830	-0.446212
6	1	0	1.757403	0.823696	-0.151345

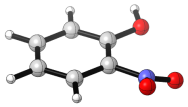
1-OH-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.424755	0.993659	0.000010
2	6	0	-0.215713	-0.262060	0.000029
3	6	0	2.546684	-0.175280	-0.000010
4	6	0	0.515524	-1.457736	0.000048
5	6	0	1.895158	-1.418570	0.000026
6	1	0	3.631172	-0.134763	-0.000024
7	1	0	-0.026091	-2.395704	0.000061
8	1	0	2.465246	-2.339914	0.000031
9	6	0	1.827938	1.006116	-0.000018
10	1	0	2.320834	1.972063	-0.000027
11	8	0	-0.197109	2.177537	0.000072
12	1	0	-1.161411	2.025322	0.000188
13	7	0	-1.660853	-0.358485	-0.000005
14	8	0	-2.179827	-1.457615	0.000018
15	8	0	-2.319296	0.688280	-0.000177

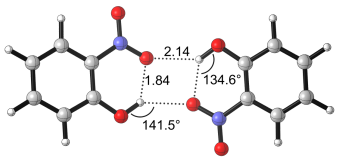
1-OH-b



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.444284	0.979486	-0.053209
2	6	0	-0.231561	-0.248889	0.016551
3	6	0	2.531465	-0.254081	0.032496
4	6	0	0.457582	-1.459855	0.081016
5	6	0	1.843050	-1.468271	0.100159
6	1	0	3.616445	-0.242650	0.040348
7	1	0	-0.115965	-2.378227	0.123317
8	1	0	2.380553	-2.406778	0.166328
9	6	0	1.844348	0.948797	-0.050003
10	1	0	2.387122	1.887362	-0.116022
11	8	0	-0.241351	2.133268	-0.158128
12	1	0	0.371690	2.871768	-0.272538
13	7	0	-1.691122	-0.312563	0.019486
14	8	0	-2.210140	-1.334309	-0.408720
15	8	0	-2.315635	0.635209	0.461861

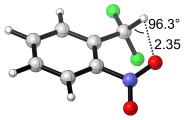
(1-OH-a)$_2$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.958676	-0.895580	0.029750
2	6	0	-3.146661	0.501187	-0.038980
3	6	0	-4.377636	1.092842	0.279123
4	6	0	-5.441938	0.305028	0.665203
5	6	0	-5.272825	-1.087131	0.736363
6	6	0	-4.060027	-1.672872	0.426933
7	7	0	-2.071137	1.381672	-0.439304
8	8	0	-1.830315	-1.556488	-0.239362
9	8	0	-1.001473	0.866595	-0.783751
10	8	0	-2.249105	2.583641	-0.430024
11	1	0	-1.119820	-0.949959	-0.519494
12	1	0	-4.465402	2.170229	0.209439
13	1	0	-6.395414	0.759159	0.907586
14	1	0	-6.103640	-1.717007	1.037678
15	1	0	-3.917005	-2.746514	0.480058
16	6	0	2.958685	0.895584	0.029643
17	6	0	3.146649	-0.501182	-0.039142
18	6	0	4.377601	-1.092873	0.278983
19	6	0	5.441904	-0.305096	0.665137
20	6	0	5.272814	1.087064	0.736345
21	6	0	4.060038	1.672839	0.426896
22	7	0	2.071136	-1.381638	-0.439554
23	8	0	1.830352	1.556533	-0.239484
24	8	0	1.001473	-0.866542	-0.783970
25	8	0	2.249131	-2.583605	-0.430376
26	1	0	1.119830	0.950045	-0.519626
27	1	0	4.465349	-2.170259	0.209257
28	1	0	6.395360	-0.759256	0.907540
29	1	0	6.103630	1.716913	1.037715
30	1	0	3.917033	2.746481	0.480058

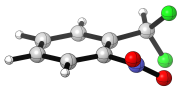
1-CF$_2$H-a



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.285248	0.592425	-0.139935
2	6	0	0.101660	1.930586	-0.103190
3	6	0	2.066858	-0.036820	0.063546
4	6	0	1.445833	2.286723	0.000775
5	1	0	-0.663752	2.696147	-0.149321
6	6	0	2.429026	1.306534	0.087438
7	1	0	2.802139	-0.829426	0.135480
8	1	0	1.719746	3.336385	0.021792
9	1	0	3.474891	1.580345	0.173648
10	6	0	-1.760140	0.243940	-0.192113
11	1	0	-2.060116	-0.321290	-1.072521
12	9	0	-2.497597	1.390349	-0.152797
13	9	0	-2.087654	-0.472671	0.919061
14	6	0	0.725948	-0.371625	-0.060962
15	7	0	0.411645	-1.811020	-0.140297
16	8	0	1.207542	-2.588130	0.349926
17	8	0	-0.611390	-2.131207	-0.719517

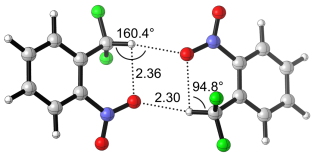
1-CF$_2$H-b



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.206722	-0.778992	0.068458
2	6	0	1.334029	-1.597211	0.096957
3	6	0	1.686234	1.156391	-0.098380
4	6	0	2.618905	-1.062577	-0.000283
5	1	0	1.203618	-2.669869	0.205724
6	6	0	2.795624	0.313807	-0.094581
7	1	0	1.792324	2.233041	-0.162923
8	1	0	3.478413	-1.723701	0.012987
9	1	0	3.791315	0.737825	-0.161605
10	6	0	-1.137045	-1.447039	0.233163
11	1	0	-1.023723	-2.462030	0.620872
12	9	0	-1.811766	-1.529766	-0.947021
13	9	0	-1.924035	-0.753947	1.105571
14	6	0	0.417443	0.599896	-0.033668
15	7	0	-0.712067	1.540753	-0.102708
16	8	0	-1.694828	1.198356	-0.730741
17	8	0	-0.576014	2.620047	0.449109

(1-CF$_2$H-a)$_2$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.969276	-0.431779	0.308858
2	6	0	-4.025723	-1.286783	0.616095
3	6	0	-4.455076	0.762388	-1.221897
4	6	0	-5.271928	-1.136346	0.008719
5	1	0	-3.864930	-2.069848	1.347253
6	6	0	-5.490417	-0.111662	-0.906732
7	1	0	-4.586927	1.575051	-1.926247
8	1	0	-6.075316	-1.820323	0.261754
9	1	0	-6.460439	0.011201	-1.375967
10	6	0	-1.642958	-0.595634	1.025841
11	1	0	-0.813920	-0.887441	0.381747
12	9	0	-1.775369	-1.532125	2.005165
13	9	0	-1.327366	0.579589	1.648472
14	6	0	-3.215418	0.581228	-0.624083
15	7	0	-2.143641	1.501793	-1.044125
16	8	0	-2.470209	2.598337	-1.454368
17	8	0	-0.996217	1.092390	-0.983910
18	1	0	0.814908	0.890365	0.377837
19	6	0	1.643470	0.599944	1.023146
20	6	0	2.969835	0.432585	0.307058
21	6	0	3.215215	-0.583448	-0.622745
22	6	0	4.027033	1.287465	0.612039
23	6	0	4.454810	-0.767608	-1.219767
24	6	0	5.273213	1.134027	0.005365
25	1	0	3.866831	2.072830	1.340855
26	6	0	5.490898	0.106458	-0.907022
27	1	0	4.586045	-1.582559	-1.921605
28	1	0	6.077201	1.817993	0.256512
29	1	0	6.460883	-0.018640	-1.375744
30	7	0	2.142575	-1.504261	-1.039963
31	8	0	2.468010	-2.602775	-1.445780
32	8	0	0.995645	-1.093070	-0.982169
33	9	0	1.776481	1.539433	1.999474
34	9	0	1.326613	-0.573053	1.649420

5.5.3. The $\Delta\bar{\chi}$ - Electronegativity Equalization Relationship

The Allen scale of electronegativity (units eV e^{-1}) was devised by averaging atomic *s*- and *p*-level energies obtained from photoelectron spectroscopy.[15] The Allen scale offers a good estimate of how the change in the average electron binding energy, $\Delta\bar{\chi}$,[16] relates to the classical Pauling electronegativity scale (Pauling units = PU, Figure S42).[17] If we choose to let the linear regression in Figure S42 intersect the origin, i.e. that zero PU = zero eV e^{-1}, the coefficient of determination, r^2, becomes 0.995, and the conversion reads as 1 PU = 6.06 eV e^{-1} = 585 kJ/mol = 140 kcal/mol. By this relationship, the $\Delta\bar{\chi}$-term expresses the binding energy change corresponding to a certain degree of "electronegativity equalization," over a chemical transformation. For a more detailed account of $\Delta\bar{\chi}$ and its uses see references [16] and [18].

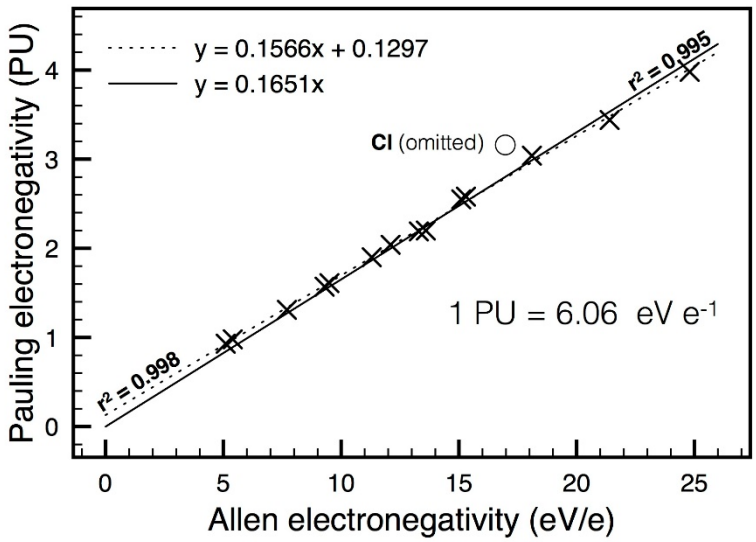


Figure S42. Allen electronegativity plotted against Pauling electronegativity for the first two rows of the periodic table; He, Ar and Cl omitted.

Table S16. Atomic charge on selected atoms and change upon bond formation.[a]

Species	Atom X in HB donor X–H	H	HB acceptor
H_2O	-1.17	0.59	-1.17
$(H_2O)_2$	-1.22	0.63	-1.18
2 $H_2O \rightarrow (H_2O)_2$	-0.05	0.04	-0.01
1-OH-b	-1.15	0.61	-0.46
1-OH-a	-1.21	0.67	-0.53
(**1-OH-a**)$_2$	-1.22	0.68	-0.55
1-OH-b → **1-OH-a**	-0.06	0.01	-0.08
2 **1-OH-a** → (**1-OH-a**)$_2$	-0.01	0.07	-0.01
1-CF_2H-b	1.29	0.06	-0.45
1-CF_2H-a	1.25	0.11	-0.48
(**1-CF_2H-a**)$_2$	1.18	0.13	-0.49
1-CF_2H-b → **1-CF_2H-a**	-0.03	0.05	-0.03
2 **1-CF_2H-a** → (**1-CF_2H-a**)$_2$	-0.08	0.02	-0.01
DMF	-	-	-1.22
2-CF_2H	1.24	0.07	-
[**2-CF_2H**···DMF]	1.20	0.11	-1.24
2-CF_2H + DMF → [**2-CF_2H**···DMF]	-0.05	0.05	-0.02
2-OH	-1.17	0.60	-
[**2-OH**···DMF]	-1.23	0.66	-1.24
2-OH + DMF → [**2-OH**···DMF]	-0.06	0.06	-0.02
Ph$\underline{CH_3}$[b]	0.04	0.01	-

[a] QTAIM-charges derived from topological analyses of M06-2X/aug-cc-pVTZ electron densities.[19] Integrations were performed on 18.5 μÅ^3 resolution grids.[20] [b] C and H charges on the methyl group in toluene given for reference when comparing with NMR-shielding measurements.

6. X-ray Crystallography Studies

6.1. CSD Structure Search and Data Analysis

All structure parameters were retrieved from the CSD using the fragment defining query tool of ConQuest. X···H distances were set to ≤ 2.6 Å and ≤ 2.7 Å, corresponding to the sum of the van der Waals radii of O···H and N···H, respectively. The data for O···H distances and C–H···O angles of methyl-containing compounds were obtained using the automatic export function of ConQuest. For difluoromethyl-containing compounds, the CF_2H···O distances and F_2C–H···O angles were measured manually using ORTEP (version 2.02) based on the corresponding .cif files. Manual inspection of the data sets allowed for consideration of possible disorder of the CF_2H groups. In some cases, the disorder had not been modeled sufficiently to allow for high accuracy measurements. Such structures were refined again to obtain reliable CF_2H···X (X = N, O) distances. Details of the re-refinement as well as the corresponding .res files are provided in Section 6.2.5.

Table S17. Summary of short $F_2C–H^{\cdots}O$ bond distances and the corresponding bond angles found in CSD.

#	CSD Refcode	$F_2CH\cdots O$ Bond distance [Å]	F_2C-H$\cdots$O Bond angle [°]	#	CSD Refcode	$CF_2CH\cdots O$ Bond distance [Å]	F_2C-H$\cdots$O Bond angle [°]
1	PUMYUN	2.490	99.44	**45**	MAPWOQ	2.664	95.85
2	ADIGEA	2.462	103.67	**46**	SASHUR	2.203	106.77
3	APITID	2.430	90.48	**47**	SASHUR	2.213	105.76
4	APITOJ	2.237	126.13	**48**	TELRUX	2.684	91.74
5	AZELIB	2.626	98.91	**49**	QUXCUJ	2.510	110.55
6	GEJRUK	2.524	98.85	**50**	TUWVEM	2.585	98.36
7	LUKMOT	2.510	93.54	**51**	TUWVEM	2.500	103.25
8	ZIJFAB	2.622	112.12	**52**	TUWVEM	2.470	103.04
9	BEBTUY	2.376	117.16	**53**	FIQXEI	2.540	129.10
10	IQOSIR	2.556	120.01	**54**	YUHGIT	2.579	103.44
11	SEPWEQ	2.457	98.21	**55**	YAPMUY	2.694	109.98
12	SOSBOS	2.529	99.26	**56**	YAWTIB	2.516	103.69
13	SOSBOS	2.544	99.46	**57**	ZAPPIR	2.513	103.15
14	TUZWUG	2.588	90.04	**58**	WEFHAS	2.352	152.78
15	XOFTIX	2.659	98.19	**59**	NAYPUZ	2.606	97.16
16	XOFTIX	2.529	96.71	**60**	HIKMIX	2.685	95.02
17	YESVUO	2.692	103.48	**61**	VEXNOC	2.361	122.68
18	AZEPOL	2.081	138.91	**62**	MOGLAV	2.238	116.99
19	AZEPOL	2.323	125.24	**63**	MOGLOJ	2.139	121.48
20	GEJRUK	2.221	127.30	**64**	POYLIZ	2.639	104.18
21	JIXQAJ	2.226	126.47	**65**	RIDCOY	2.658	131.72
22	TIJZOC	2.310	118.65	**66**	WOHJAG	2.167	132.30
23	HALNIT	2.261	108.53	**67**	LUVJOC	2.229	119.44
24	HALNIT	2.243	110.85	**68**	LUVJOC	2.390	110.49
25	HALNIT	2.414	159.39	**69**	ZECBIU	2.677	91.57
26	QEZLUE	2.392	111.18	**70**	APIVAX	2.347	92.36
27	XOCVIW	2.128	130.00	**71**	AZEPUR	2.201	131.31
28	XOCVIW	2.194	124.18	**72**	XIRXOM	2.564	90.61
29	XOCVIW	2.200	123.05	**73**	XIRXUS	2.654	92.34
30	XOCVIW	2.145	127.67	**74**	IHEPES	2.500	96.84
31	QUWQOQ	2.509	98.46	**75**	JIXQEN	2.318	129.61
32	BAXCIN	2.277	113.15				
33	BAXCIN	2.344	109.54				
34	DIDZUL	2.386	139.27				
35	ELUGUO	2.265	126.02				
36	HALNOZ	2.292	106.41				
37	SEFFIU	2.217	128.27				
38	SEFFIU	2.419	125.43				
39	CEFZAP	2.527	96.14				
40	GAPYIG	2.403	95.67				
41	IFOZUZ	2.261	104.69				
42	MAPWEG	2.481	100.78				
43	MAPWEG	2.654	93.23				
44	MAPWEG	2.535	96.36				

Table S18. Selected short $H_2C–H^{\cdots}O$ bond distances and the corresponding bond angles found in CSD.

#	CSD Refcode	$H_2CH\cdots O$ Bond distance [Å]	H_2C-H$\cdots$O Bond angle [°]	#	CSD Refcode	$H_2CH\cdots O$ Bond distance [Å]	H_2C-H$\cdots$O Bond angle [°]
1	FUVSEW	2.677	134.691	**45**	NEMCAK	2.466	105.57
2	GUNRAK	2.627	142.957	**46**	NEQSEI	2.391	114.026
3	RUMFEM	2.589	144.421	**47**	NIFMUM	2.626	98.682
4	ALEYAS	2.593	153.641	**48**	NIYKEN	2.433	116.224
5	BIFNOU	2.703	132.607	**49**	OBOGAO	2.431	130.585
6	CENBIH	2.705	117.813	**50**	ODIDEM	2.626	170.894
7	DIKWUQ	2.638	161.969	**51**	OGAKOX	2.66	114.117
8	DOPKAU	2.546	124.38	**52**	OHESUR	2.669	142.08
9	DOYPEM	2.642	108.989	**53**	PIBQAU	2.506	124.347
10	ENOYEM	2.511	154.161	**54**	QAZLIM	2.396	156.438
11	EVADOU	2.706	121.723	**55**	RASXEQ	2.226	145.709
12	EZOJIN	2.394	106.244	**56**	REJDOB	2.285	126.62
13	FEWMEA	2.658	136.262	**57**	SABWOI	2.636	115.886
14	FIHQOC	2.316	126.142	**58**	SEQWOA01	2.648	114.275
15	FILYOP	2.643	138.349	**59**	SOWZEK	2.415	134.142
16	GIVQOS	2.661	115.982	**60**	SUJCOR	2.712	137.784
17	HOCWOM	2.639	159.287	**61**	TIDKOH	2.448	122.532
18	HOTSOZ	2.705	113.6	**62**	TOKNOY	2.299	143.072
19	ICAGEA	2.567	153.007	**63**	TURGUI	2.415	122.859
20	INIBUC	2.342	121.979	**64**	UGALEV	2.416	159.616
21	IQETON	2.54	114.67	**65**	VEYYEF	2.518	173.889
22	IVUPAR	2.45	113.544	**66**	VOZYIU	2.669	98.373
23	JIVJOO	2.498	148.28	**67**	WEVFUZ	2.56	149.426
24	JIXKEG	2.471	112.903	**68**	XALHEZ	2.454	123.188
25	KANDOU01	2.394	122.658	**69**	XURRIL	2.486	120.306
26	KAWLEA	2.581	135.566	**70**	YONKIW	2.348	124.862
27	KEDSUI	2.627	118.121	**71**	YUSJAX	2.664	111.804
28	KISCUL	2.511	103.163	**72**	ZUZRUH	2.546	121.286
29	LACFAW02	2.514	126.216	**73**	RUJQUK	2.714	109.769
30	LEJXOP	2.301	124.289	**74**	WUYXIZ	2.488	142.828
31	LIFWOM	2.669	117.31	**75**	YUTREM	2.36	125.188
32	LILVAF	2.49	121.648				
33	LIYDEC	2.593	122.966				
34	LOPHUU	2.452	123.233				
35	LOTWOG	2.652	128.659				
36	LUKKOS	2.512	119.49				
37	LUNKEL	2.507	120.015				
38	MEJCUA	2.508	128.097				
39	MEPYEM	2.564	159.772				
40	MIGHEQ	2.712	109.613				
41	MOKKOM	2.695	136.898				
42	MUDTIP	2.586	143.962				
43	NAJCOS	2.598	93.003				
44	NARQII	2.314	159.104				

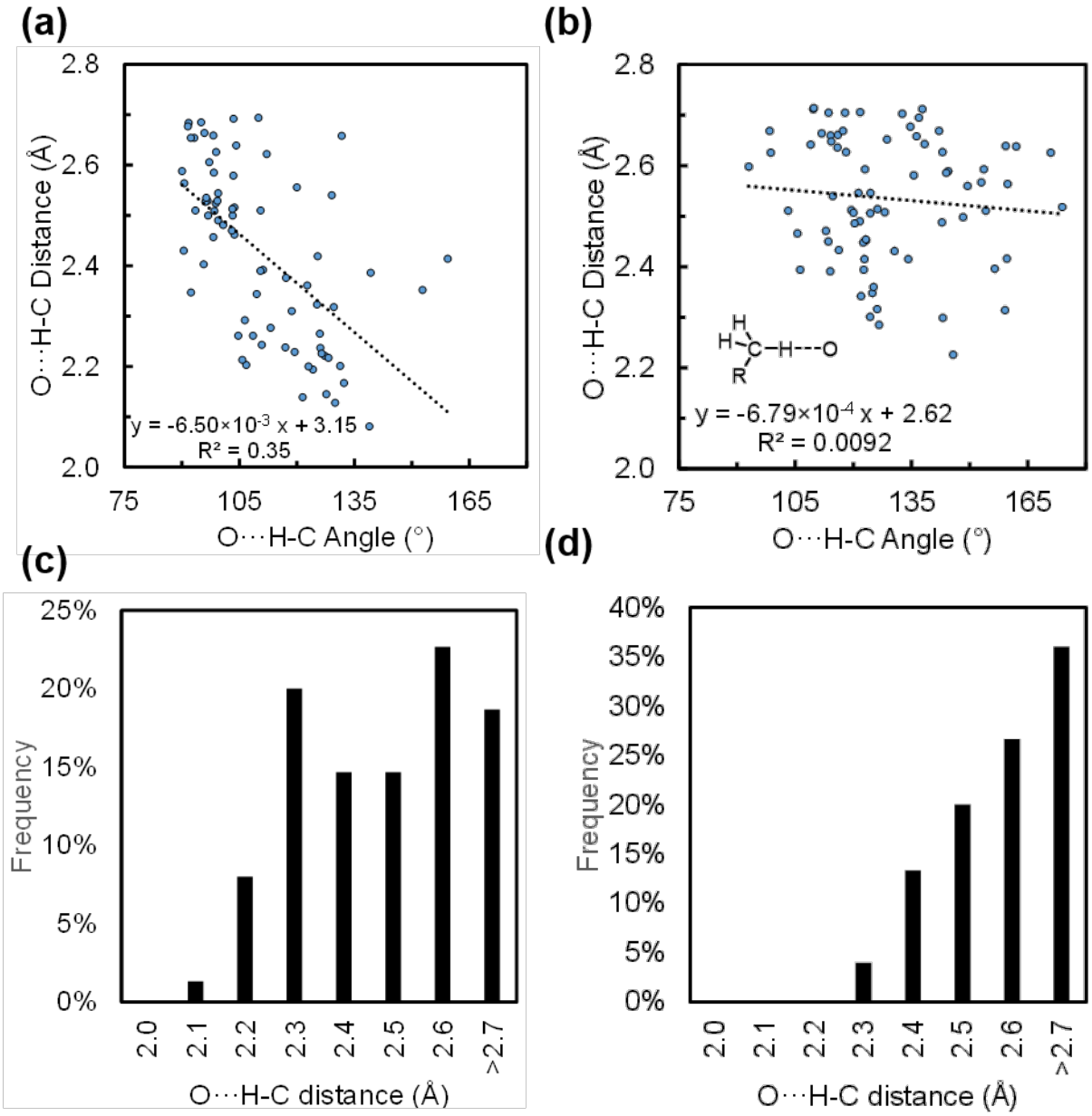


Figure S43. A) Correlation between short $F_2C–H^{\cdots}O$ bond distances and the corresponding $F_2C–H^{\cdots}O$ bond angles; b) Correlation between short $H_2C–H^{\cdots}O$ bond distances and the corresponding $H_2C–H^{\cdots}O$ bond angles; C) Histogram showing the distribution of short $F_2C–H^{\cdots}O$ distances; D) Histogram showing the distribution of short $F_2C–H^{\cdots}O$ distances.

A one-tailed Student *t*-test was performed on the bond angle/distance correlations to determine the significance of the results. A *t* value for the correlation coefficient (*r*) was determined using equation S2 for a population of size *n*.

$$t = r\sqrt{\frac{n-2}{1-r^2}} \qquad \text{Eq. (S2)}$$

For the $F_2C–H^{\cdots}O$ correlation, $t = 6.27$ corresponding to a *p*-value of 1.1×10^{-8}. For the $H_2C–H^{\cdots}O$ correlation, $t = 0.82$ corresponding to a *p*-value of 0.21. These results indicate a significant correlation ($r > 0$) between the

bond distances and angles for $F_2C–H^{\cdots}O$ interactions, but no significant correlation (r = 0) for $H_2C–H^{\cdots}O$ interactions. These results are consistent with the proposed weak $F_2C–H^{\cdots}O$ bonding interactions but negligible $H_2C–H^{\cdots}O$ interactions.

6.2. Experimental Details of the Crystal Structure Refinement

Single crystals of **1-CF_2H**, **1-OH**, and **5-CF_2H** were mounted on loops with Paratone-N oil and transferred to an N_2 cold stream (100 K) with a KRYO-FLEX low-temperature apparatus. The crystal of **2-CF_2H** was mounted at low temperature and transferred to the N_2 cold stream with a dry ice device. Data sets were collected at 100 K. Data collection was carried out using a Bruker SMART APEX CCD X-ray diffractometer equipped with a Bruker APEX2 CCD detector with Mo K_α radiation (λ = 0.71073 Å) controlled by the APEX2 software package.[21]Reduction of the data of **1-CF_2H**, **1-OH**, and **5-CF_2H** was performed with SAINT.[22] Empirical absorption corrections were calculated with SADABS.[23] Reduction of the data of **2-CF_2H** was performed with CELL_NOW and empirical absorption correction was applied with TWINABS.[23] The space groups were determined by XPREP[22] through analysis of metric symmetry and systematic absences. The structures were solved with SHELXT.[24] All structures were refined by full-matrix least-squares based on F^2 using SHELXL (Re. 789).[25] Each structure was checked for higher symmetry using PLATON.[26] All non-hydrogen atoms were located and refined anisotropically. If not otherwise noted, the isotropic displacement parameters of the hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms, to which they are attached. Distance and anisotropic displacement parameter restraints were applied to disordered atoms. Figures were generated using the program ORTEP and Mercury.[27] See Figures S44-47 and Tables S19-38 below for crystallographic data and refinement details. Specific details and discussion about refinement, including disorder, are provided below for selected structures.

6.2.1. *o*-Nitro-α,α-difluorotoluene (1-CF_2H)

o-Nitro-α,α-difluorotoluene crystallized in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. As governed by the symmetry operations of the space group, the densest packing of the layers is achieved by a glide plane and a twofold screw-axis rotation. The distance between the two indicated aromatic rings was determined to be 3.472(42) Å (see Figure S44 B).

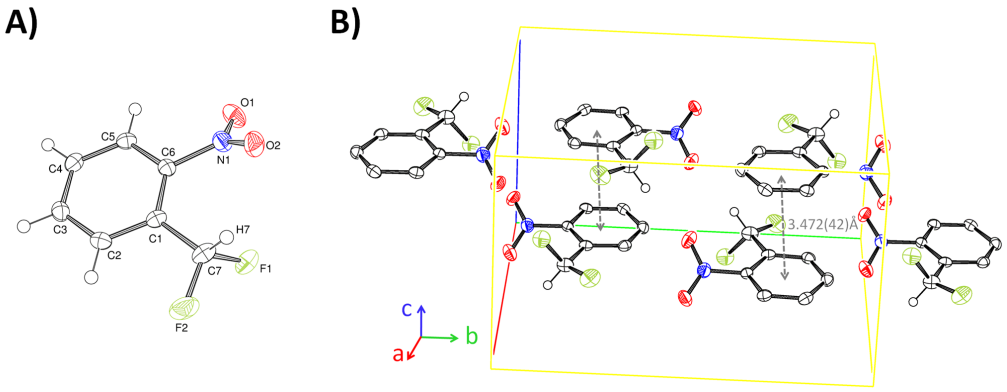


Figure S44. ORTEP representation of 1-difluoromethyl-2-nitro-benzene (**A**). (**B**) shows the packing of the unit cell, hydrogen atoms, except H7, were deleted for clarity. Thermal ellipsoids are set at 50% probability.

Coordinates for H7, the hydrogen atom of the CF_2H group, were taken from the difference Fourier synthesis. H7 was subsequently refined semi-freely with the U_{iso} value constrained to 1.2 times the U_{eq} value of the carbon atom to which it is attached. The relatively high residual electron density of 1.21 of H7 was unexpected.

We searched the CSD for other examples of CF_2H-containing molecules in order to compare the residual electron density of the H-atoms. Because of the limited availability of .cif files containing .res- and .hkl-files necessary for this comparison a thorough analysis was not possible. It is conceivable that the relatively high residual electron density of H7 is associated with the blue-shifted nature of the hydrogen bonding interaction. In order to pursue this hypothesis, we synthesized and crystallized *p*-bromo-α,α-difluorotoluene (**2-CF_2H**), a CF_2H containing compound that does not show hydrogen bonding interactions. Thorough analysis of the residual electron density of the CF_2H hydrogen atom was impeded by a statistical disorder of the CF_2H moiety and the bromide (see §6.2.3.). To avoid this issue we synthesized and crystallized 1-benzyloxy-4-(difluoromethyl)benzene (**5-CF_2H,** see §6.2.4.). Indeed, the crystal did not exhibit disorder. In contrast to the residual electron density of the CF_2H hydrogen atom in **1-CF_2H**, the residual electron density of this CF_2H hydrogen atom was similar to those of other hydrogen atoms in the structure. Thus, the relatively high residual electron density of the CF_2H hydrogen atom in **1-CF_2H** is unique. At the moment, we do not have an explanation for this phenomenon.

Table S19. Crystal data and structure refinement for *o*-nitro-α,α-difluorotoluene (**1-CF_2H**).

CCDC number	1552715
Empirical formula	$C_7H_5F_2NO_2$
Formula weight	173.12
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a = 8.007(2) Å	
b = 12.905(3) Å	β = 113.188(4)°
c = 7.3562(18) Å	
Volume	698.7(3) $Å^{-3}$
Z	4
Density (calculated)	1.646 Mg/m^3
Absorption coefficient	0.155 mm^{-1}
F(000)	352
Crystal size	0.250 x 0.200 x 0.070 mm^3
Theta range for data collection	2.768 to 28.281°
Index ranges	-10<=h<=10, -17<=k<=17, -9<=l<=9
Reflections collected	12289
Independent reflections	1728 [R(int) = 0.0521]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6422
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1728 / 0 / 112
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1197
R indices (all data)	R1 = 0.0541, wR2 = 0.1279
Largest diff. peak and hole	0.657 and -0.288 $e.Å^{-3}$

Table S20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *o*-nitro-α,α-difluorotoluene (**1-CF_2H**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	3973(1)	6045(1)	1539(2)	34(1)
O(1)	8735(2)	4982(1)	2870(2)	32(1)
N(1)	7794(2)	5451(1)	3571(2)	26(1)
C(1)	6330(2)	7170(1)	3427(2)	18(1)
F(2)	3253(1)	7410(1)	2829(2)	40(1)
O(2)	6910(2)	5020(1)	4381(2)	33(1)
C(2)	6497(2)	8241(1)	3468(2)	21(1)
C(3)	8120(2)	8705(1)	3636(2)	22(1)
C(4)	9583(2)	8106(1)	3750(2)	22(1)
C(5)	9445(2)	7037(1)	3701(2)	20(1)
C(6)	7839(2)	6585(1)	3556(2)	18(1)
C(7)	4541(2)	6682(1)	3168(3)	26(1)

Table S21. Bond distances [Å] and angles [°] for *o*-nitro-α,α-difluorotoluene (**1-CF_2H**).

Bond distance (Å)		Bond angle (°)			Bond angle (°)
F(1)-C(7)	1.375(2)	O(2)-N(1)-O(1)	123.32(15)	C(4)-C(5)-H(5)	120.4
O(1)-N(1)	1.2269(18)	O(2)-N(1)-C(6)	118.59(14)	C(5)-C(6)-C(1)	122.20(14)
N(1)-O(2)	1.2242(18)	O(1)-N(1)-C(6)	117.95(13)	C(5)-C(6)-N(1)	116.61(13)
N(1)-C(6)	1.464(2)	C(2)-C(1)-C(6)	117.61(13)	C(1)-C(6)-N(1)	121.18(13)
C(1)-C(2)	1.389(2)	C(2)-C(1)-C(7)	119.83(14)	F(2)-C(7)-F(1)	106.87(13)
C(1)-C(6)	1.396(2)	C(6)-C(1)-C(7)	122.51(14)	F(2)-C(7)-C(1)	110.70(14)
C(1)-C(7)	1.506(2)	C(1)-C(2)-C(3)	120.62(14)	F(1)-C(7)-C(1)	109.35(13)
F(2)-C(7)	1.343(2)	C(1)-C(2)-H(2)	119.7	F(2)-C(7)-H(7)	107.5(12)
C(2)-C(3)	1.391(2)	C(3)-C(2)-H(2)	119.7	F(1)-C(7)-H(7)	101.0(13)
C(2)-H(2)	0.95	C(4)-C(3)-C(2)	120.35(14)	C(1)-C(7)-H(7)	120.4(12)
C(3)-C(4)	1.378(2)	C(4)-C(3)-H(3)	119.8		
C(3)-H(3)	0.95	C(2)-C(3)-H(3)	119.8		
C(4)-C(5)	1.383(2)	C(3)-C(4)-C(5)	120.07(14)		
C(4)-H(4)	0.95	C(3)-C(4)-H(4)	120		
C(5)-C(6)	1.377(2)	C(5)-C(4)-H(4)	120		
C(5)-H(5)	0.95	C(6)-C(5)-C(4)	119.15(14)		
C(7)-H(7)	0.96(2)	C(6)-C(5)-H(5)	120.4		

Table S22. Anisotropic displacement parameters ($Å^2 \times 10^3$) for *o*-nitro-α,α-difluorotoluene (**1-CF_2H**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	25(1)	41(1)	29(1)	-6(1)	5(1)	-9(1)
O(1)	46(1)	23(1)	31(1)	-2(1)	18(1)	9(1)
N(1)	28(1)	22(1)	25(1)	1(1)	9(1)	0(1)
C(1)	16(1)	25(1)	14(1)	1(1)	6(1)	0(1)
F(2)	20(1)	52(1)	51(1)	-6(1)	15(1)	3(1)
O(2)	35(1)	26(1)	36(1)	5(1)	13(1)	-8(1)
C(2)	22(1)	24(1)	16(1)	1(1)	8(1)	6(1)
C(3)	28(1)	18(1)	17(1)	1(1)	6(1)	-1(1)
C(4)	20(1)	26(1)	18(1)	2(1)	6(1)	-5(1)
C(5)	17(1)	25(1)	17(1)	3(1)	7(1)	2(1)
C(6)	21(1)	18(1)	15(1)	1(1)	7(1)	1(1)
C(7)	17(1)	36(1)	24(1)	-1(1)	7(1)	-2(1)

Table S23. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for *o*-nitro-α,α-difluorotoluene (**1-CF_2H**).

	x	y	z	U(eq)
H(2)	5494	8662	3380	25
H(3)	8220	9439	3672	26
H(4)	10687	8427	3863	26
H(5)	10445	6620	3767	24
H(7)	4460(30)	6221(17)	4160(30)	31

6.2.2. *o*-Nitrophenol (1-OH)

o-Nitrophenol (**1-OH**) crystallized in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. Packing of the unit cell of *o*-nitrophenol is similar to that of *o*-nitro-α,α-difluorotoluene (**1-CF_2H**); however, the distance between the two indicated aromatic rings is 3.329(15) Å, which is shorter than that of *o*-nitro-α,α-difluorotoluene (**1-CF_2H**). Coordinates for H1, the hydrogen atom of the hydroxyl group, were taken from the difference Fourier synthesis. H1 was subsequently refined freely to obtain good geometry parameters for the hydrogen bonding.

Table S24. Crystal data and structure refinement for *o*-nitrophenol (**1-OH**).

CCDC number	1552716
Empirical formula	$C_6H_5NO_3$
Formula weight	139.11
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a = 6.3511(6) Å	
b = 14.3305(14) Å	β = 103.348(2)°
c = 6.6757(6) Å	
Volume	591.17(10) $Å^3$
Z	4
Density (calculated)	1.563 Mg/m^3
Absorption coefficient	0.128 mm^{-1}
F(000)	288
Crystal size	0.170 x 0.160 x 0.120 mm^3
Theta range for data collection	2.843 to 30.624°
Index ranges	-8<=h<=9, -20<=k<=20, -8<=l<=9
Reflections collected	11483
Independent reflections	1710 [R(int) = 0.0259]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.6901
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1710 / 0 / 95
Goodness-of-fit on F^2	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0981
R indices (all data)	R1 = 0.0445, wR2 = 0.1045
Largest diff. peak and hole	0.368 and -0.268 e. $Å^{-3}$

Table S25. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *o*-nitrophenol (**1-OH**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3855(1)	6748(1)	5413(1)	23(1)
N(1)	8293(1)	6038(1)	6695(1)	18(1)
C(1)	5588(2)	7318(1)	5907(2)	17(1)
O(2)	6794(1)	5453(1)	6269(1)	24(1)
C(2)	7751(2)	7021(1)	6515(2)	15(1)
O(3)	10192(1)	5808(1)	7274(1)	26(1)
C(3)	9459(2)	7657(1)	6992(2)	17(1)
C(4)	9033(2)	8604(1)	6898(2)	19(1)
C(5)	6882(2)	8909(1)	6316(2)	20(1)
C(6)	5192(2)	8281(1)	5818(2)	20(1)

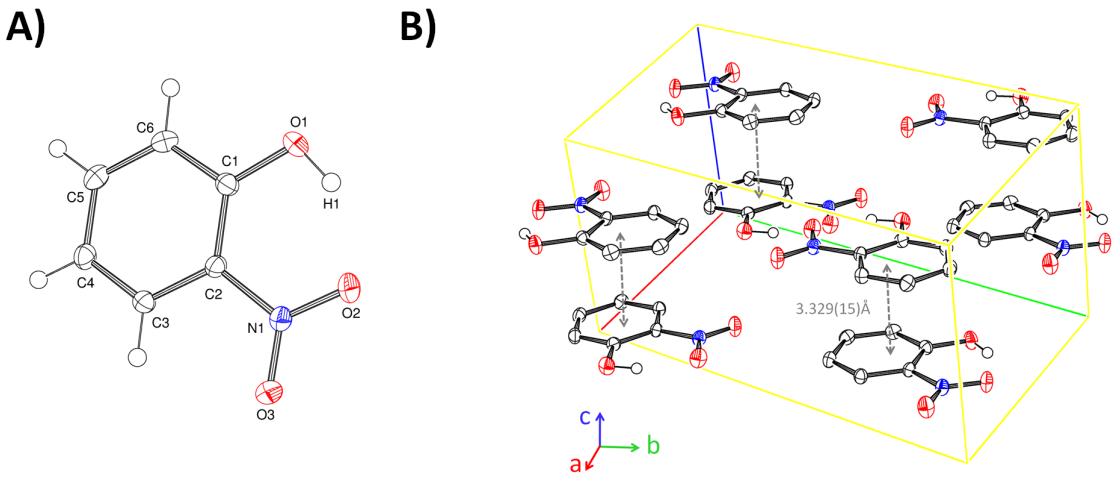


Figure S45. ORTEP representation of *o*-nitrophenol **(1-OH, A**). (**B**) shows the packing of the unit cell, hydrogen atoms, except H1, were deleted for clarity. The distance between the layers was determined to be 3.329(15) Å. Thermal ellipsoids are set at 50% probability.

Table S26. Bond distances [Å] and angles [°] for *o*-nitrophenol (**1-OH**).

	Bond distance (Å)		Bond angle (°)		Bond angle (°)
O(1)-C(1)	1.3486(12)	C(1)-O(1)-H(1)	104.4(13)	C(5)-C(4)-H(4)	120.4
O(1)-H(1)	0.91(2)	O(3)-N(1)-O(2)	122.23(9)	C(6)-C(5)-C(4)	121.10(9)
N(1)-O(3)	1.2237(11)	O(3)-N(1)-C(2)	119.12(8)	C(6)-C(5)-H(5)	119.4
N(1)-O(2)	1.2513(11)	O(2)-N(1)-C(2)	118.65(8)	C(4)-C(5)-H(5)	119.4
N(1)-C(2)	1.4487(12)	O(1)-C(1)-C(6)	117.19(9)	C(5)-C(6)-C(1)	120.63(10)
C(1)-C(6)	1.4011(14)	O(1)-C(1)-C(2)	125.15(9)	C(5)-C(6)-H(6)	119.7
C(1)-C(2)	1.4053(13)	C(6)-C(1)-C(2)	117.66(9)	C(1)-C(6)-H(6)	119.7
C(2)-C(3)	1.3960(13)	C(3)-C(2)-C(1)	121.64(9)		
C(3)-C(4)	1.3812(14)	C(3)-C(2)-N(1)	117.30(9)		
C(3)-H(3)	0.95	C(1)-C(2)-N(1)	121.05(9)		
C(4)-C(5)	1.4017(14)	C(4)-C(3)-C(2)	119.79(9)		
C(4)-H(4)	0.95	C(4)-C(3)-H(3)	120.1		
C(5)-C(6)	1.3815(15)	C(2)-C(3)-H(3)	120.1		
C(5)-H(5)	0.95	C(3)-C(4)-C(5)	119.17(9)		
C(6)-H(6)	0.95	C(3)-C(4)-H(4)	120.4		

Table S27. Anisotropic displacement parameters ($Å^2 \times 10^3$) for *o*-nitrophenol (**1-OH**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	14(1)	22(1)	29(1)	0(1)	1(1)	-4(1)
N(1)	18(1)	14(1)	20(1)	0(1)	3(1)	-1(1)
C(1)	15(1)	18(1)	16(1)	1(1)	3(1)	-1(1)
O(2)	23(1)	16(1)	32(1)	-1(1)	2(1)	-6(1)
C(2)	16(1)	12(1)	16(1)	0(1)	2(1)	0(1)
O(3)	18(1)	17(1)	41(1)	3(1)	3(1)	3(1)
C(3)	15(1)	16(1)	19(1)	-1(1)	2(1)	0(1)
C(4)	21(1)	14(1)	20(1)	-1(1)	3(1)	-2(1)
C(5)	25(1)	15(1)	19(1)	1(1)	4(1)	3(1)
C(6)	18(1)	19(1)	21(1)	2(1)	3(1)	5(1)

Table S28. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for *o*-nitrophenol (**1-OH**).

	x	y	z	U(eq)
H(1)	4430(30)	6160(15)	5560(30)	55(5)
H(3)	10909	7440	7381	20
H(4)	10184	9042	7223	23
H(5)	6580	9559	6264	24
H(6)	3747	8503	5411	24

6.2.3. *p*-Bromo-α,α-difluorotoluene (2-CF_2H)

2-CF_2H crystallized as a non merohedral twin. Three components were identified with CELL_NOW and refined using the hkl5 file. The batch scale factor (BASF) was refined and converged to a composition consisting of 59.1% of the first, 26.7% of the second, and 14.2% of the third twin domain.

The structure was solved in the monoclinic space group $P2_1/c$ with half a molecule in the asymmetric unit. The bromo- and CF_2H motifs were found to be disordered statistically across two positions, a result which is likely due to the similar space requirements of the CF_2H and bromo motifs. Because half of the molecule is generated through crystallographic symmetry, the occupancies of the disordered motifs were set to 50% to generate the full disordered molecule.

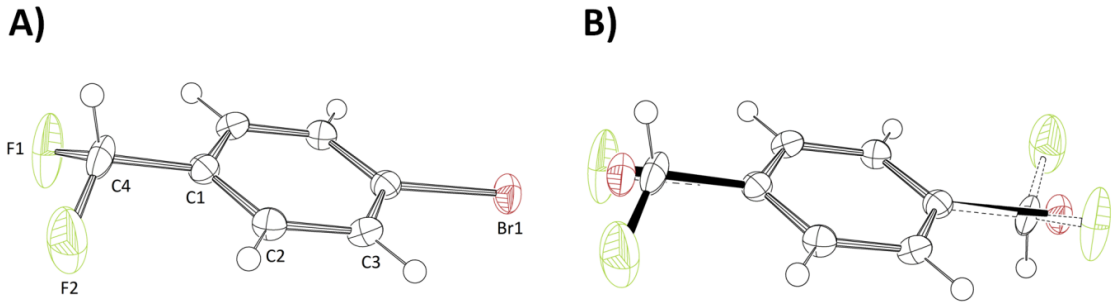


Figure S46. ORTEP representation of *p*-bromo-α,α-difluorotoluene (**2-CF_2H**) (A). Thermal ellipsoids are set at 50% probability. Disordered motifs are highlighted with bold/dashed bonds (B).

Table S29. Crystal data and structure refinement for *p*-bromo-α,α-difluorotoluene (**2-CF_2H**).

CCDC number	1552717
Empirical formula	$C_7H_5BrF_2$
Formula weight	207.02
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a = 7.962(2) Å	
b = 7.097(2) Å	β = 92.557(4)°
c = 6.1966(18) Å	
Volume	349.76(17) $Å^3$
Z	2
Density (calculated)	1.966 Mg/m^3
Absorption coefficient	5.825 mm^{-1}
F(000)	200
Crystal size	0.700 x 0.400 x 0.400 mm^3
Theta range for data collection	2.561 to 29.477°.
Index ranges	-8<=h<=9, -20<=k<=20, -8<=l<=9
Reflections collected	1066
Independent reflections	066 [R(int) = ?]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745882 and 0.257008
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1066 / 96 / 69
Goodness-of-fit on F^2	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0578, wR2 = 0.1367
R indices (all data)	R1 = 0.0824, wR2 = 0.1549
Largest diff. peak and hole	0.888 and -0.669 e. $Å^{-3}$

Table S30. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for *p*-bromo-α,α-difluorotoluene (**2-CF_2H**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	8496(2)	5518(2)	7992(2)	28(1)
C(1)	6489(5)	5240(5)	6196(7)	20(1)
C(3)	5027(5)	4220(6)	2928(7)	22(1)
C(2)	6522(5)	4473(6)	4145(7)	20(1)
C(4)	8126(15)	5570(20)	7395(18)	28(3)
F(2)	9251(8)	4251(12)	6904(12)	58(2)
F(1)	7914(8)	5388(13)	9508(10)	59(2)

Table S31. Bond distances [Å] and angles [°] for *p*-bromo-α,α-difluorotoluene (**2-CF_2H**).

Bond distance (Å)		Bond angle (°)			Bond angle (°)
Br(1)-C(1)	1.916(4)	C(2)-C(1)-C(3)#1	121.1(4)	C(3)-C(2)-H(2)	120.1
C(1)-C(2)	1.384(6)	C(2)-C(1)-C(4)	117.9(5)	F(1)-C(4)-F(2)	105.7(11)
C(1)-C(3)#1	1.398(5)	C(3)#1-C(1)-C(4)	120.9(6)	F(1)-C(4)-C(1)	109.2(9)
C(1)-C(4)	1.490(11)	C(2)-C(1)-Br(1)	121.6(3)	F(2)-C(4)-C(1)	110.9(9)
C(3)-C(2)	1.392(6)	C(3)#1-C(1)-Br(1)	117.3(3)	F(1)-C(4)-H(4)	110.3
C(3)-H(3)	0.9500	C(2)-C(3)-C(1)#1	119.1(4)	F(2)-C(4)-H(4)	110.3
C(2)-H(2)	0.9500	C(2)-C(3)-H(3)	120.5	C(1)-C(4)-H(4)	110.3
C(4)-F(1)	1.333(12)	C(1)#1-C(3)-H(3)	120.5		
C(4)-F(2)	1.340(13)	C(1)-C(2)-C(3)	119.8(3)		
C(4)-H(4)	1.0000	C(1)-C(2)-H(2)	120.1		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S32. Anisotropic displacement parameters ($Å^2 \times 10^3$) for *p*-bromo-α,α-difluorotoluene (**2-CF_2H**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	23(1)	35(1)	26(1)	2(1)	-8(1)	-4(1)
C(1)	18(2)	17(2)	24(2)	1(2)	0(1)	-2(1)
C(3)	23(2)	18(2)	24(2)	-4(2)	2(2)	-1(1)
C(2)	18(2)	21(2)	22(2)	0(2)	4(1)	1(1)
C(4)	31(6)	35(5)	17(5)	-2(5)	-8(4)	-9(4)
F(2)	32(3)	96(6)	45(4)	-17(4)	-8(3)	20(3)
F(1)	33(3)	123(7)	22(3)	-7(4)	-8(2)	-4(4)

Table S33. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for *p*-bromo-α,α-difluorotoluene (**2-CF_2H**).

	x	y	z	U(eq)
H(3)	5036	3689	1522	26
H(2)	7562	4120	3570	24
H(4)	8565	6854	7069	34

6.2.4. 1-Benzyloxy-4-(difluoromethyl)benzene (5-CF_2H)

5-CF_2H crystallized in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The coordinates of the CF_2H hydrogen were taken from the Fourier synthesis and refined freely. All other hydrogen atoms were attached to idealized positions and their isotropic displacement parameters were fixed to 1.2 times the U_{eq} value of the atoms to which they are attached.

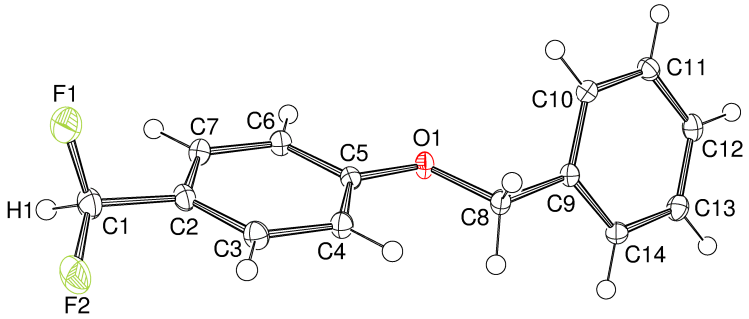


Figure S47. ORTEP representation of 1-benzyloxy-4-(difluoromethyl)benzene (5-CF_2H). Thermal ellipsoids are set at 50% probability.

Table S34. Crystal data and structure refinement for 1-benzyloxy-4-(difluoromethyl)benzene (5-CF_2H).

CCDC number	1552718
Empirical formula	$C_{14}H_{12}F_2O$
Formula weight	234.24
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a = 14.4147(11) Å	
b = 10.6790(8) Å	β = 103.7140(10)
c = 7.5441(6) Å	
Volume	1128.19(15) $Å^3$
Z	4
Density (calculated)	1.379 Mg/m^3
Absorption coefficient	0.108 mm^{-1}
F(000)	488
Crystal size	0.400 x 0.300 x 0.300 mm^3
Theta range for data collection	1.454 to 30.905°
Index ranges	-20<=h<=20, -15<=k<=14, -10<=l<=10
Reflections collected	24098
Independent reflections	3407 [R(int) = 0.0264]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.7038
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3407 / 0 / 158
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.1015
R indices (all data)	R1 = 0.0433, wR2 = 0.1064
Largest diff. peak and hole	0.451 and -0.292 e. $Å^{-3}$

Table S35. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1-benzyl-oxy-4-(difluoromethyl)benzene (**5-CF_2H**).U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	-562(1)	3116(1)	6562(1)	34(1)
O(1)	3832(1)	3617(1)	7816(1)	14(1)
C(1)	-47(1)	3790(1)	8039(1)	20(1)
F(2)	-446(1)	4954(1)	7850(1)	30(1)
C(2)	984(1)	3819(1)	7992(1)	15(1)
C(3)	1372(1)	4806(1)	7208(1)	16(1)
C(4)	2328(1)	4782(1)	7118(1)	15(1)
C(5)	2890(1)	3752(1)	7819(1)	12(1)
C(6)	2501(1)	2758(1)	8613(1)	14(1)
C(7)	1554(1)	2796(1)	8703(1)	16(1)
C(8)	4275(1)	4628(1)	7054(1)	14(1)
C(9)	5279(1)	4245(1)	7081(1)	12(1)
C(10)	5449(1)	3176(1)	6136(1)	14(1)
C(11)	6376(1)	2831(1)	6117(1)	16(1)
C(12)	7147(1)	3555(1)	7043(1)	17(1)
C(13)	6984(1)	4628(1)	7965(1)	17(1)
C(14)	6051(1)	4972(1)	7987(1)	14(1)

Table S36. Bond distances [Å] and angles [°] for 1-benzyloxy-4-(difluoromethyl)benzene (**5-CF_2H**).

	Bond distance (Å)		Bond angle (°)		Bond angle (°)
F(1)-C(1)	1.3845(12)	C(5)-O(1)-C(8)	117.12(7)	H(8A)-C(8)-H(8B)	108.4
O(1)-C(5)	1.3667(10)	F(2)-C(1)-F(1)	104.92(8)	C(14)-C(9)-C(10)	119.29(8)
O(1)-C(8)	1.4408(10)	F(2)-C(1)-C(2)	112.07(8)	C(14)-C(9)-C(8)	120.65(8)
C(1)-F(2)	1.3632(12)	F(1)-C(1)-C(2)	109.77(8)	C(10)-C(9)-C(8)	120.02(8)
C(1)-C(2)	1.4944(12)	F(2)-C(1)-H(1)	106.9(8)	C(11)-C(10)-C(9)	120.40(8)
C(1)-H(1)	0.962(13)	F(1)-C(1)-H(1)	106.9(8)	C(11)-C(10)-H(10)	119.8
C(2)-C(3)	1.3906(13)	C(2)-C(1)-H(1)	115.6(8)	C(9)-C(10)-H(10)	119.8
C(2)-C(7)	1.3955(12)	C(3)-C(2)-C(7)	119.80(8)	C(10)-C(11)-C(12)	120.09(8)
C(3)-C(4)	1.3965(12)	C(3)-C(2)-C(1)	121.90(8)	C(10)-C(11)-H(11)	120.0
C(3)-H(3)	0.9500	C(7)-C(2)-C(1)	118.26(8)	C(12)-C(11)-H(11)	120.0
C(4)-C(5)	1.3937(12)	C(2)-C(3)-C(4)	120.53(8)	C(13)-C(12)-C(11)	119.82(8)
C(4)-H(4)	0.9500	C(2)-C(3)-H(3)	119.7	C(13)-C(12)-H(12)	120.1
C(5)-C(6)	1.3993(12)	C(4)-C(3)-H(3)	119.7	C(11)-C(12)-H(12)	120.1
C(6)-C(7)	1.3836(12)	C(5)-C(4)-C(3)	119.20(8)	C(12)-C(13)-C(14)	120.01(8)
C(6)-H(6)	0.9500	C(5)-C(4)-H(4)	120.4	C(12)-C(13)-H(13)	120.0
C(7)-H(7)	0.9500	C(3)-C(4)-H(4)	120.4	C(14)-C(13)-H(13)	120.0
C(8)-C(9)	1.5005(12)	O(1)-C(5)-C(4)	124.79(8)	C(9)-C(14)-C(13)	120.39(8)
C(8)-H(8A)	0.9900	O(1)-C(5)-C(6)	114.84(7)	C(9)-C(14)-H(14)	119.8
C(8)-H(8B)	0.9900	C(4)-C(5)-C(6)	120.36(8)	C(13)-C(14)-H(14)	119.8
C(9)-C(14)	1.3947(12)	C(7)-C(6)-C(5)	119.91(8)		
C(9)-C(10)	1.3978(12)	C(7)-C(6)-H(6)	120.0		
C(10)-C(11)	1.3895(12)	C(5)-C(6)-H(6)	120.0		
C(10)-H(10)	0.9500	C(6)-C(7)-C(2)	120.19(8)		
C(11)-C(12)	1.3976(13)	C(6)-C(7)-H(7)	119.9		
C(11)-H(11)	0.9500	C(2)-C(7)-H(7)	119.9		
C(12)-C(13)	1.3897(13)	O(1)-C(8)-C(9)	107.90(7)		
C(12)-H(12)	0.9500	O(1)-C(8)-H(8A)	110.1		
C(13)-C(14)	1.3971(12)	C(9)-C(8)-H(8A)	110.1		
C(13)-H(13)	0.9500	O(1)-C(8)-H(8B)	110.1		
C(14)-H(14)	0.9500	C(9)-C(8)-H(8B)	110.1		

Table S37. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 1-benzyloxy-4-(difluoromethyl)benzene (**5-CF_2H**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	14(1)	45(1)	41(1)	-16(1)	5(1)	-5(1)
O(1)	11(1)	15(1)	18(1)	4(1)	6(1)	1(1)
C(1)	14(1)	24(1)	23(1)	0(1)	6(1)	1(1)
F(2)	18(1)	29(1)	43(1)	1(1)	12(1)	8(1)
C(2)	12(1)	19(1)	15(1)	-1(1)	4(1)	0(1)
C(3)	14(1)	17(1)	18(1)	2(1)	4(1)	3(1)
C(4)	14(1)	15(1)	16(1)	2(1)	5(1)	1(1)
C(5)	11(1)	15(1)	11(1)	0(1)	3(1)	0(1)
C(6)	14(1)	15(1)	15(1)	2(1)	4(1)	1(1)
C(7)	14(1)	17(1)	16(1)	2(1)	5(1)	-2(1)
C(8)	12(1)	14(1)	17(1)	2(1)	6(1)	0(1)
C(9)	12(1)	13(1)	12(1)	2(1)	4(1)	0(1)
C(10)	14(1)	14(1)	15(1)	0(1)	4(1)	-2(1)
C(11)	17(1)	15(1)	17(1)	0(1)	7(1)	2(1)
C(12)	13(1)	20(1)	18(1)	4(1)	6(1)	2(1)
C(13)	13(1)	20(1)	16(1)	1(1)	2(1)	-3(1)
C(14)	15(1)	15(1)	14(1)	-1(1)	3(1)	-1(1)

Table S38. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for 1-benzyloxy-4-(difluoromethyl)benzene (**5-CF_2H**).

	x	y	z	U(eq)
H(1)	-184(9)	3425(12)	9114(17)	17(3)
H(3)	984	5504	6729	20
H(4)	2593	5459	6586	18
H(6)	2887	2058	9089	17
H(7)	1292	2124	9250	19
H(8A)	4277	5399	7785	17
H(8B)	3916	4799	5787	17
H(10)	4926	2682	5503	17
H(11)	6485	2102	5474	19
H(12)	7781	3314	7042	20
H(13)	7506	5129	8581	20
H(14)	5942	5704	8622	17

6.2.5. Experimental details of the crystal structure re-refinement of published structures

Two structures were re-refined and a more detailed disorder model was applied to obtain hydrogen bonding parameters with a higher accuracy. All structures were re-refined by full-matrix least-squares based on F^2 using SHELXL (Re. 789).[25] Each structure was checked for higher symmetry using PLATON.[26] All non-hydrogen atoms were located and refined anisotropically. If not otherwise noted, the isotropic displacement parameters of the hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms to which they are attached. Figures were

generated using the program ORTEP. See Figures S51-S52 and Tables S39-S48 below for crystallographic data and refinement details.

6.2.5.1. CCDC Entry SUQQEC

SUQQEC crystallized in the orthorhombic space group *Pbcn* with one molecule in the asymmetric unit. Coordinates for H2n, the hydrogen atom of the amino group, were taken from the difference Fourier synthesis. H2n was subsequently refined freely. All other hydrogen atoms including H15, the hydrogen atom of the CF_2H group, were attached to idealized positions. Their isotropic displacement parameters were fixed to 1.2 times the U_{eq} value of the atoms to which they are attached. The CF_2H group was modeled across two positions. The major component of the disorder refined to an occupancy of 63.3%. The CFClH group was also found to be disordered and was subsequently modeled across two positions. The major part refined to an occupancy of 75.7%. Distance and anisotropic displacement parameter restraints were applied to all disordered atoms.

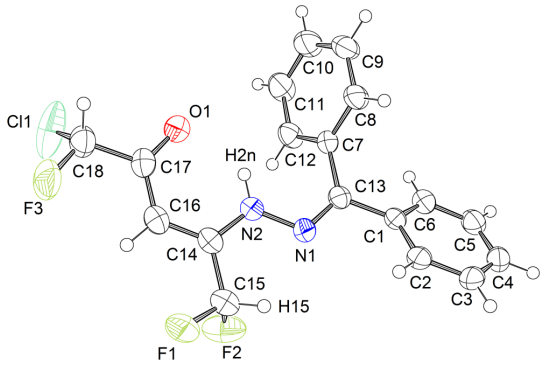


Figure S48. ORTEP representation of SUQQEC. Thermal ellipsoids are set at 50% probability.

res-file for the re-refinement of SUQQEC:

```
TITL import in P c n b transformed to space group : Pbcn
CELL  0.71073  10.0193  20.3405  16.9296   90.000   90.000   90.000
ZERR     8.00   0.0003   0.0006   0.0004    0.000    0.000    0.000
LATT   1
SYMM  1/2 - X, 1/2 - Y, 1/2 + Z
SYMM  1/2 + X, 1/2 - Y, - Z
SYMM  - X,   Y, 1/2 - Z
SFAC C H N O F CL
UNIT 144 112 16 8 24 8
LIST 4
FMAP 2
PLAN 5
ACTA
BOND $H
OMIT  0   2   0  ! beamstop
OMIT  1   1   0  ! beamstop
```

```
OMIT  0   2   1  ! beamstop
OMIT  1   1   1  ! Outlier
HTAB
HTAB N2 O1
RIGU
SADI C15 F1 C15 F2 C15 F1B C15 F2B C18 F3 C18 F3B
SADI C18 C11 C18 C11B
DFIX 0.88 N2 H2N
SIZE 0.40x0.35x0.30
L.S. 10
TEMP -100.00
WGHT    0.067400    2.395100
FVAR       0.36612   0.63255   0.75704
O1    4    0.392743    0.927444    0.179835    11.00000    0.04609    0.04195 =
         0.04347   -0.00327    0.00124   -0.00103
N1    3    0.417444    0.741529    0.118093    11.00000    0.03165    0.03448 =
         0.04076   -0.00184    0.00348    0.00126
N2    3    0.385233    0.799168    0.157013    11.00000    0.03527    0.03502 =
         0.03889    0.00023    0.00526   -0.00102
H2N   2    0.412795    0.837476    0.140864    11.00000   -1.20000
C1    1    0.522101    0.686363    0.012694    11.00000    0.02326    0.03433 =
         0.04221   -0.00056    0.00232   -0.00101
C2    1    0.551190    0.629850    0.056176    11.00000    0.03004    0.03666 =
         0.04497   -0.00006    0.00098   -0.00356
AFIX  43
H2    2    0.545867    0.630843    0.112190    11.00000   -1.20000
AFIX   0
C3    1    0.587701    0.572448    0.018192    11.00000    0.03364    0.03324 =
         0.06257    0.00017    0.00240   -0.00327
AFIX  43
H3    2    0.608378    0.534342    0.048242    11.00000   -1.20000
AFIX   0
C4    1    0.594268    0.570239   -0.063431    11.00000    0.03868    0.03983 =
         0.06262   -0.01230    0.01085   -0.00336
AFIX  43
H4    2    0.619021    0.530686   -0.089429    11.00000   -1.20000
AFIX   0
C5    1    0.564763    0.625625   -0.106741    11.00000    0.04546    0.05010 =
         0.04536   -0.00765    0.01109   -0.00516
AFIX  43
H5    2    0.567951    0.623922   -0.162787    11.00000   -1.20000
AFIX   0
C6    1    0.530468    0.683820   -0.069428    11.00000    0.03654    0.04235 =
         0.04324    0.00032    0.00393    0.00088
AFIX  43
H6    2    0.512619    0.722064   -0.099858    11.00000   -1.20000
AFIX   0
C7    1    0.515436    0.811779    0.014050    11.00000    0.03144    0.03328 =
         0.03635   -0.00061    0.00301    0.00247
C8    1    0.647574    0.827627   -0.001337    11.00000    0.03070    0.04136 =
         0.06399    0.00754    0.00623    0.00487
```

```
AFIX  43
H8    2    0.716538    0.798068    0.013557    11.00000   -1.20000
AFIX   0
C9    1    0.679333    0.885977   -0.038086    11.00000    0.03988    0.04763 =
         0.08723    0.01454    0.01903   -0.00025
AFIX  43
H9    2    0.770119    0.896522   -0.048160    11.00000   -1.20000
AFIX   0
C10   1    0.580242    0.929158   -0.060335    11.00000    0.06296    0.04615 =
         0.07664    0.02268    0.02039    0.00632
AFIX  43
H10   2    0.602237    0.969328   -0.085832    11.00000   -1.20000
AFIX   0
C11   1    0.449233    0.913496   -0.045246    11.00000    0.05231    0.05435 =
         0.06156    0.02273    0.00985    0.01725
AFIX  43
H11   2    0.380711    0.943253   -0.060283    11.00000   -1.20000
AFIX   0
C12   1    0.415930    0.855444   -0.008739    11.00000    0.03328    0.05013 =
         0.04664    0.01081    0.00251    0.00776
AFIX  43
H12   2    0.324898    0.845151    0.000925    11.00000   -1.20000
AFIX   0
C13   1    0.481109    0.747953    0.052265    11.00000    0.02387    0.03555 =
         0.03920    0.00132   -0.00229    0.00156
C14   1    0.318747    0.797388    0.225492    11.00000    0.03287    0.04606 =
         0.03829    0.00107    0.00349    0.00032
C15   1    0.273138    0.730169    0.252770    11.00000    0.05751    0.05183 =
         0.05199    0.00372    0.01714   -0.00541
PART 1
AFIX  13
H15A  2    0.344996    0.697061    0.242858    21.00000   -1.20000
AFIX  13
PART 2
H15B  2    0.233865    0.710010    0.204167   -21.00000   -1.20000
AFIX   0
PART 0
C16   1    0.292075    0.852941    0.268470    11.00000    0.04151    0.05176 =
         0.03489   -0.00210    0.00466    0.00191
AFIX  43
H16   2    0.244245    0.849107    0.316703    11.00000   -1.20000
AFIX   0
C17   1    0.333873    0.915775    0.242904    11.00000    0.03665    0.04717 =
         0.03843   -0.00731   -0.00388    0.00430
C18   1    0.307243    0.974407    0.296609    11.00000    0.05296    0.05527 =
         0.04803   -0.01295    0.00401    0.00099
PART 1
AFIX  13
H18A  2    0.392520    0.999315    0.303420    31.00000   -1.20000
AFIX  13
PART 2
```

```
H18B  2    0.326885    0.965388    0.353499   -31.00000   -1.20000
AFIX   0
PART 0
PART 1
F1    5    0.245446    0.733560    0.333930    21.00000    0.07718    0.06202 =
         0.04620    0.01243    0.01660   -0.00762
F2    5    0.167445    0.712928    0.218181    21.00000    0.08169    0.07993 =
         0.06589    0.01567   -0.01633   -0.03636
CL1   6    0.189103    1.026991    0.255561    31.00000    0.15047    0.09510 =
         0.08628   -0.03659   -0.03275    0.07557
F3    5    0.261369    0.956359    0.370184    31.00000    0.13288    0.06698 =
         0.05277   -0.01743    0.02881    0.00398
PART 2

F1B   5    0.370555    0.692195    0.269774   -21.00000    0.08697    0.05532 =
         0.05771    0.01785   -0.01721   -0.00251
F2B   5    0.172034    0.734342    0.301212   -21.00000    0.11218    0.07520 =
         0.11504   -0.02063    0.08113   -0.02979
CL1B  6    0.143821    0.995781    0.279435   -31.00000    0.06371    0.07015 =
         0.10772   -0.03841    0.01701    0.00413
F3B   5    0.377611    1.029539    0.266122   -31.00000    0.12636    0.05415 =
         0.07787   -0.02142    0.02179   -0.03254
PART 0
HKLF    4

REM  import in P c n b transformed to space group : Pbcn
REM R1 =  0.0626 for    2706 Fo > 4sig(Fo)  and  0.0975 for all    3959 data
REM    267 parameters refined using    227 restraints

END

WGHT      0.0674      2.3951

REM Instructions for potential hydrogen bonds
HTAB N2 O1
EQIV $1 -x+1, y, -z+1/2
HTAB C18 O1_$1

REM Highest difference peak  0.496,  deepest hole -0.473,  1-sigma level  0.050
Q1    1   0.1711  0.9598  0.3341  11.00000  0.05    0.50
Q2    1   0.2854  1.0417  0.2625  11.00000  0.05    0.33
Q3    1   0.1015  0.7473  0.2499  11.00000  0.05    0.30
Q4    1   0.3076  0.7050  0.3071  11.00000  0.05    0.21
Q5    1   0.4968  0.7845  0.0343  11.00000  0.05    0.20
```

Table S39. Crystal data and structure refinement for SUQQEC.

Empirical formula	$C_{18}H_{14}ClF_3N_2O$
Formula weight	366.76
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	
a = 10.0193(3) Å	
b = 20.3405(6) Å	
c = 16.9296(4) Å	
Volume	3450.21(17) $Å^3$
Z	8
Density (calculated)	1.412 Mg/m^3
Absorption coefficient	0.260 mm^{-1}
F(000)	1504
Crystal size	0.400 x 0.350 x 0.300 mm^3
Theta range for data collection	2.406 to 27.509°
Index ranges	-10<=h<=13, -19<=k<=26, -21<=l<=21
Reflections collected	23579
Independent reflections	3959 [R(int) = 0.0629]
Completeness to theta = 25.242°	99.80%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3959 / 227 / 267
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1475
R indices (all data)	R1 = 0.0975, wR2 = 0.1656
Largest diff. peak and hole	0.496 and -0.473 $e.Å^{-3}$

Table S40. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for SUQQEC. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	X	Y	Z	U(eq)
O(1)	3927(2)	9274(1)	1798(1)	44(1)
N(1)	4174(2)	7415(1)	1181(1)	36(1)
N(2)	3852(2)	7992(1)	1570(1)	36(1)
C(1)	5221(2)	6864(1)	127(1)	33(1)
C(2)	5512(2)	6298(1)	562(1)	37(1)
C(3)	5877(2)	5724(1)	182(2)	43(1)
C(4)	5943(2)	5702(1)	-634(2)	47(1)
C(5)	5648(2)	6256(1)	-1067(2)	47(1)
C(6)	5305(2)	6838(1)	-694(1)	41(1)
C(7)	5154(2)	8118(1)	141(1)	34(1)
C(8)	6476(2)	8276(1)	-13(2)	45(1)
C(9)	6793(3)	8860(1)	-381(2)	58(1)
C(10)	5802(3)	9292(1)	-603(2)	62(1)
C(11)	4492(3)	9135(1)	-452(2)	56(1)
C(12)	4159(2)	8554(1)	-87(1)	43(1)
C(13)	4811(2)	7480(1)	523(1)	33(1)
C(14)	3187(2)	7974(1)	2255(1)	39(1)
C(15)	2731(3)	7302(1)	2528(2)	54(1)
C(16)	2921(2)	8529(1)	2685(1)	43(1)
C(17)	3339(2)	9158(1)	2429(1)	41(1)
C(18)	3072(3)	9744(1)	2966(2)	52(1)
F(1)	2454(4)	7336(2)	3339(2)	62(1)
F(2)	1674(3)	7129(2)	2182(2)	76(1)
Cl(1)	1891(3)	10270(1)	2556(1)	111(1)
F(3)	2614(3)	9564(1)	3702(1)	84(1)
F(1B)	3706(5)	6922(2)	2698(3)	67(2)
F(2B)	1720(9)	7343(4)	3012(5)	101(3)
Cl(1B)	1438(4)	9958(3)	2794(4)	80(2)
F(3B)	3776(9)	10295(3)	2661(5)	86(3)

Table S41. Bond distances [Å] and angles [°] for SUQQEC.

Bond distance (Å)		Bond angle (°)			Bond angle (°)
O(1)-C(17)	1.243(3)	C(13)-N(1)-N(2)	116.16(18)	F(1B)-C(15)-F(2B)	119.4(6)
N(1)-C(13)	1.291(3)	C(14)-N(2)-N(1)	120.41(19)	F(2)-C(15)-F(1)	107.6(3)
N(1)-N(2)	1.383(3)	C(14)-N(2)-H(2N)	117.0(17)	F(2)-C(15)-C(14)	111.3(3)
N(2)-C(14)	1.338(3)	N(1)-N(2)-H(2N)	122.3(17)	F(1B)-C(15)-C(14)	112.6(3)
N(2)-H(2N)	0.871(16)	C(6)-C(1)-C(2)	118.9(2)	F(2B)-C(15)-C(14)	111.5(4)
C(1)-C(6)	1.394(3)	C(6)-C(1)-C(13)	120.0(2)	F(1)-C(15)-C(14)	108.3(3)
C(1)-C(2)	1.396(3)	C(2)-C(1)-C(13)	121.1(2)	F(2)-C(15)-H(15A)	109.9
C(1)-C(13)	1.479(3)	C(3)-C(2)-C(1)	120.4(2)	F(1)-C(15)-H(15A)	109.9
C(2)-C(3)	1.382(3)	C(3)-C(2)-H(2)	119.8	C(14)-C(15)-H(15A)	109.9
C(2)-H(2)	0.9500	C(1)-C(2)-H(2)	119.8	F(1B)-C(15)-H(15B)	103.8
C(3)-C(4)	1.384(4)	C(2)-C(3)-C(4)	120.3(2)	F(2B)-C(15)-H(15B)	103.8
C(3)-H(3)	0.9500	C(2)-C(3)-H(3)	119.9	C(14)-C(15)-H(15B)	103.8
C(4)-C(5)	1.376(4)	C(4)-C(3)-H(3)	119.9	C(14)-C(16)-C(17)	121.7(2)
C(4)-H(4)	0.9500	C(5)-C(4)-C(3)	119.7(2)	C(14)-C(16)-H(16)	119.1
C(5)-C(6)	1.385(3)	C(5)-C(4)-H(4)	120.2	C(17)-C(16)-H(16)	119.1
C(5)-H(5)	0.9500	C(3)-C(4)-H(4)	120.2	O(1)-C(17)-C(16)	125.2(2)
C(6)-H(6)	0.9500	C(4)-C(5)-C(6)	120.7(2)	O(1)-C(17)-C(18)	116.5(2)
C(7)-C(8)	1.387(3)	C(4)-C(5)-H(5)	119.7	C(16)-C(17)-C(18)	118.3(2)
C(7)-C(12)	1.390(3)	C(6)-C(5)-H(5)	119.7	F(3)-C(18)-C(17)	112.9(2)
C(7)-C(13)	1.491(3)	C(5)-C(6)-C(1)	120.1(2)	F(3B)-C(18)-C(17)	108.3(3)
C(8)-C(9)	1.377(4)	C(5)-C(6)-H(6)	119.9	F(3B)-C(18)-Cl(1B)	102.2(5)
C(8)-H(8)	0.9500	C(1)-C(6)-H(6)	119.9	C(17)-C(18)-Cl(1B)	105.3(2)
C(9)-C(10)	1.378(4)	C(8)-C(7)-C(12)	118.9(2)	F(3)-C(18)-Cl(1)	107.3(2)
C(9)-H(9)	0.9500	C(8)-C(7)-C(13)	120.27(19)	C(17)-C(18)-Cl(1)	111.22(18)
C(10)-C(11)	1.375(4)	C(12)-C(7)-C(13)	120.8(2)	F(3)-C(18)-H(18A)	108.4
C(10)-H(10)	0.9500	C(9)-C(8)-C(7)	120.4(2)	C(17)-C(18)-H(18A)	108.4
C(11)-C(12)	1.374(4)	C(9)-C(8)-H(8)	119.8	Cl(1)-C(18)-H(18A)	108.4
C(11)-H(11)	0.9500	C(7)-C(8)-H(8)	119.8		
C(12)-H(12)	0.9500	C(8)-C(9)-C(10)	120.4(2)		
C(14)-C(16)	1.370(3)	C(8)-C(9)-H(9)	119.8		
C(14)-C(15)	1.514(4)	C(10)-C(9)-H(9)	119.8		
C(15)-F(2)	1.260(4)	C(11)-C(10)-C(9)	119.3(2)		
C(15)-F(1B)	1.278(5)	C(11)-C(10)-H(10)	120.3		
C(15)-F(2B)	1.306(6)	C(9)-C(10)-H(10)	120.3		
C(15)-F(1)	1.403(4)	C(12)-C(11)-C(10)	121.0(2)		
C(15)-H(15A)	1.0000	C(12)-C(11)-H(11)	119.5		
C(15)-H(15B)	1.0000	C(10)-C(11)-H(11)	119.5		
C(16)-C(17)	1.413(4)	C(11)-C(12)-C(7)	120.0(2)		
C(16)-H(16)	0.9500	C(11)-C(12)-H(12)	120.0		
C(17)-C(18)	1.523(3)	C(7)-C(12)-H(12)	120.0		
C(18)-F(3)	1.378(3)	N(1)-C(13)-C(1)	116.27(19)		
C(18)-F(3B)	1.422(7)	N(1)-C(13)-C(7)	125.23(19)		
C(18)-Cl(1B)	1.719(6)	C(1)-C(13)-C(7)	118.49(18)		
C(18)-Cl(1)	1.740(3)	N(2)-C(14)-C(16)	122.3(2)		
C(18)-H(18A)	1.0000	N(2)-C(14)-C(15)	116.1(2)		
C(18)-H(18B)	1.0000	C(16)-C(14)-C(15)	121.6(2)		

Table S42. Anisotropic displacement parameters ($Å^2 \times 10^3$) for SUQQEC. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	46(1)	42(1)	44(1)	-3(1)	1(1)	-1(1)
N(1)	32(1)	34(1)	41(1)	-2(1)	4(1)	1(1)
N(2)	35(1)	35(1)	39(1)	0(1)	5(1)	-1(1)
C(1)	23(1)	34(1)	42(1)	-1(1)	2(1)	-1(1)
C(2)	30(1)	37(1)	45(1)	0(1)	1(1)	-4(1)
C(3)	34(1)	33(1)	63(2)	0(1)	2(1)	-3(1)
C(4)	39(1)	40(1)	63(2)	-12(1)	11(1)	-3(1)
C(5)	45(1)	50(1)	45(1)	-8(1)	11(1)	-5(1)
C(6)	36(1)	42(1)	43(1)	0(1)	4(1)	1(1)
C(7)	31(1)	33(1)	36(1)	-1(1)	3(1)	2(1)
C(8)	31(1)	41(1)	64(2)	7(1)	6(1)	5(1)
C(9)	40(1)	48(2)	87(2)	14(1)	19(1)	0(1)
C(10)	63(2)	46(2)	77(2)	23(1)	20(2)	6(1)
C(11)	52(2)	54(2)	62(2)	23(1)	10(1)	17(1)
C(12)	33(1)	50(1)	47(1)	11(1)	2(1)	8(1)
C(13)	24(1)	36(1)	39(1)	1(1)	-2(1)	2(1)
C(14)	33(1)	46(1)	38(1)	1(1)	4(1)	0(1)
C(15)	58(2)	52(2)	52(1)	4(1)	17(1)	-5(1)
C(16)	42(1)	52(1)	35(1)	-2(1)	5(1)	2(1)
C(17)	37(1)	47(1)	38(1)	-7(1)	-4(1)	4(1)
C(18)	53(2)	55(2)	48(1)	-13(1)	4(1)	1(1)
F(1)	77(2)	62(2)	46(2)	12(1)	17(1)	-8(2)
F(2)	82(2)	80(2)	66(2)	16(2)	-16(2)	-36(2)
Cl(1)	150(2)	95(1)	86(1)	-37(1)	-33(1)	76(1)
F(3)	133(2)	67(2)	53(1)	-17(1)	29(1)	4(2)
F(1B)	87(3)	55(3)	58(3)	18(2)	-17(2)	-3(2)
F(2B)	112(5)	75(4)	115(7)	-21(4)	81(5)	-30(4)
Cl(1B)	64(2)	70(3)	108(4)	-38(3)	17(2)	4(2)
F(3B)	126(7)	54(4)	78(5)	-21(3)	22(4)	-33(4)

Table S43. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for SUQQEC.

	X	Y	Z	U(eq)
H(2N)	4130(20)	8375(9)	1409(14)	44
H(2)	5459	6308	1122	45
H(3)	6084	5343	482	52
H(4)	6190	5307	-894	56
H(5)	5680	6239	-1628	56
H(6)	5126	7221	-999	49
H(8)	7165	7981	136	54
H(9)	7701	8965	-482	70
H(10)	6022	9693	-858	74
H(11)	3807	9433	-603	67
H(12)	3249	8452	9	52
H(15A)	3450	6971	2429	65
H(15B)	2339	7100	2042	65
H(16)	2442	8491	3167	51
H(18A)	3925	9993	3034	63
H(18B)	3269	9654	3535	63

6.2.5.2. CCDC Entry SUQQIG

SUQQIG crystallized in the orthorhombic space group *Pbcn* with two molecules in the asymmetric unit. Coordinates for H2n, the hydrogen atom of the amino group, were taken from the difference Fourier synthesis and H2n was subsequently refined freely. All other hydrogen atoms including H19, the hydrogen atom of the CF_2H group, were attached to idealized positions. Their isotropic displacement parameters were fixed to 1.2 times the U_{eq} value of the atoms, to which they are attached. The CF_2H group was modeled across two positions. The major component of the disorder refined to an occupancy of 64.2%. The terminal $CFHCF_3$ moiety was also modeled across two positions. The major part refined to an occupancy of 56.9%. Distance and anisotropic displacement parameter restraints were applied to all disordered atoms.

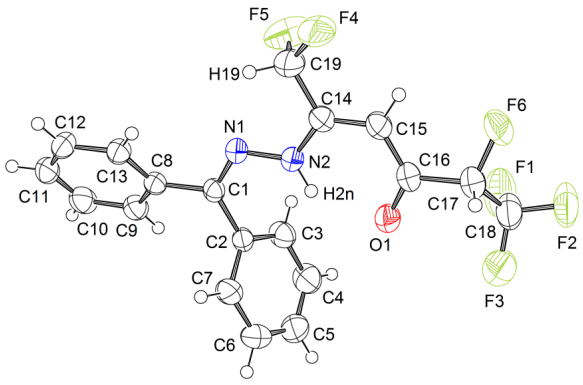


Figure S49. ORTEP representation of SUQQIG. Thermal ellipsoids are set at 50% probability.

res-file for the re-refinement of SUQQIG:

```
TITL suqqig_a.res in Pbcn
CELL  0.71073   9.9803  20.8362  17.5990   90.000   90.000   90.000
ZERR   8.000   0.0020   0.0042   0.0035    0.000    0.000    0.000
LATT  1
SYMM 1/2-X, 1/2-Y, 1/2+Z
SYMM -X, Y, 1/2-Z
SYMM 1/2+X, 1/2-Y, -Z
SFAC C H N O F
UNIT 152 112 16 8 48
L.S. 10
BOND $H
LIST 4
ACTA
FMAP 2
PLAN 5
HTAB
HTAB N2 O1
EQIV $1 -x, +y, 1/2-z
FREE F1A F1A_$1
SIMU
RIGU
SADI C18 F1 C18 F2 C18 F3 C18a F1a C18a F2a C18a F3a
SADI 0.04 F1 F2 F2 F3 F3 F1 F1A F2A F2A F3A F3A F1A
SADI C17 F6 C17 F6A
SADI C19 F4 C19 F5 C19 F4a C19 F5a
DFIX 0.89 N2 H2n
WGHT    0.065400    1.037700
FVAR       0.34263   0.56912   0.64207
O1    4    0.390092    0.570803    0.319142    11.00000    0.05849    0.04002 =
         0.04639   -0.00422   -0.01117   -0.00030
N1    3    0.408340    0.752995    0.379722    11.00000    0.03981    0.03194 =
         0.04179   -0.00251   -0.00485   -0.00252
N2    3    0.379466    0.696597    0.342258    11.00000    0.04252    0.03119 =
         0.04162   -0.00131   -0.00799   -0.00070
H2N   2    0.406336    0.657770    0.357945    11.00000   -1.20000
C1    1    0.470258    0.747103    0.443765    11.00000    0.02757    0.03242 =
         0.03785   -0.00163    0.00243   -0.00323
C2    1    0.504576    0.684885    0.479944    11.00000    0.03527    0.03278 =
         0.03565   -0.00184   -0.00353   -0.00418
C3    1    0.405134    0.644424    0.506912    11.00000    0.03971    0.05120 =
         0.05194    0.00988   -0.00128   -0.00811
AFIX  43
H3    2    0.315640    0.656192    0.502156    11.00000   -1.20000
AFIX   0
C4    1    0.437922    0.586928    0.540693    11.00000    0.06296    0.05479 =
         0.06528    0.02293   -0.00885   -0.01625
AFIX  43
H4    2    0.370376    0.560224    0.558739    11.00000   -1.20000
AFIX   0
```

```
C5    1    0.568436    0.568826    0.547906    11.00000    0.08009    0.04389 =
         0.07320    0.01553   -0.02692   -0.00407
AFIX  43
H5    2    0.589859    0.529772    0.570421    11.00000   -1.20000
AFIX   0
C6    1    0.668090    0.608387    0.521857    11.00000    0.05360    0.05393 =
         0.10254    0.00974   -0.02580    0.00710
AFIX  43
H6    2    0.757258    0.596167    0.526977    11.00000   -1.20000
AFIX   0
C7    1    0.636725    0.666442    0.487963    11.00000    0.03570    0.04717 =
         0.07939    0.00721   -0.00686   -0.00397
AFIX  43
H7    2    0.704862    0.693098    0.470544    11.00000   -1.20000
AFIX   0
C8    1    0.509007    0.807482    0.482429    11.00000    0.02769    0.03413 =
         0.04461   -0.00290   -0.00055    0.00000
C9    1    0.524276    0.808785    0.560916    11.00000    0.04290    0.04489 =
         0.04378   -0.00388   -0.00364    0.00099
AFIX  43
H9    2    0.512005    0.771518    0.589153    11.00000   -1.20000
AFIX   0
C10   1    0.557922    0.865860    0.597204    11.00000    0.05183    0.05876 =
         0.05286   -0.01864   -0.01123    0.00777
AFIX  43
H10   2    0.565760    0.866858    0.649848    11.00000   -1.20000
AFIX   0
C11   1    0.579576    0.920581    0.555914    11.00000    0.04717    0.04008 =
         0.07732   -0.02285   -0.01368    0.00659
AFIX  43
H11   2    0.603085    0.958419    0.580570    11.00000   -1.20000
AFIX   0
C12   1    0.566643    0.919797    0.477817    11.00000    0.04319    0.03154 =
         0.07485   -0.00337   -0.00224    0.00151
AFIX  43
H12   2    0.582117    0.956953    0.449883    11.00000   -1.20000
AFIX   0
C13   1    0.530507    0.863461    0.441066    11.00000    0.03690    0.03538 =
         0.04973   -0.00325    0.00004   -0.00005
AFIX  43
H13   2    0.520611    0.863122    0.388523    11.00000   -1.20000
AFIX   0
C14   1    0.314075    0.697692    0.275970    11.00000    0.04108    0.04162 =
         0.04100    0.00053   -0.00559   -0.00137
C15   1    0.287567    0.643355    0.234454    11.00000    0.05024    0.04489 =
         0.03678   -0.00182   -0.00984   -0.00215
AFIX  43
H15   2    0.240916    0.647050    0.188919    11.00000   -1.20000
AFIX   0
C16   1    0.329199    0.582102    0.259027    11.00000    0.04345    0.04327 =
         0.03873   -0.00623   -0.00271   -0.00589
```

```
C17   1    0.301842    0.524518    0.207237    11.00000    0.05797    0.04937 =
         0.04781   -0.01189   -0.00965   -0.00378
PART 1
AFIX  13
H17A  2    0.383590    0.516804    0.177771    21.00000   -1.20000
AFIX  13
PART 2
H17B  2    0.383785    0.499393    0.199719   -21.00000   -1.20000
AFIX   0
PART 1
F4    5    0.247202    0.760957    0.171770    31.00000    0.11399    0.06027 =
         0.05510    0.01519   -0.02918    0.01113
F5    5    0.161868    0.780402    0.281162    31.00000    0.10511    0.08874 =
         0.10732    0.02087    0.01296    0.04554
F6    5    0.199551    0.538049    0.155319    21.00000    0.12727    0.06392 =
         0.09265   -0.00206   -0.07221   -0.01017
PART 2
F4A   5    0.168393    0.757443    0.199154   -31.00000    0.16074    0.07297 =
         0.15814   -0.02466   -0.12571    0.03824
F5A   5    0.373623    0.795473    0.227597   -31.00000    0.12071    0.05973 =
         0.08446    0.02803    0.02694    0.00035
F6A   5    0.249594    0.541148    0.141050   -21.00000    0.15632    0.06536 =
         0.04278   -0.01534   -0.02659   -0.01543
PART 1
F1    5    0.173582    0.472345    0.298606    21.00000    0.10519    0.08914 =
         0.08504   -0.01597    0.02517   -0.04073
F2    5    0.219630    0.421476    0.195334    21.00000    0.12150    0.05463 =
         0.07756   -0.01266   -0.02219   -0.03142
F3    5    0.375922    0.438886    0.275344    21.00000    0.13883    0.06495 =
         0.11690   -0.01302   -0.05730    0.01545
C18   1    0.267256    0.464996    0.243817    21.00000    0.08373    0.05200 =
         0.05600   -0.00671   -0.01368   -0.01437
PART 2
F1A   5    0.082296    0.515013    0.257657   -21.00000    0.07225    0.13053 =
         0.17281   -0.06084    0.01638   -0.03347
F2A   5    0.156182    0.434603    0.199164   -21.00000    0.12721    0.08197 =
         0.08414   -0.03655   -0.01025   -0.04183
F3A   5    0.235603    0.457301    0.307337   -21.00000    0.17357    0.09719 =
         0.07670    0.01549   -0.02798   -0.06511
C18A  1    0.191766    0.482818    0.242861   -21.00000    0.08470    0.06450 =
         0.05476   -0.02469   -0.00030   -0.02190
PART 0
C19   1    0.270142    0.763114    0.247965    11.00000    0.07242    0.04876 =
         0.05479    0.00332   -0.01907    0.00594
PART 1
AFIX  13
H19A  2    0.340719    0.794553    0.258613    31.00000   -1.20000
AFIX  13
PART 2
H19B  2    0.233668    0.785362    0.292453   -31.00000   -1.20000
PART 0
```

```
AFIX   0
HKLF 4

REM  suqqig_a.res in Pbcn
REM R1 =  0.0580 for    2606 Fo > 4sig(Fo)  and  0.1140 for all    4419 data
REM    321 parameters refined using    608 restraints

END

WGHT      0.0654      1.0377

REM Instructions for potential hydrogen bonds
HTAB N2 O1
EQIV $2 -x+1, y, -z+1/2
HTAB C17 O1_$2

REM Highest difference peak  0.316,  deepest hole -0.170,  1-sigma level  0.039
Q1    1   0.4001  0.4751  0.2302  11.00000  0.05    0.32
Q2    1   0.0916  0.7429  0.2541  11.00000  0.05    0.25
Q3    1   0.5008  0.7768  0.4630  11.00000  0.05    0.24
Q4    1   0.3127  0.5515  0.2359  11.00000  0.05    0.21
Q5    1   0.4859  0.7190  0.4618  11.00000  0.05    0.21
```

Table S44. Crystal data and structure refinement for SUQQIG.

Empirical formula	$C_{19}H_{14}F_6N_2O$
Formula weight	400.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	
a = 9.980(2) Å	
b = 20.836(4) Å	
c = 17.599(4) Å	
Volume	3659.7(13) $Å^3$
Z	8
Density (calculated)	1.453 Mg/m^3
Absorption coefficient	0.133 mm^{-1}
F(000)	1632
Crystal size	0.450 x 0.150 x 0.100 mm^3
Theta range for data collection	2.263 to 28.022°
Index ranges	-13<=h<=12, -27<=k<=10, -9<=l<=23
Reflections collected	18813
Independent reflections	4417 [R(int) = 0.0682]
Completeness to theta = 25.242°	99.90%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4417 / 608 / 321
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1294
R indices (all data)	R1 = 0.1137, wR2 = 0.1528
Largest diff. peak and hole	0.319 and -0.167 $e.Å^{-3}$

Table S45. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for SUQQIG. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	X	Y	X	U(eq)
O(1)	3901(2)	5708(1)	3191(1)	48(1)
N(1)	4083(2)	7530(1)	3797(1)	38(1)
N(2)	3795(2)	6966(1)	3423(1)	38(1)
C(1)	4703(2)	7471(1)	4438(1)	33(1)
C(2)	5046(2)	6849(1)	4799(1)	35(1)
C(3)	4051(2)	6444(1)	5069(1)	48(1)
C(4)	4379(3)	5869(1)	5407(1)	61(1)
C(5)	5684(3)	5688(1)	5479(2)	66(1)
C(6)	6681(3)	6083(1)	5219(2)	70(1)
C(7)	6367(2)	6664(1)	4880(1)	54(1)
C(8)	5090(2)	8075(1)	4824(1)	36(1)
C(9)	5243(2)	8088(1)	5609(1)	44(1)
C(10)	5579(2)	8659(1)	5972(1)	54(1)
C(11)	5796(2)	9206(1)	5559(2)	55(1)
C(12)	5666(2)	9198(1)	4778(1)	50(1)
C(13)	5305(2)	8635(1)	4411(1)	41(1)
C(14)	3141(2)	6977(1)	2760(1)	41(1)
C(15)	2876(2)	6433(1)	2344(1)	44(1)
C(16)	3292(2)	5821(1)	2590(1)	42(1)
C(17)	3018(3)	5245(1)	2072(1)	52(1)
F(4)	2472(4)	7609(2)	1718(2)	76(1)
F(5)	1619(3)	7804(2)	2812(2)	100(1)
F(6)	1996(9)	5380(5)	1553(4)	95(3)
F(4A)	1685(9)	7575(4)	1991(6)	131(4)
F(5A)	3736(6)	7955(2)	2276(3)	88(2)
F(6A)	2495(12)	5412(7)	1411(5)	88(3)
F(1)	1736(7)	4724(4)	2986(4)	93(2)
F(2)	2196(6)	4215(3)	1954(4)	84(2)
F(3)	3759(5)	4389(2)	2753(2)	107(2)
C(18)	2673(7)	4650(3)	2438(3)	64(1)
F(1A)	823(5)	5150(3)	2577(4)	125(2)
F(2A)	1562(9)	4347(5)	1991(6)	98(3)
F(3A)	2355(11)	4573(6)	3073(5)	116(4)
C(18A)	1918(10)	4828(4)	2429(4)	68(2)
C(19)	2701(3)	7631(1)	2480(1)	59(1)

Table S46. Bond distances [Å] and angles [°] for SUQQIG.

Bond distance (Å)		Bond angle (°)			Bond angle (°)
O(1)-C(16)	1.242(2)	C(1)-N(1)-N(2)	115.87(17)	F(6)-C(17)-C(18)	106.9(5)
N(1)-C(1)	1.291(2)	C(14)-N(2)-N(1)	120.31(17)	F(6A)-C(17)-C(16)	112.9(6)
N(1)-N(2)	1.378(2)	C(14)-N(2)-H(2N)	115.3(14)	F(6)-C(17)-C(16)	111.2(5)
N(2)-C(14)	1.337(2)	N(1)-N(2)-H(2N)	124.3(14)	C(18)-C(17)-C(16)	116.8(3)
N(2)-H(2N)	0.901(16)	N(1)-C(1)-C(8)	116.41(17)	F(6A)-C(17)-C(18A)	103.0(6)
C(1)-C(8)	1.482(3)	N(1)-C(1)-C(2)	124.60(17)	C(16)-C(17)-C(18A)	109.1(3)
C(1)-C(2)	1.485(3)	C(8)-C(1)-C(2)	118.99(16)	F(6)-C(17)-H(17A)	107.1
C(2)-C(7)	1.381(3)	C(7)-C(2)-C(3)	118.6(2)	C(18)-C(17)-H(17A)	107.1
C(2)-C(3)	1.386(3)	C(7)-C(2)-C(1)	120.49(18)	C(16)-C(17)-H(17A)	107.1
C(3)-C(4)	1.377(3)	C(3)-C(2)-C(1)	120.87(19)	F(6A)-C(17)-H(17B)	110.5
C(3)-H(3)	0.93	C(4)-C(3)-C(2)	120.5(2)	C(16)-C(17)-H(17B)	110.5
C(4)-C(5)	1.362(4)	C(4)-C(3)-H(3)	119.8	C(18A)-C(17)-H(17B)	110.5
C(4)-H(4)	0.93	C(2)-C(3)-H(3)	119.8	F(2)-C(18)-F(3)	106.2(5)
C(5)-C(6)	1.370(4)	C(5)-C(4)-C(3)	120.6(2)	F(2)-C(18)-F(1)	106.6(6)
C(5)-H(5)	0.93	C(5)-C(4)-H(4)	119.7	F(3)-C(18)-F(1)	108.2(6)
C(6)-C(7)	1.385(4)	C(3)-C(4)-H(4)	119.7	F(2)-C(18)-C(17)	112.7(5)
C(6)-H(6)	0.93	C(4)-C(5)-C(6)	119.8(2)	F(3)-C(18)-C(17)	110.0(5)
C(7)-H(7)	0.93	C(4)-C(5)-H(5)	120.1	F(1)-C(18)-C(17)	112.8(6)
C(8)-C(9)	1.390(3)	C(6)-C(5)-H(5)	120.1	F(1A)-C(18A)-F(2A)	106.3(7)
C(8)-C(13)	1.392(3)	C(5)-C(6)-C(7)	120.4(2)	F(1A)-C(18A)-F(3A)	108.0(9)
C(9)-C(10)	1.391(3)	C(5)-C(6)-H(6)	119.8	F(2A)-C(18A)-F(3A)	106.5(9)
C(9)-H(9)	0.93	C(7)-C(6)-H(6)	119.8	F(1A)-C(18A)-C(17)	112.9(6)
C(10)-C(11)	1.369(4)	C(2)-C(7)-C(6)	120.2(2)	F(2A)-C(18A)-C(17)	112.7(7)
C(10)-H(10)	0.93	C(2)-C(7)-H(7)	119.9	F(3A)-C(18A)-C(17)	109.9(8)
C(11)-C(12)	1.380(3)	C(6)-C(7)-H(7)	119.9	F(5A)-C(19)-F(4A)	118.5(6)
C(11)-H(11)	0.93	C(9)-C(8)-C(13)	119.11(19)	F(5)-C(19)-F(4)	108.5(3)
C(12)-C(13)	1.388(3)	C(9)-C(8)-C(1)	120.10(18)	F(5)-C(19)-C(14)	110.5(3)
C(12)-H(12)	0.93	C(13)-C(8)-C(1)	120.80(17)	F(5A)-C(19)-C(14)	109.3(3)
C(13)-H(13)	0.93	C(8)-C(9)-C(10)	120.0(2)	F(4A)-C(19)-C(14)	110.5(4)
C(14)-C(15)	1.373(3)	C(8)-C(9)-H(9)	120	F(4)-C(19)-C(14)	109.8(3)
C(14)-C(19)	1.515(3)	C(10)-C(9)-H(9)	120	F(5)-C(19)-H(19A)	109.4
C(15)-C(16)	1.410(3)	C(11)-C(10)-C(9)	120.4(2)	F(4)-C(19)-H(19A)	109.4
C(15)-H(15)	0.93	C(11)-C(10)-H(10)	119.8	C(14)-C(19)-H(19A)	109.4
C(16)-C(17)	1.531(3)	C(9)-C(10)-H(10)	119.8	F(5A)-C(19)-H(19B)	105.9
C(17)-F(6A)	1.322(9)	C(10)-C(11)-C(12)	120.3(2)	F(4A)-C(19)-H(19B)	105.9
C(17)-F(6)	1.399(7)	C(10)-C(11)-H(11)	119.9	C(14)-C(19)-H(19B)	105.9
C(17)-C(18)	1.439(6)	C(12)-C(11)-H(11)	119.9		
C(17)-C(18A)	1.534(9)	C(11)-C(12)-C(13)	119.9(2)		
C(17)-H(17A)	0.9800	C(11)-C(12)-H(12)	120.1		
C(17)-H(17B)	0.9800	C(13)-C(12)-H(12)	120.1		
F(4)-C(19)	1.361(4)	C(12)-C(13)-C(8)	120.3(2)		
F(5)-C(19)	1.280(4)	C(12)-C(13)-H(13)	119.8		
F(4A)-C(19)	1.335(6)	C(8)-C(13)-H(13)	119.8		
F(5A)-C(19)	1.285(5)	N(2)-C(14)-C(15)	122.96(19)		
F(1)-C(18)	1.352(8)	N(2)-C(14)-C(19)	116.14(18)		

F(2)-C(18)	1.333(6)	C(15)-C(14)-C(19)	120.90(18)
F(3)-C(18)	1.334(7)	C(14)-C(15)-C(16)	121.76(18)
F(1A)-C(18A)	1.308(9)	C(14)-C(15)-H(15)	119.1
F(2A)-C(18A)	1.314(8)	C(16)-C(15)-H(15)	119.1
F(3A)-C(18A)	1.327(10)	O(1)-C(16)-C(15)	125.20(19)
C(19)-H(19A)	0.9800	O(1)-C(16)-C(17)	116.49(19)
C(19)-H(19B)	0.9800	C(15)-C(16)-C(17)	118.29(18)

Table S47. Anisotropic displacement parameters ($Å^2 \times 10^3$) for SUQQIG. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	58(1)	40(1)	46(1)	-4(1)	-11(1)	0(1)
N(1)	40(1)	32(1)	42(1)	-2(1)	-5(1)	-2(1)
N(2)	42(1)	31(1)	42(1)	-1(1)	-8(1)	-1(1)
C(1)	28(1)	32(1)	38(1)	-2(1)	2(1)	-3(1)
C(2)	35(1)	33(1)	36(1)	-2(1)	-4(1)	-4(1)
C(3)	40(1)	51(1)	52(1)	10(1)	-1(1)	-8(1)
C(4)	63(2)	55(2)	65(2)	23(1)	-9(1)	-16(1)
C(5)	80(2)	44(1)	73(2)	16(1)	-27(1)	-4(1)
C(6)	54(2)	54(2)	102(2)	10(2)	-26(2)	7(1)
C(7)	36(1)	47(1)	79(2)	7(1)	-7(1)	-4(1)
C(8)	28(1)	34(1)	45(1)	-3(1)	-1(1)	0(1)
C(9)	43(1)	45(1)	44(1)	-4(1)	-4(1)	1(1)
C(10)	52(1)	59(2)	53(1)	-19(1)	-11(1)	8(1)
C(11)	47(1)	40(1)	77(2)	-23(1)	-14(1)	7(1)
C(12)	43(1)	32(1)	75(2)	-3(1)	-2(1)	2(1)
C(13)	37(1)	35(1)	50(1)	-3(1)	0(1)	0(1)
C(14)	41(1)	42(1)	41(1)	1(1)	-6(1)	-1(1)
C(15)	50(1)	45(1)	37(1)	-2(1)	-10(1)	-2(1)
C(16)	44(1)	43(1)	39(1)	-6(1)	-3(1)	-6(1)
C(17)	58(2)	49(1)	48(1)	-12(1)	-10(1)	-4(1)
F(4)	114(3)	60(2)	55(1)	15(1)	-29(2)	11(2)
F(5)	105(2)	89(2)	107(2)	21(2)	13(2)	45(2)
F(6)	128(5)	64(3)	93(5)	-2(3)	-73(5)	-10(4)
F(4A)	161(7)	73(4)	159(8)	-25(5)	-126(6)	39(5)
F(5A)	121(4)	60(3)	85(3)	28(2)	27(3)	0(3)
F(6A)	157(9)	65(4)	43(2)	-15(2)	-27(4)	-16(5)
F(1)	105(4)	89(4)	85(4)	-16(3)	25(3)	-41(3)
F(2)	122(5)	54(2)	77(2)	-13(2)	-22(3)	-31(3)
F(3)	139(4)	64(2)	117(3)	-13(2)	-57(3)	16(2)
C(18)	83(4)	52(3)	56(3)	-7(2)	-14(3)	-14(3)
F(1A)	73(3)	130(5)	173(5)	-61(4)	17(3)	-34(3)
F(2A)	128(6)	82(5)	84(3)	-37(3)	-11(4)	-42(4)
F(3A)	174(10)	97(6)	77(4)	16(3)	-28(5)	-65(6)
C(18A)	85(5)	64(4)	55(3)	-25(3)	0(3)	-22(3)
C(19)	72(2)	49(2)	55(1)	3(1)	-19(1)	6(1)

Table S48. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for SUQQIG.

	X	Y	Z	U(eq)
H(2N)	4060(20)	6574(8)	3579(12)	46
H(3)	3156	6561	5021	57
H(4)	3704	5602	5587	73
H(5)	5898	5297	5704	79
H(6)	7572	5961	5269	84
H(7)	7049	6931	4706	65
H(9)	5120	7715	5892	53
H(10)	5658	8669	6498	65
H(11)	6031	9584	5806	66
H(12)	5821	9570	4499	60
H(13)	5206	8632	3885	49
H(15)	2409	6470	1889	53
H(17A)	3836	5168	1778	62
H(17B)	3838	4994	1997	62
H(19A)	3407	7946	2586	70
H(19B)	2336	7854	2925	70

7. NMR Spectra

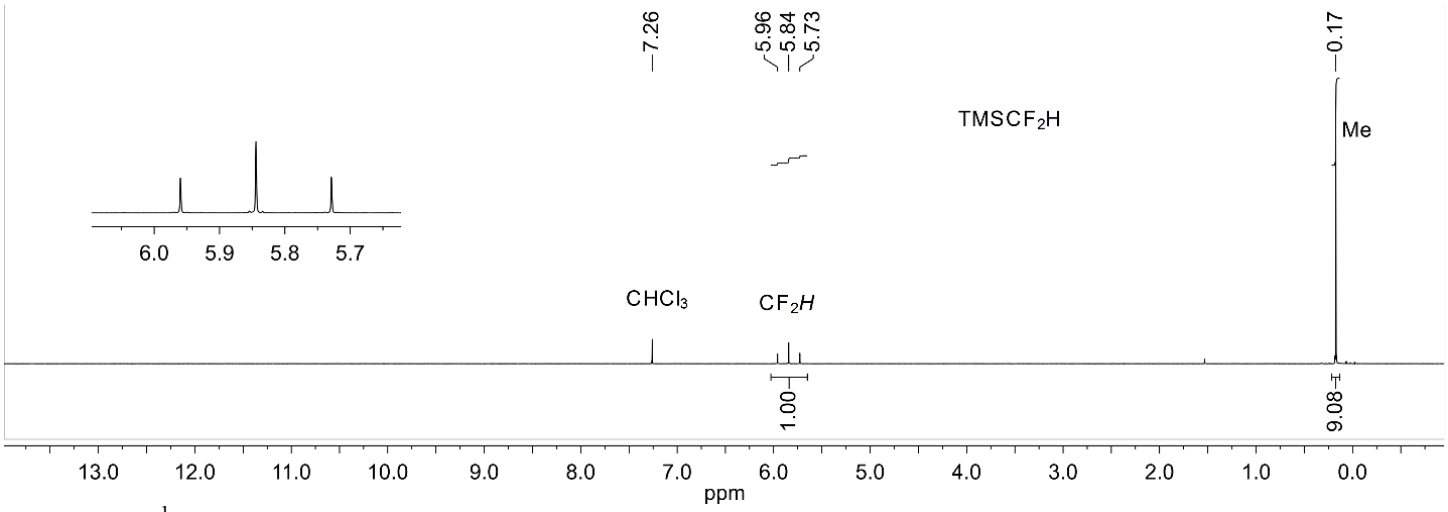


Figure S50. ^{1}H NMR spectrum of $TMSCF_2H$.

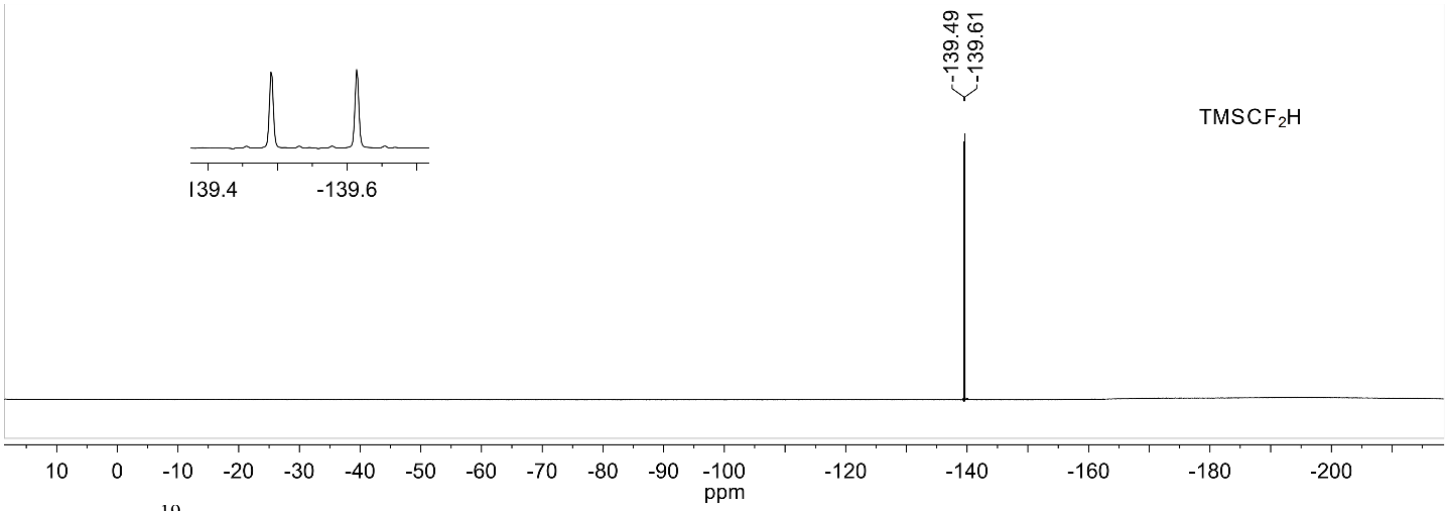


Figure S51. ^{19}F NMR spectrum of $TMSCF_2H$.

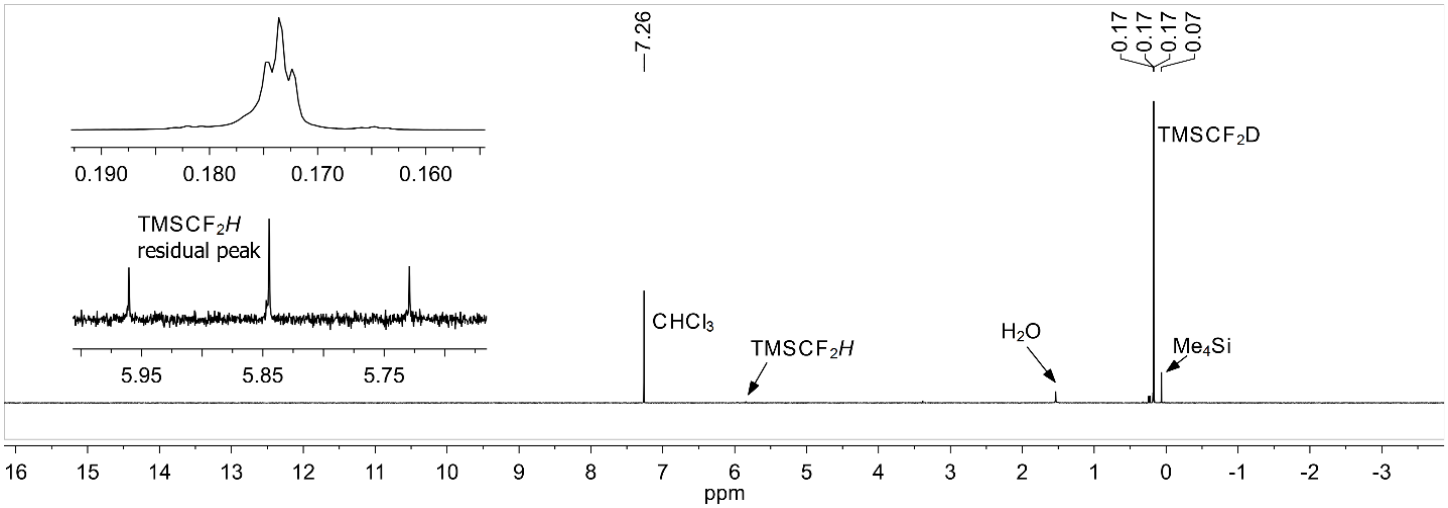


Figure S52. ^{1}H NMR spectrum of $TMSCF_2D$.

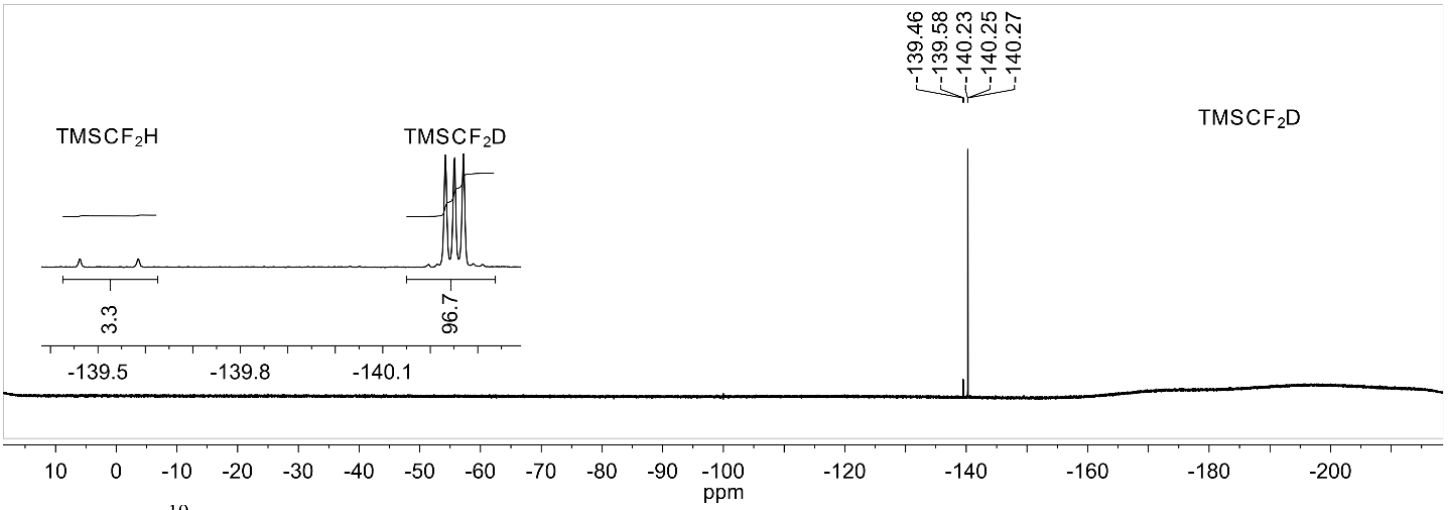


Figure S53. ^{19}F NMR spectrum of $TMSCF_2D$.

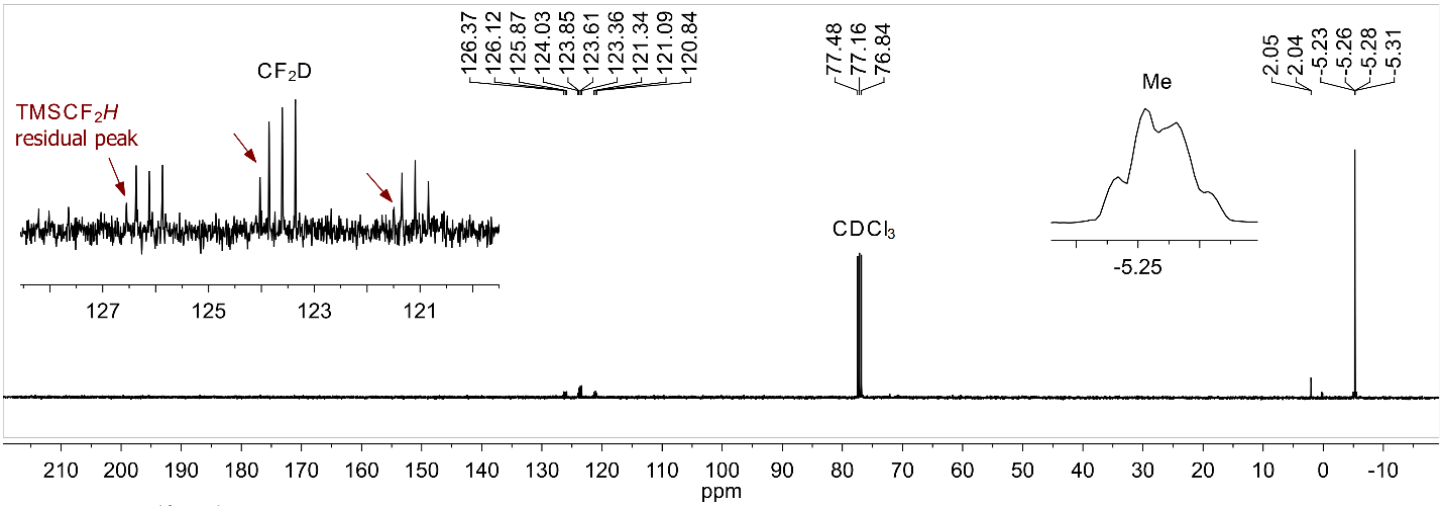


Figure S54. $^{13}C\{^1H\}$ NMR spectrum of $TMSCF_2D$.

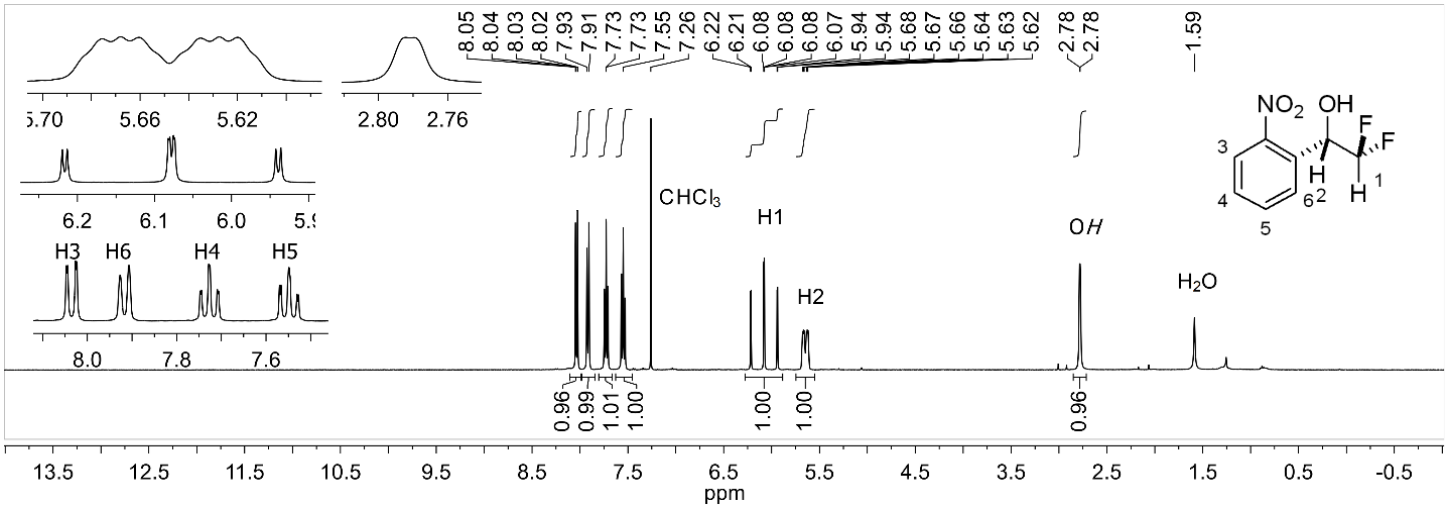


Figure S55. ^1H NMR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethan-1-ol (**3-NO_2**).

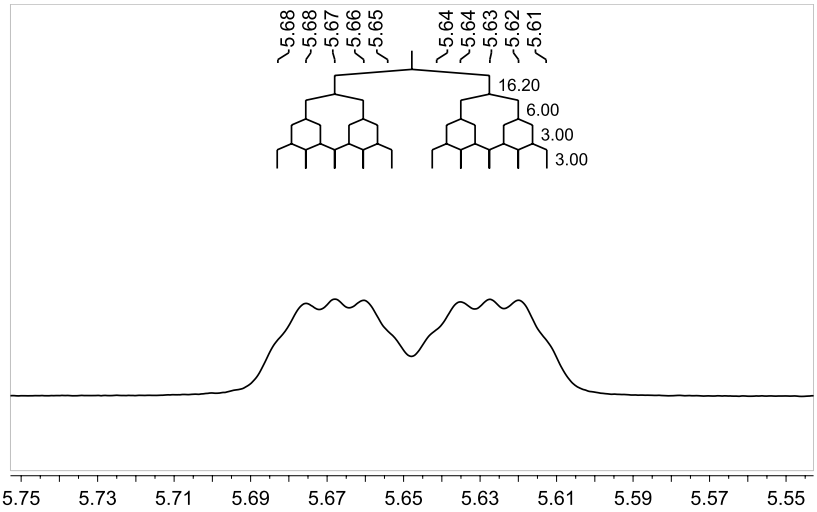


Figure S56. Splitting diagram for H2 of 2,2-difluoro-1-(2-nitrophenyl)ethan-1-ol (**3-NO$_2$**).

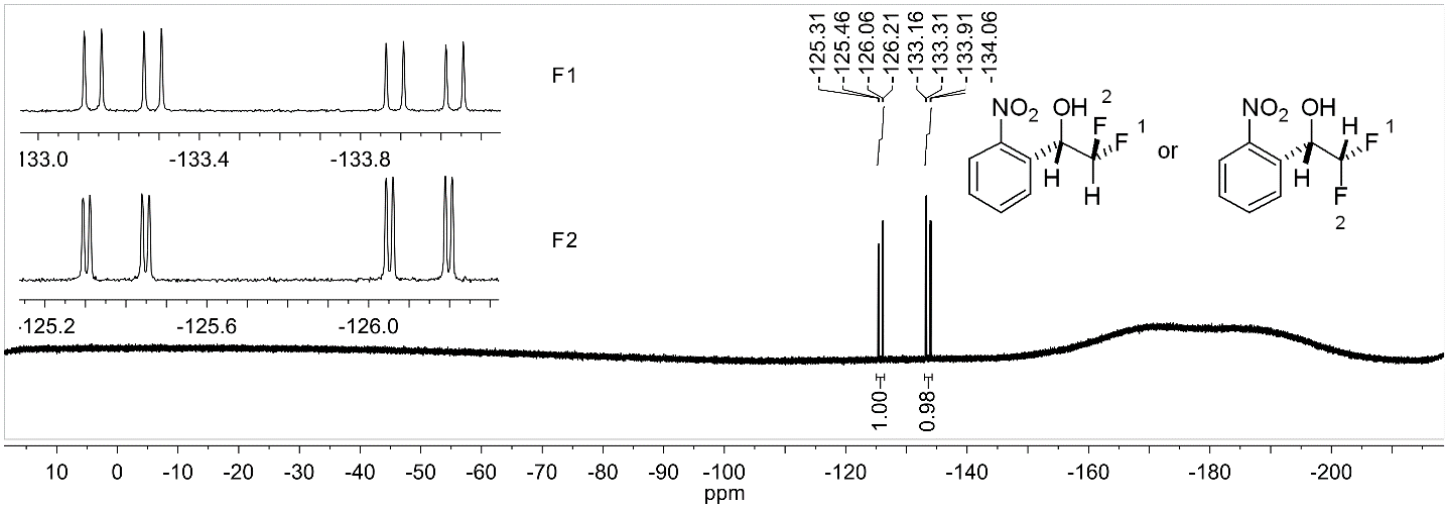


Figure S57. ^{19}F NMR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethan-1-ol (**3-NO$_2$**).

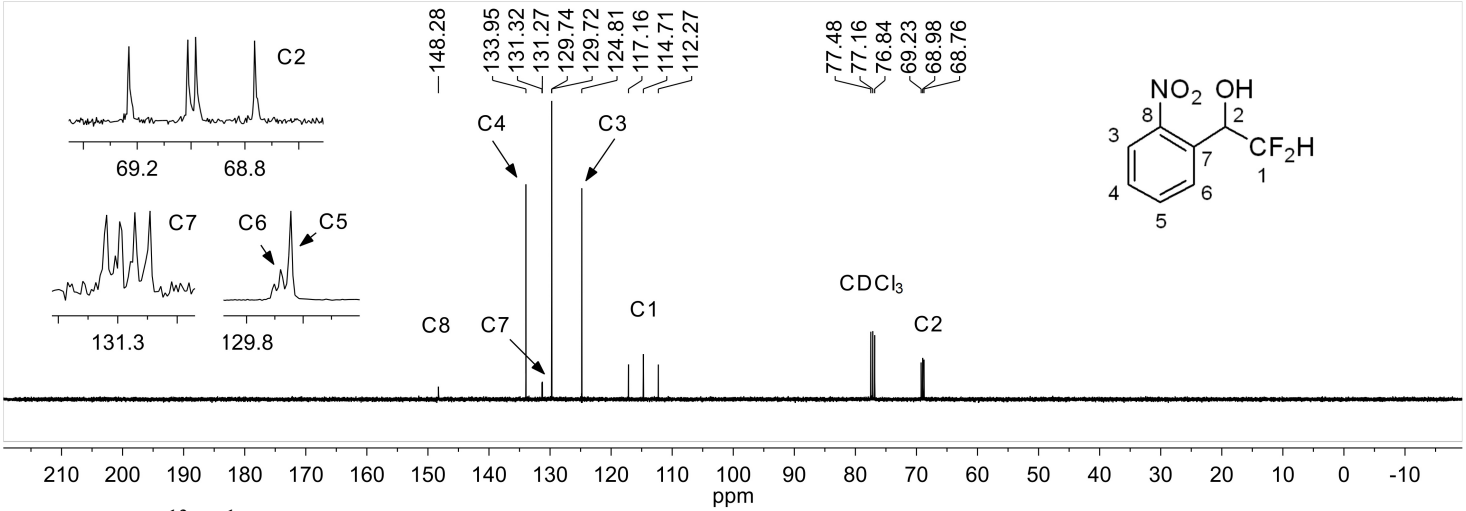


Figure S58. ^{13}C{^{1}H} NMR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethan-1-ol (**3-NO$_2$**).

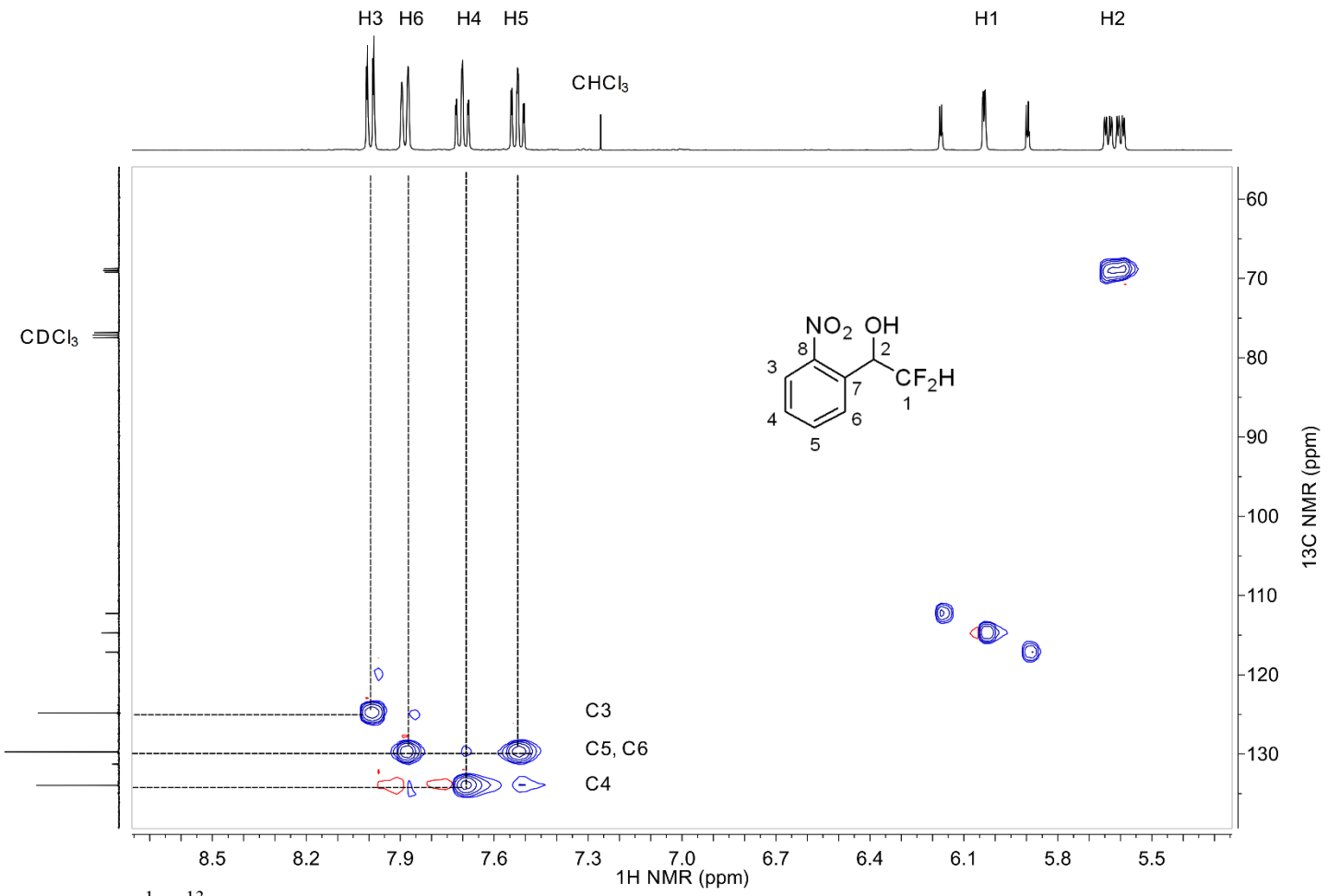


Figure S59. ^{1}H-^{13}C HSQC spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethan-1-ol (**3-NO$_2$**).

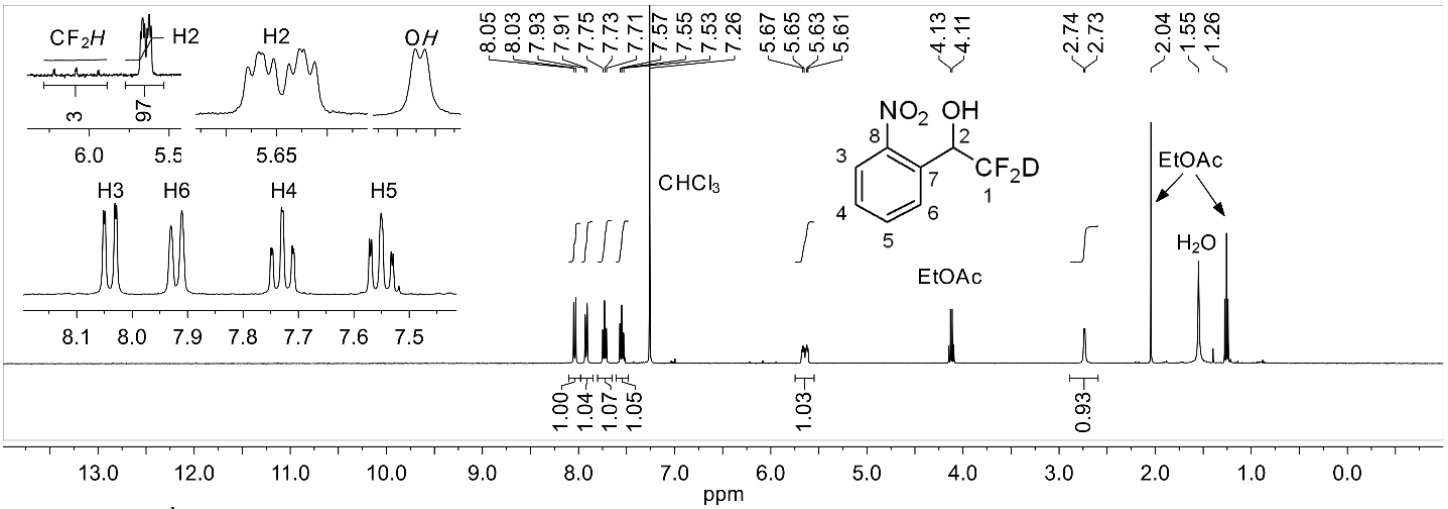


Figure S60. ^{1}H NMR spectrum of 2,2-difluoro-2-deutero-1-(2-nitrophenyl)ethan-1-ol (**3-NO$_2$-D**).

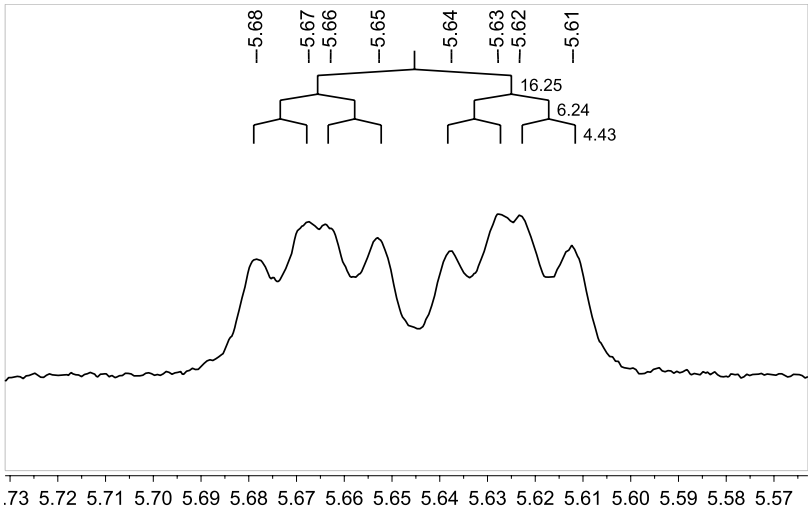


Figure S61. Splitting diagram for H2 of 2,2-difluoro-2-deutero-1-(2-nitrophenyl)ethan-1-ol (**3-NO_2-D**).

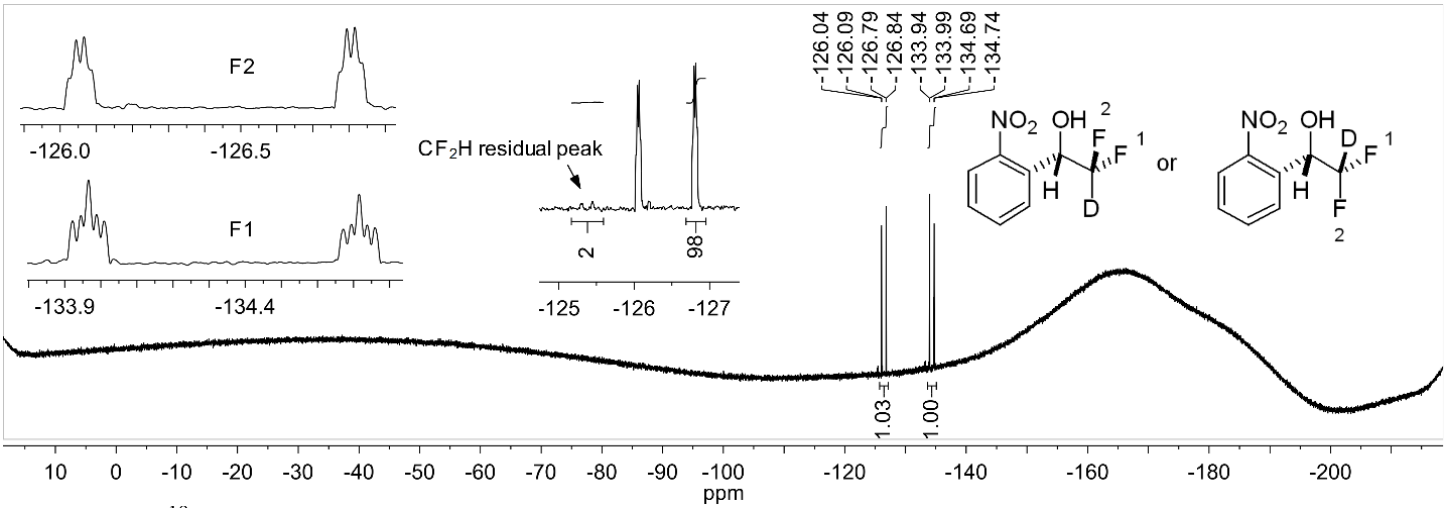


Figure S62. ^{19}F NMR spectrum of 2,2-difluoro-2-deutero-1-(2-nitrophenyl)ethan-1-ol (**3-NO_2-D**).

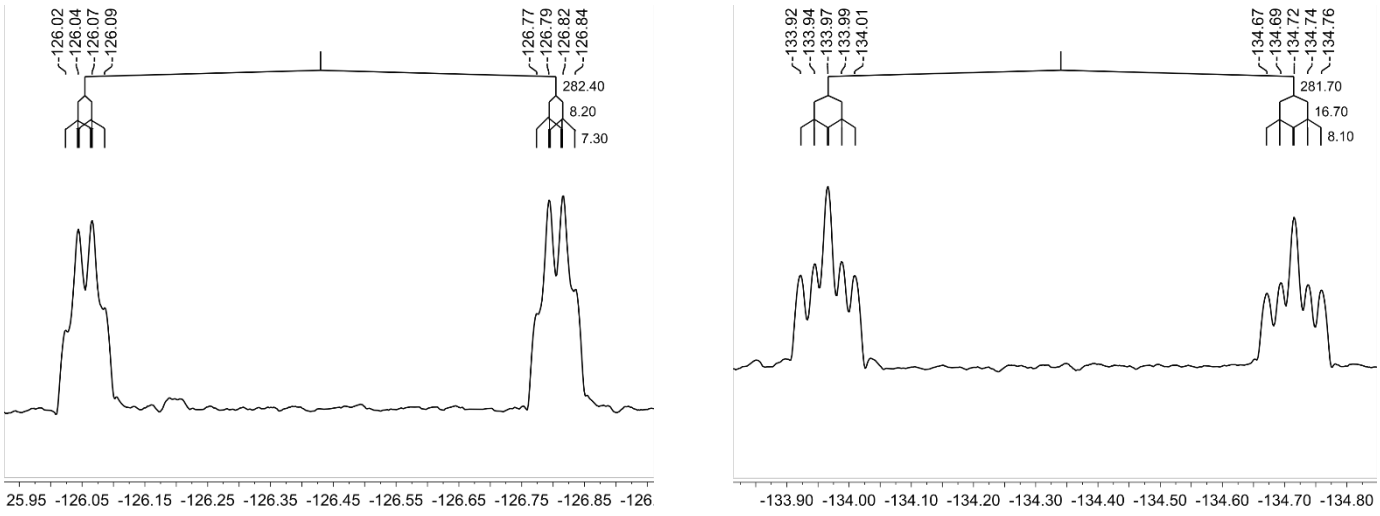


Figure S63. Splitting diagrams for F2 (left) and F1 (right) of 2,2-difluoro-2-deutero-1-(2-nitrophenyl)ethan-1-ol (**3-NO_2-D**).

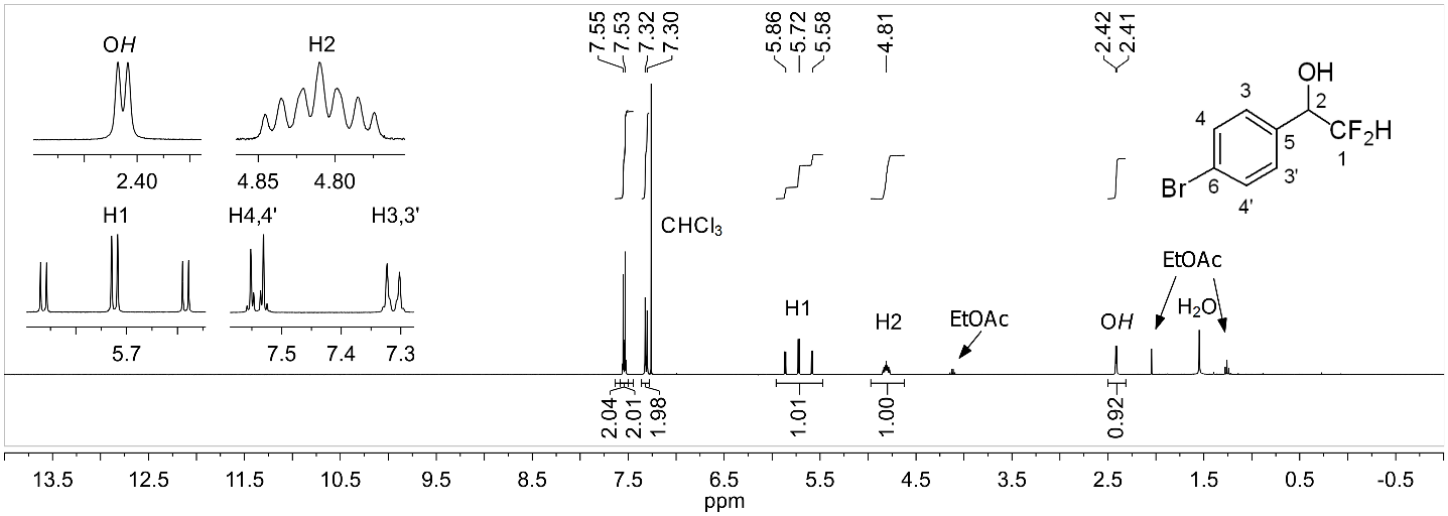


Figure S64. ^{1}H NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethan-1-ol (**3-Br**).

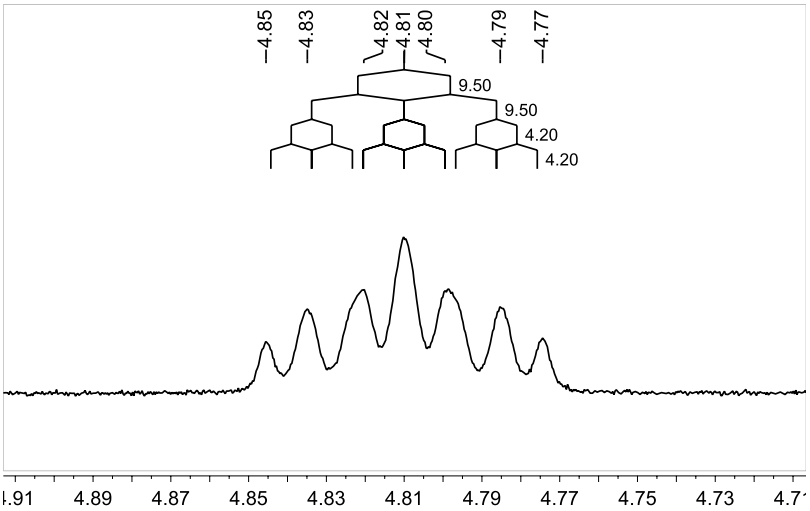


Figure S65. Splitting diagram for H2 of 1-(4-bromophenyl)-2,2-difluoroethan-1-ol (**3-Br**).

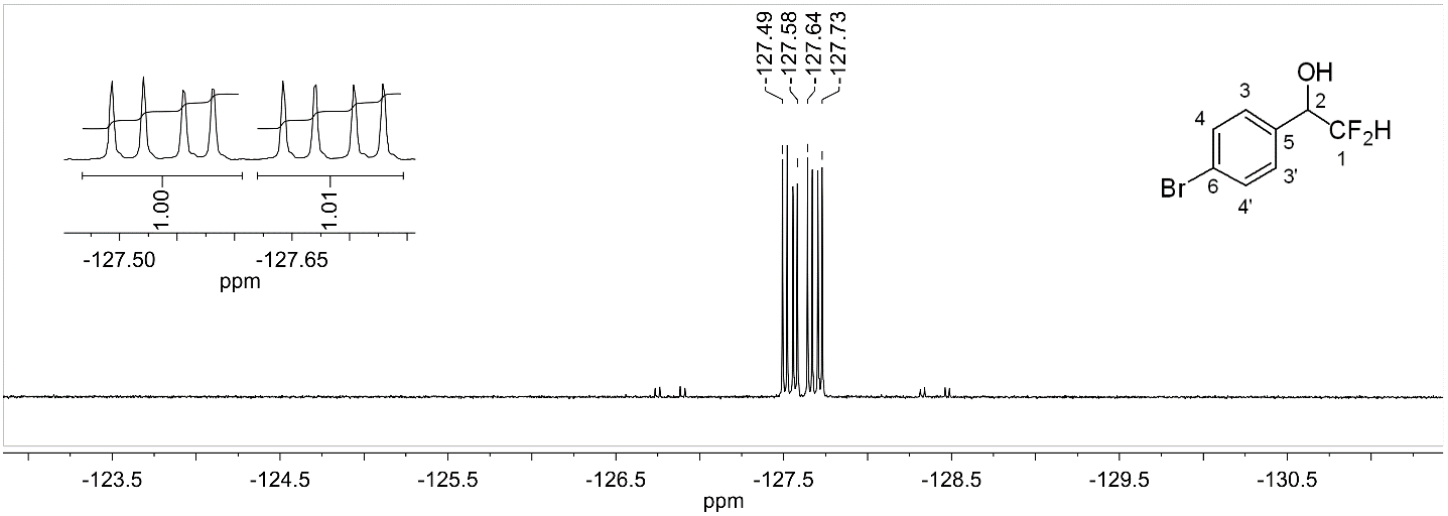


Figure S66. ^{19}F NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethan-1-ol (**3-Br**).

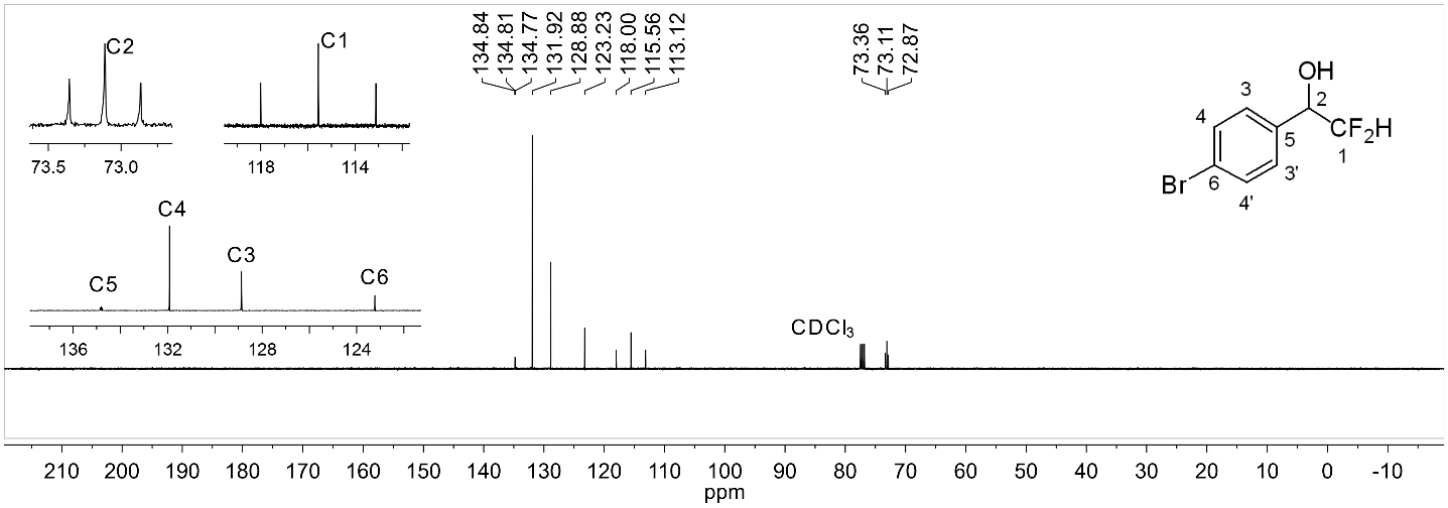


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethan-1-ol (**3-Br**).

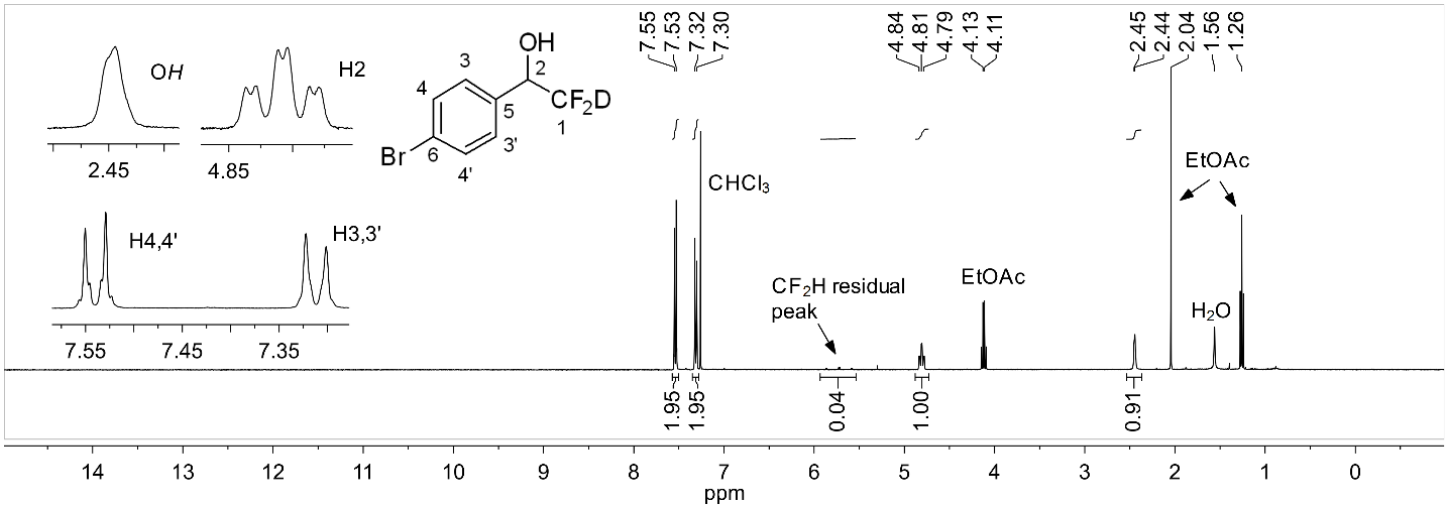


Figure S68. ^{1}H NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethan-2-deutero-1-ol (**3-Br-D**).

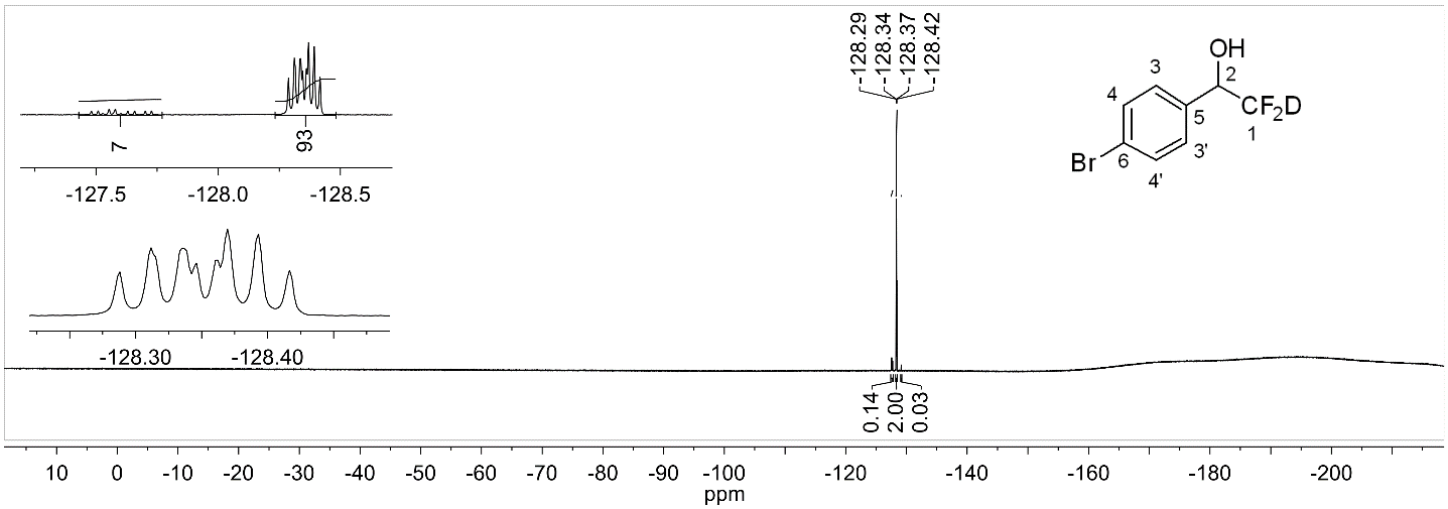


Figure S69. ^{19}F NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethan-2-deutero-1-ol (**3-Br-D**).

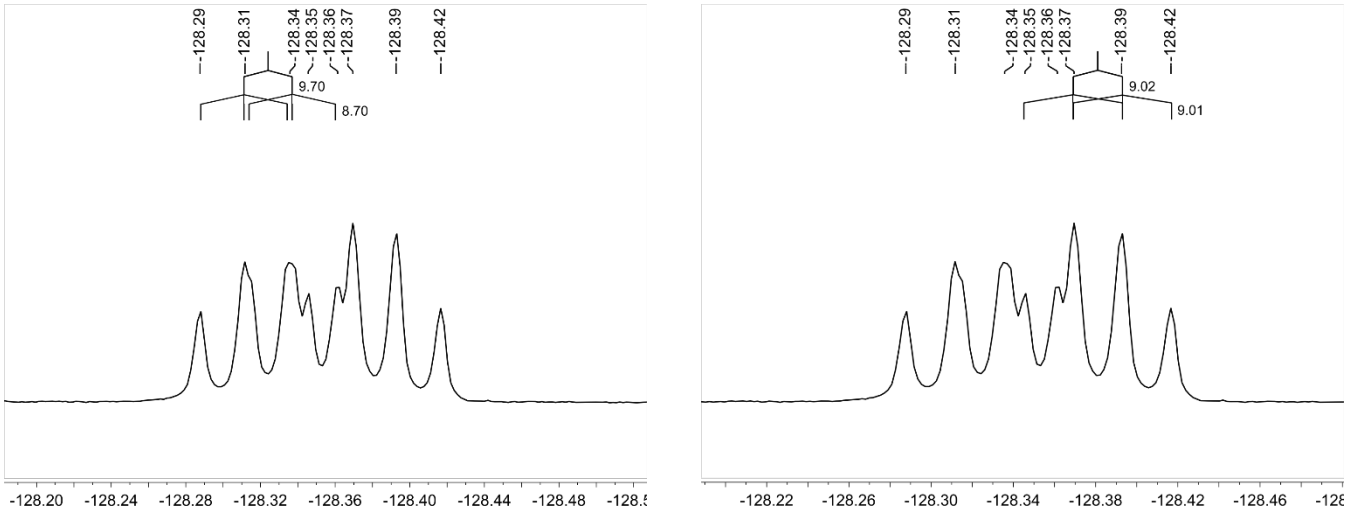


Figure S70. Splitting diagrams for Fa (left) and Fb (right) of 2,2-difluoro-2-deuterio-1-(2-nitrophenyl)ethan-1-ol (**3-Br-D**).

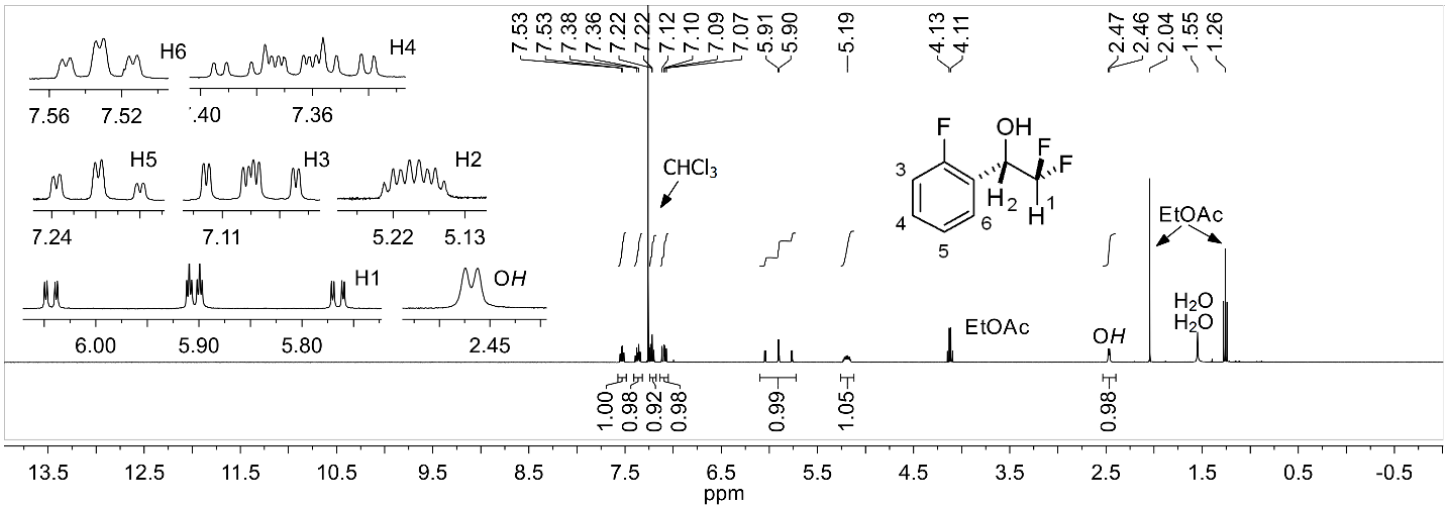


Figure S71. ^{1}H NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

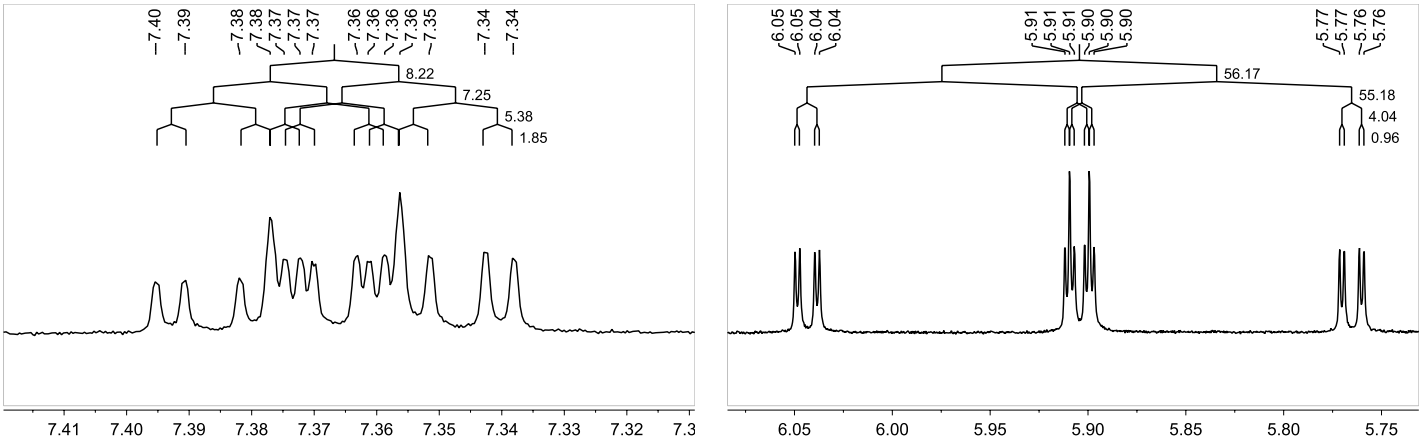


Figure S72. Splitting diagrams for H4 (left) and H1 (right) of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

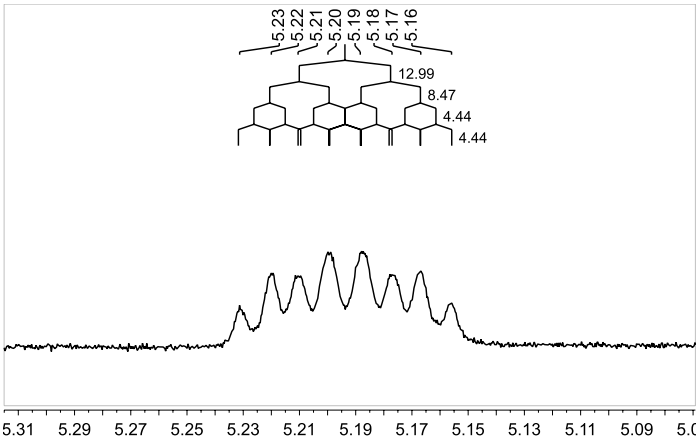


Figure S73. Splitting diagram for H2 of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

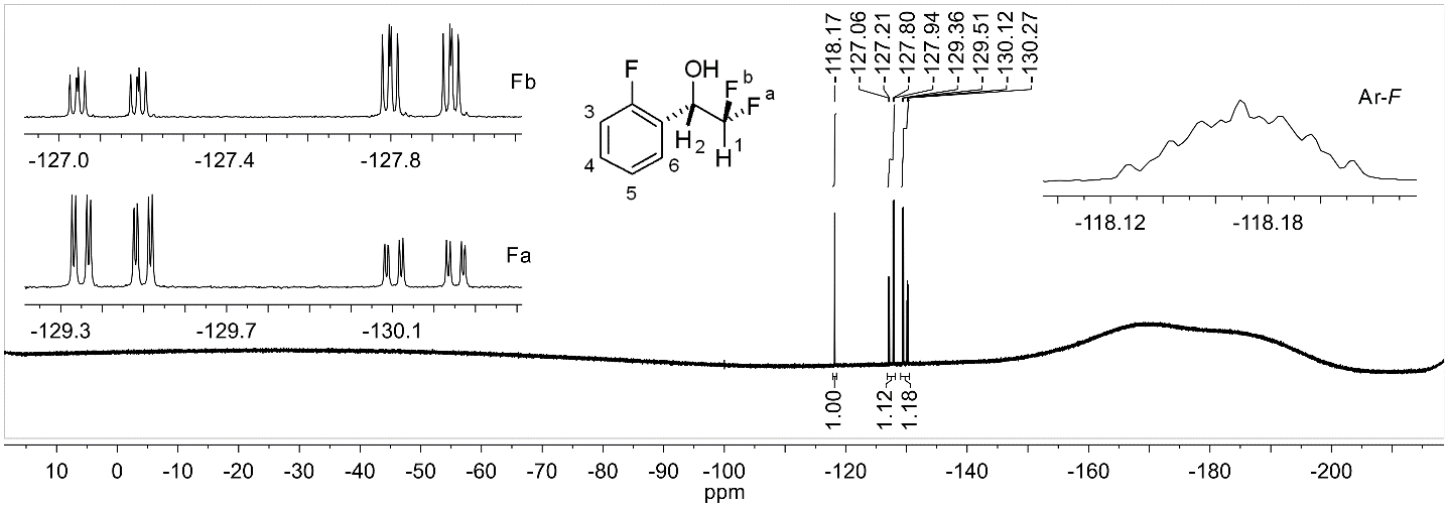


Figure S74. ^{19}F NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

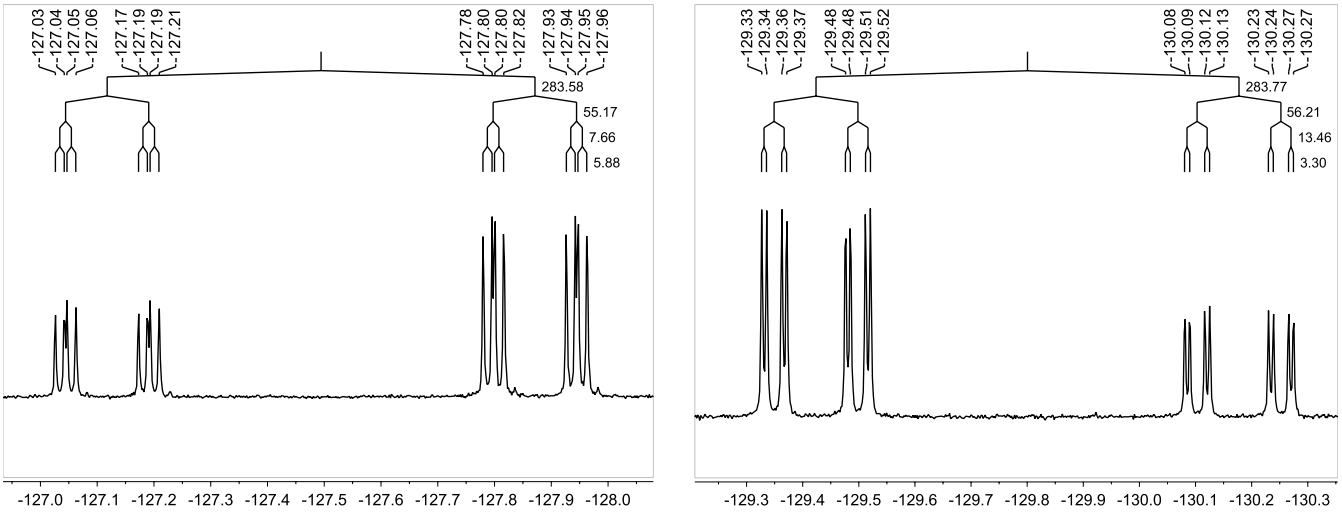


Figure S75. Splitting diagrams for Fb (left) and Fa (right) of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

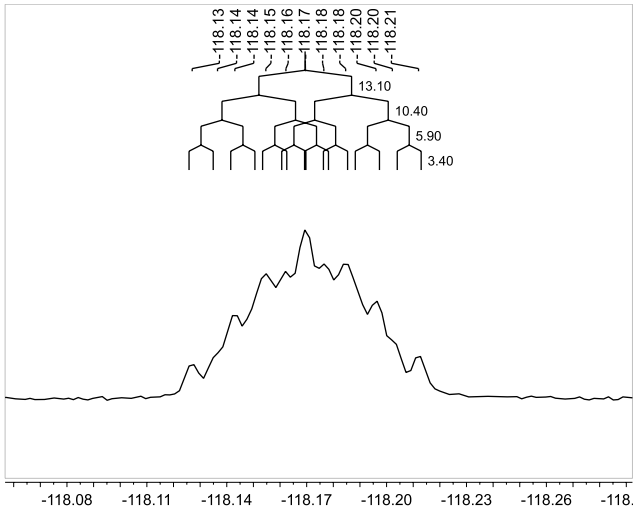


Figure S76. Splitting diagram for F_{Ar} of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

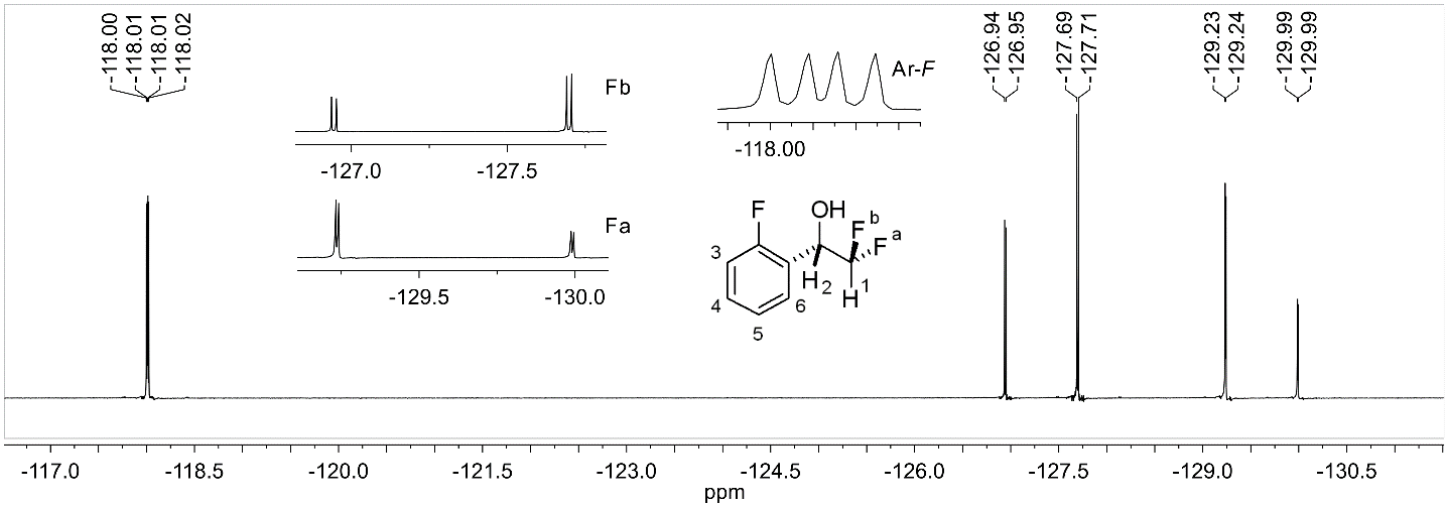


Figure S77. $^{19}F\{^{1}H\}$ NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

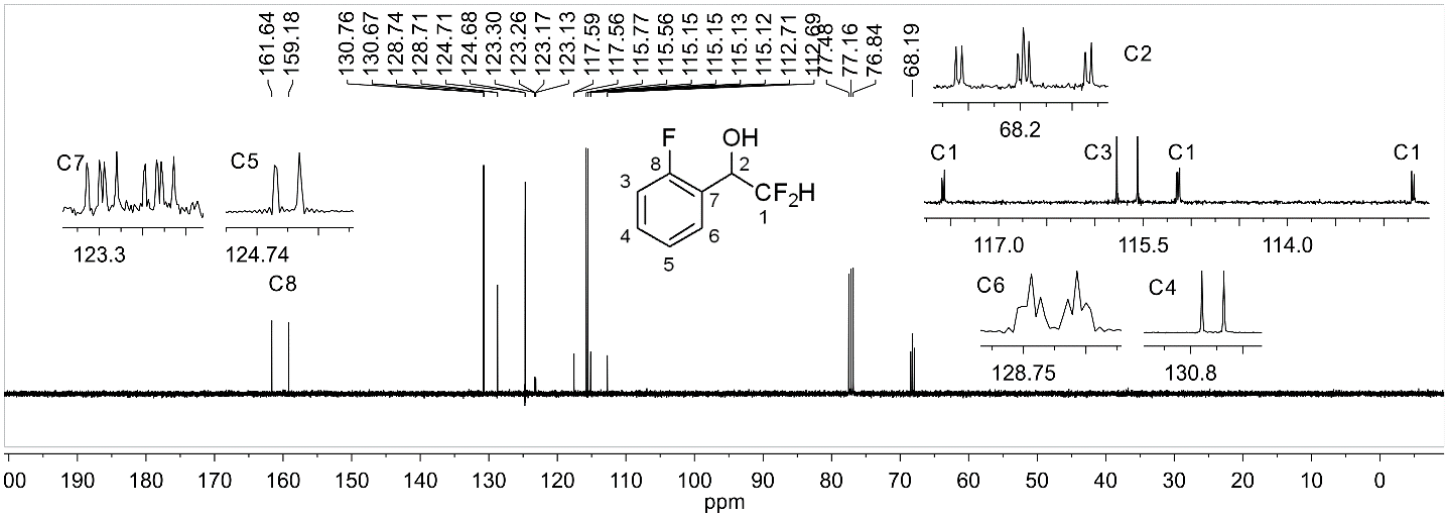


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**3-F**).

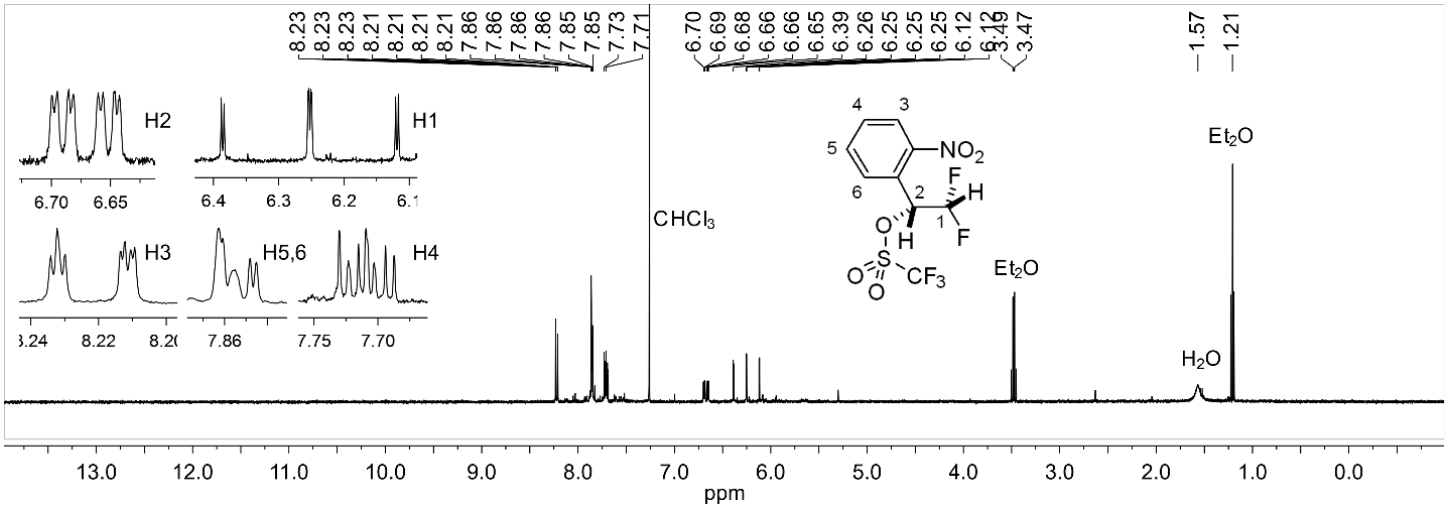


Figure S79. ^{1}H NMR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO$_2$**).

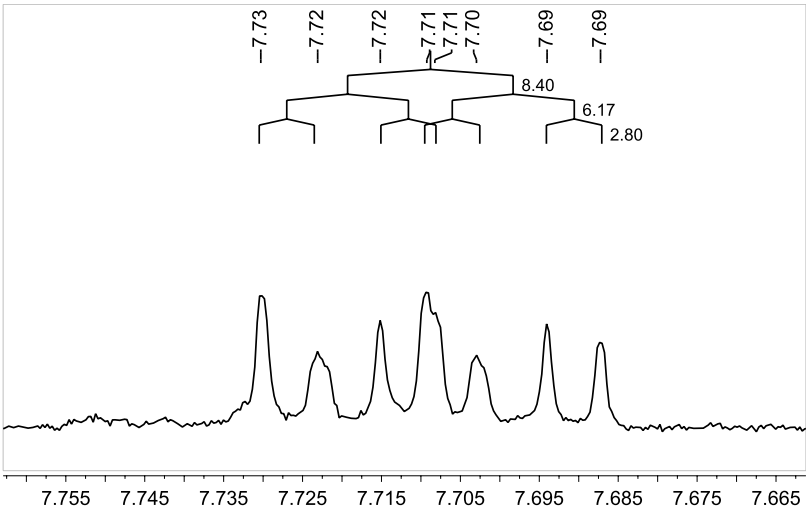


Figure S80. Splitting diagram for H4 of 2,2-difluoro-1-(2-fluorophenyl)ethan-1-ol (**4-NO$_2$**).

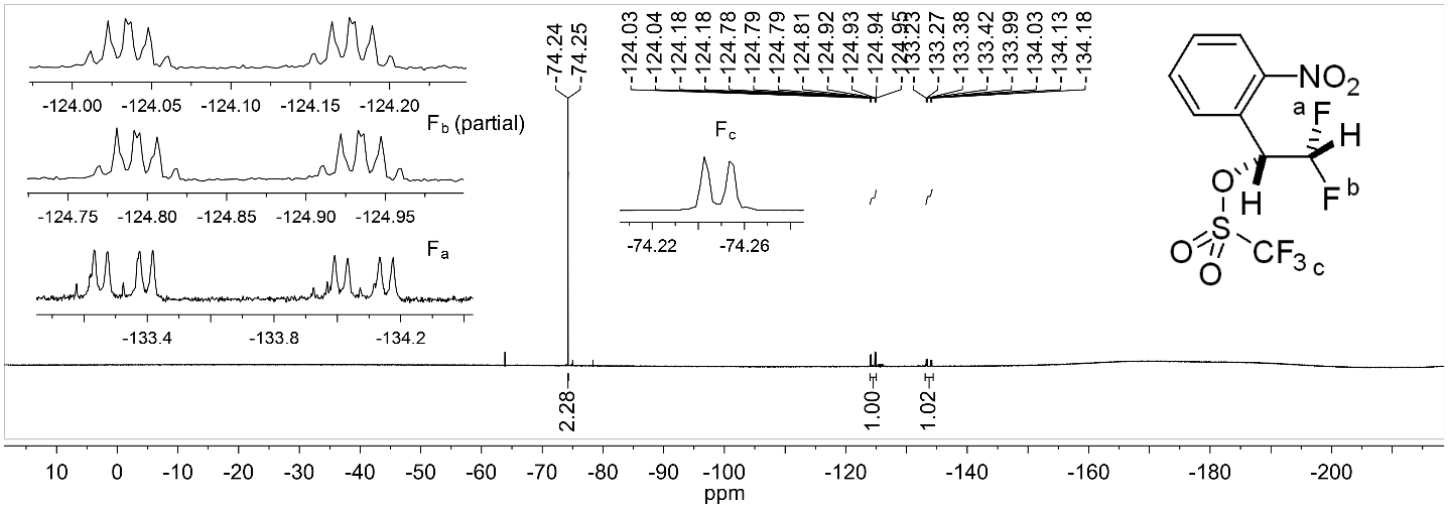


Figure S81. ^{19}F NMR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO$_2$**).

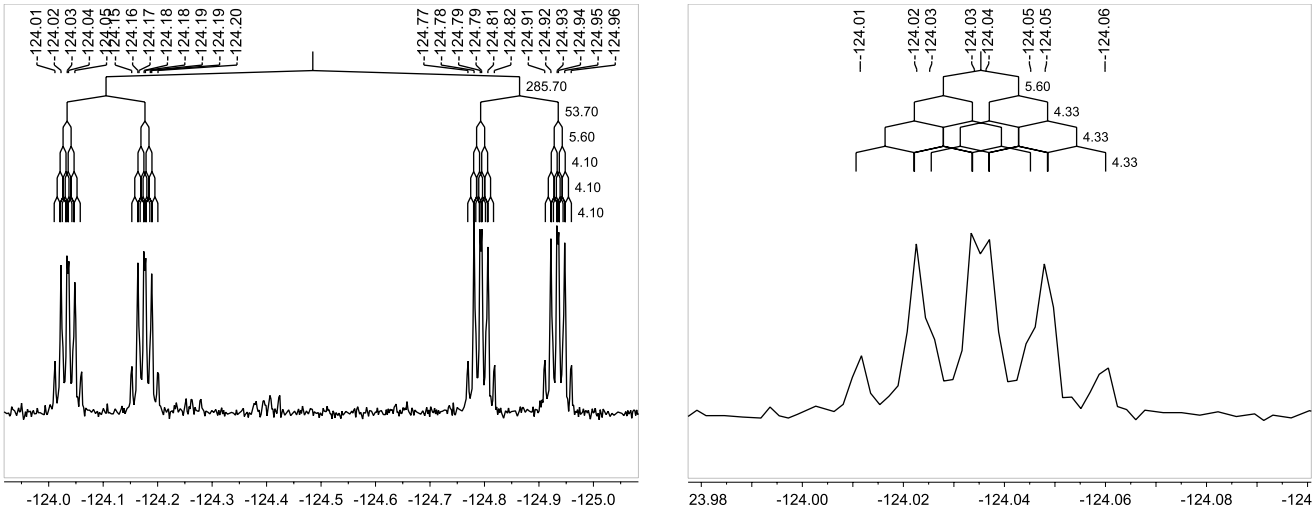


Figure S82. Splitting diagrams for Fb of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO$_2$**). Left: full signal; right: expansion of the part of the signal.

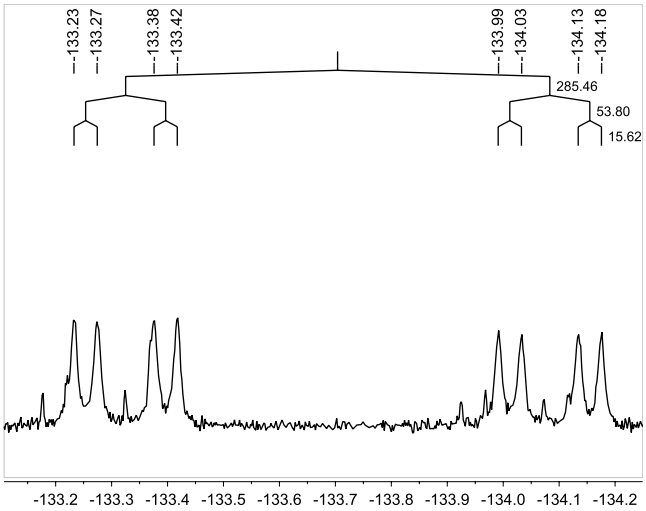


Figure S83. Splitting diagram for Fa of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO$_2$**).

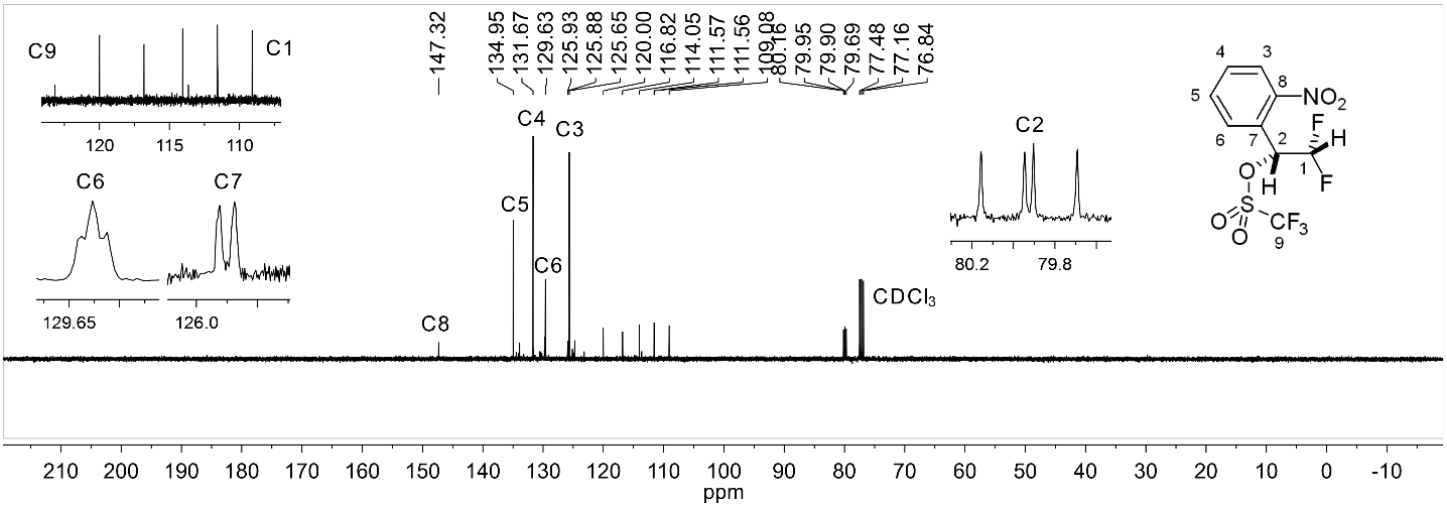


Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO$_2$**).

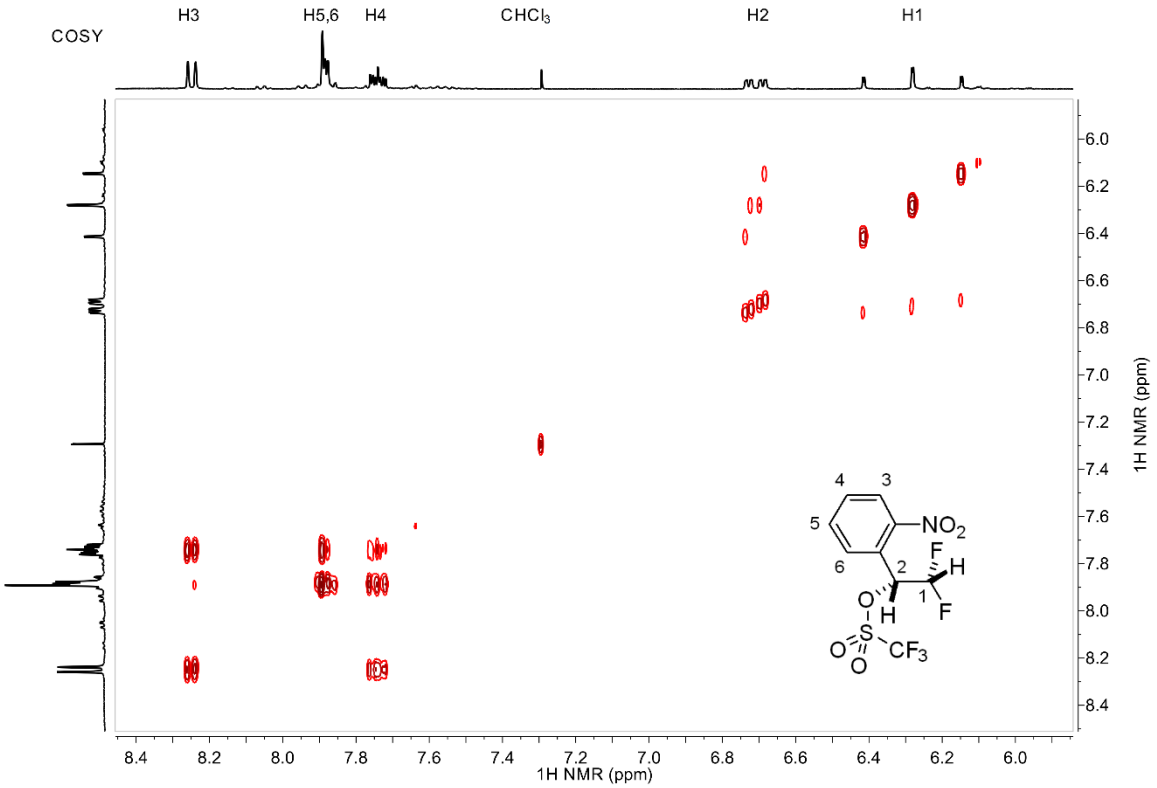


Figure S85. ^{1}H-^{1}H COSY spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO$_2$**).

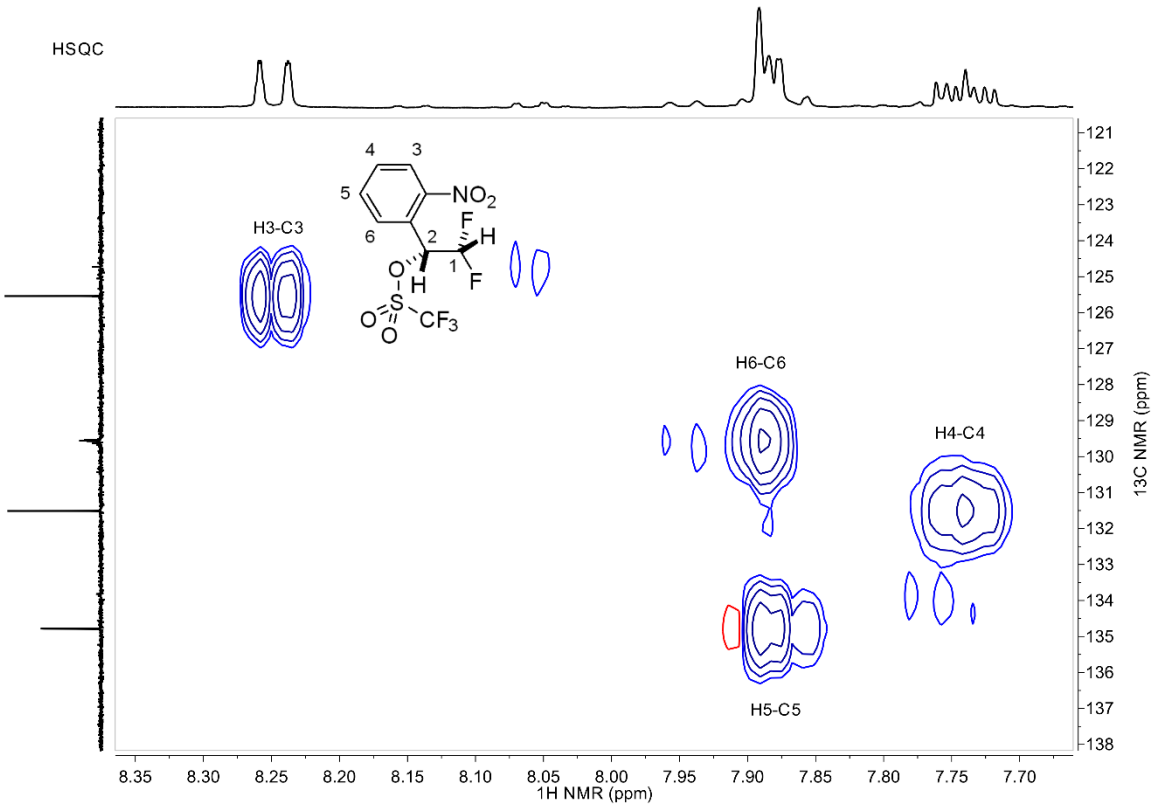


Figure S86. ^{1}H-^{13}C HSQC spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO$_2$**).

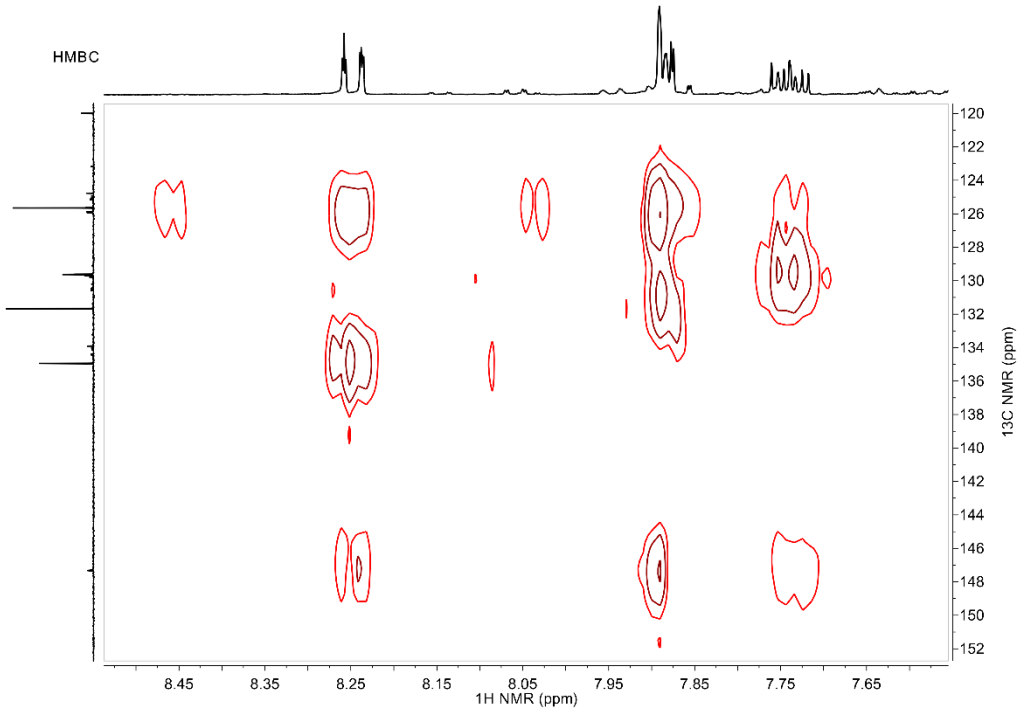


Figure S87. ^{1}H-^{13}C HMBC spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO_2**).

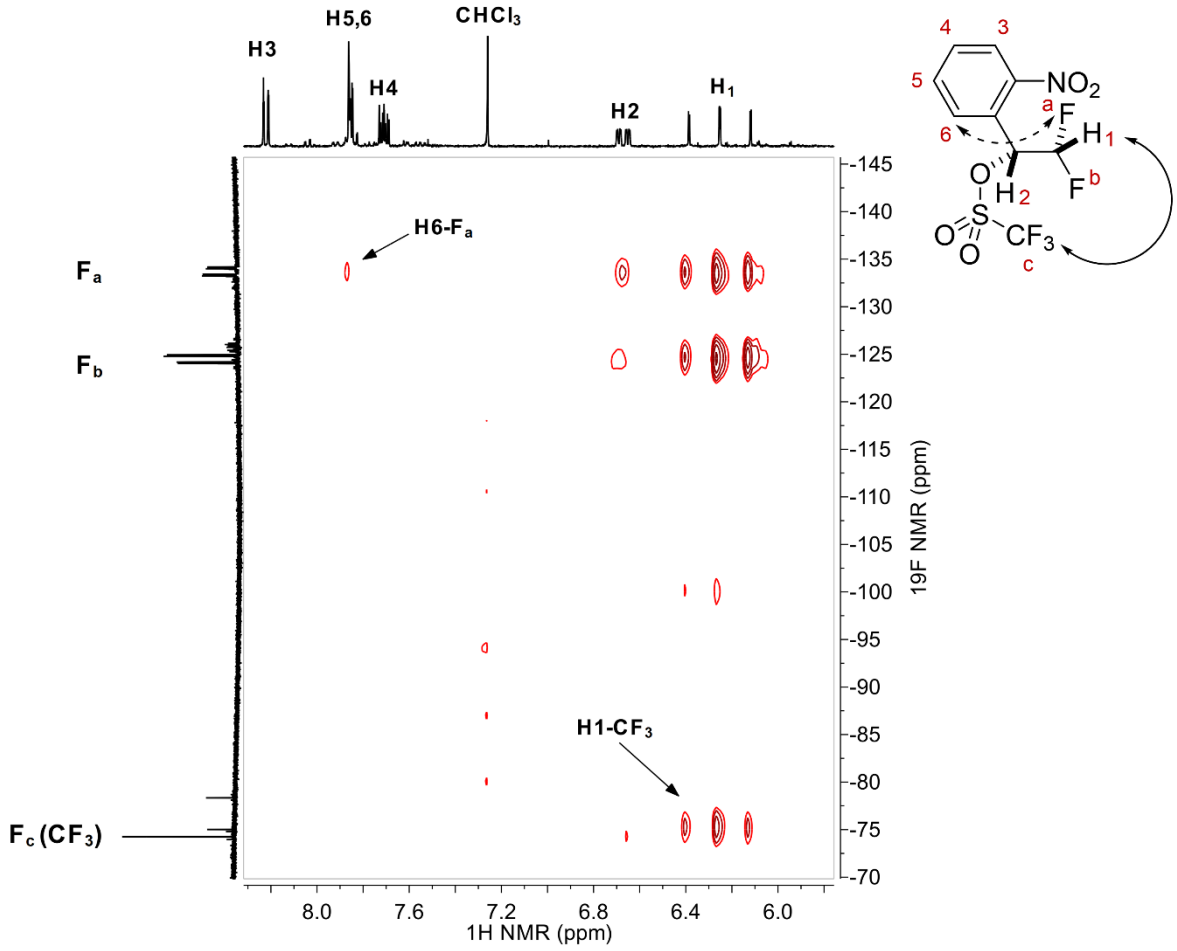


Figure S88. ^{1}H-^{19}F HOESY spectrum of 2,2-difluoro-1-(2-nitrophenyl)ethyl triflate (**4-NO_2**).

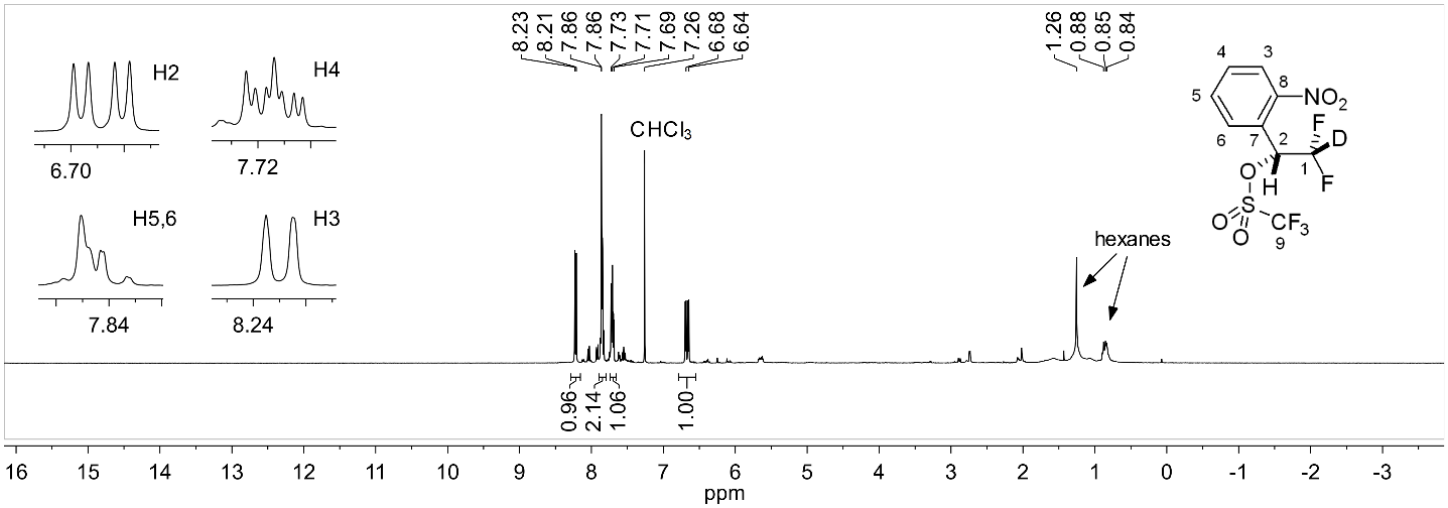


Figure S89. ^{1}H NMR spectrum of 2,2-difluoro-2-deuero-1-(2-nitrophenyl)ethyl triflate (**4-NO_2-D**).

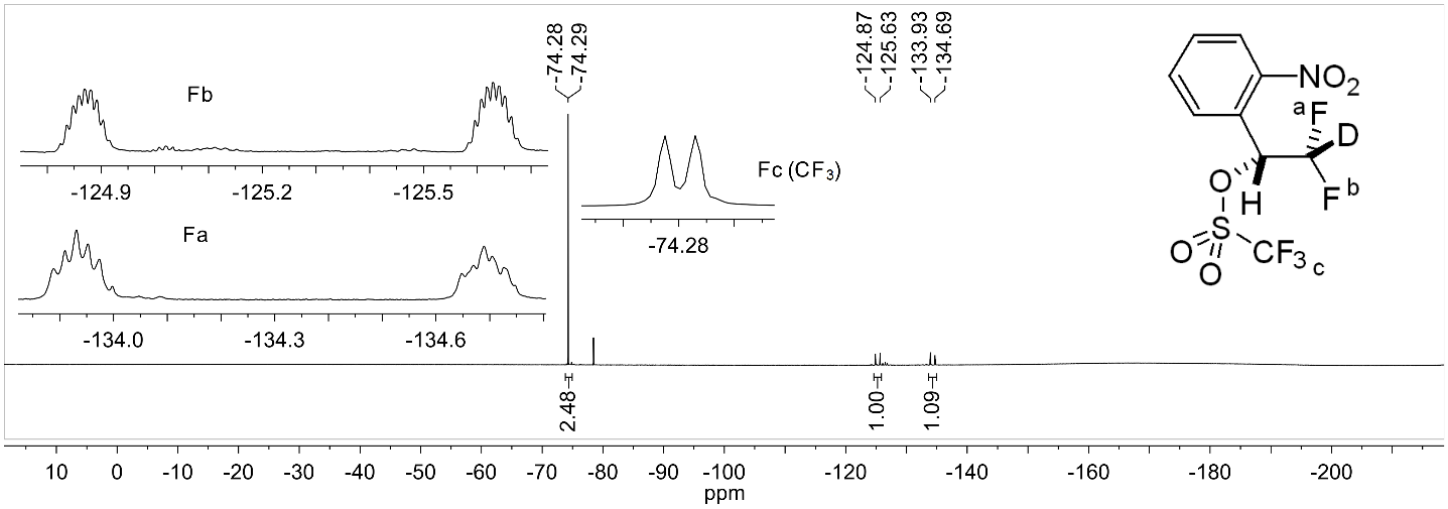


Figure S90. ^{19}F NMR spectrum of 2,2-difluoro-2-deuero-1-(2-nitrophenyl)ethyl triflate (**4-NO_2-D**).

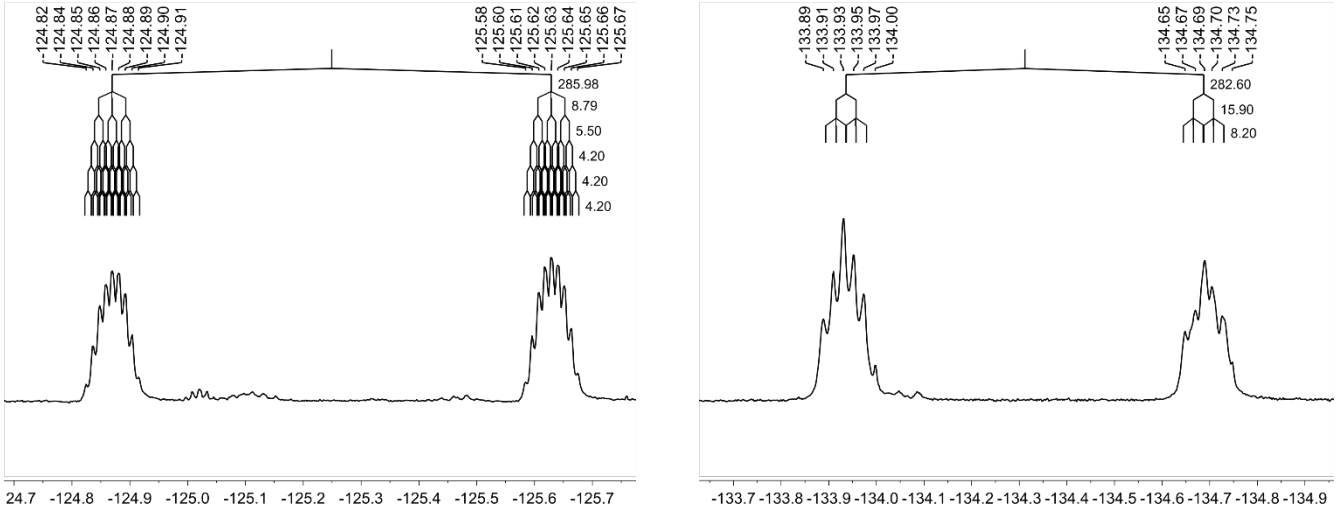


Figure S91. Splitting diagrams for Fb (left) and Fa (right) of 2,2-difluoro-2-deuero-1-(2-nitrophenyl)ethyl triflate (**4-NO_2-D**).

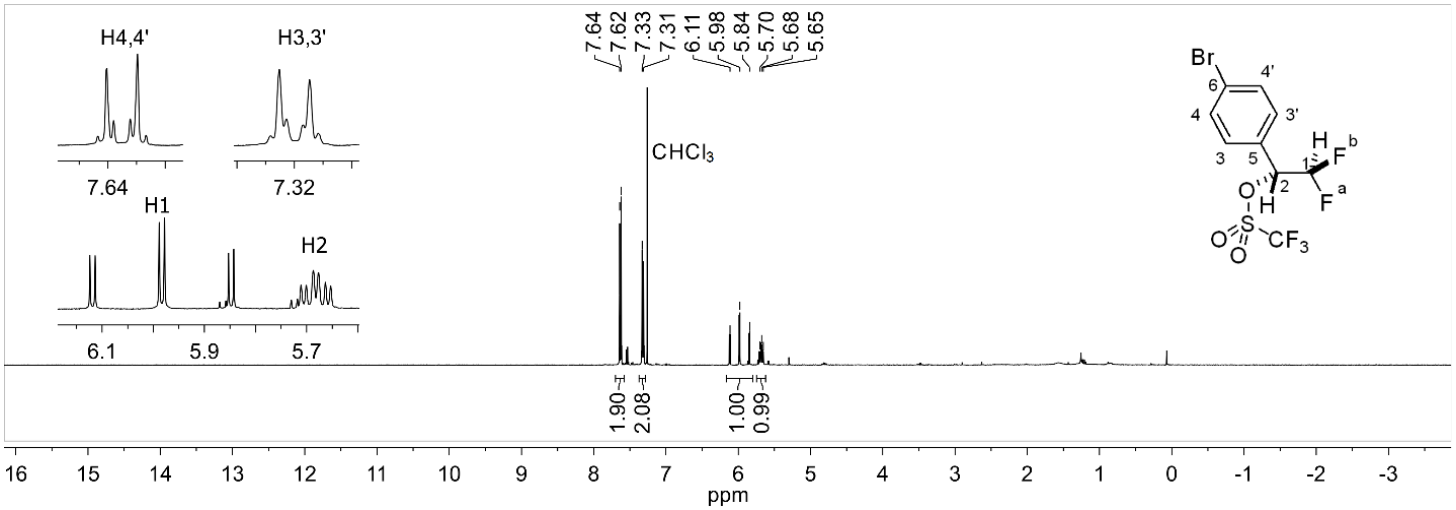


Figure S92. ^{1}H NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethyl triflate (**4-Br**).

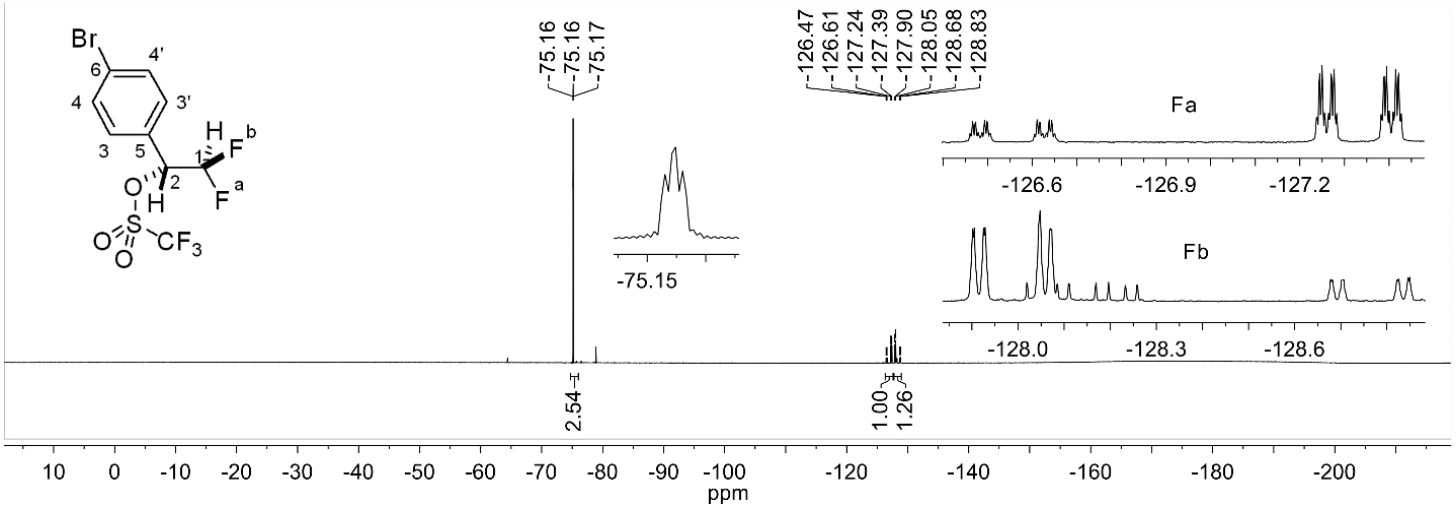


Figure S93. ^{19}F NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethyl triflate (**4-Br**).

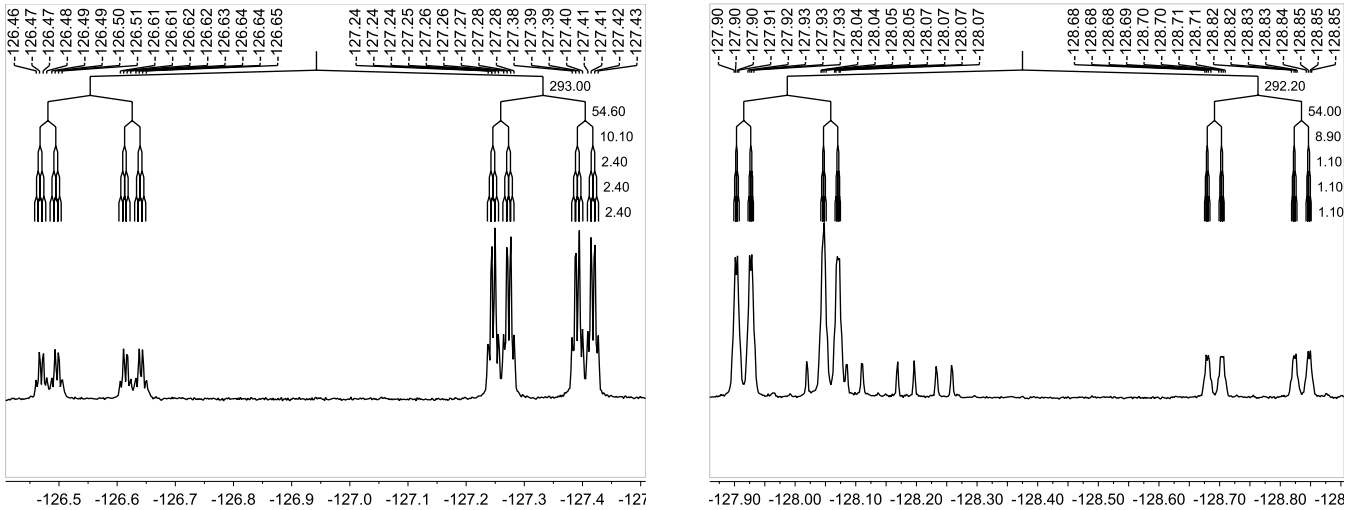


Figure S94. Splitting diagrams for Fa (left) and Fb (right) of 1-(4-bromophenyl)-2,2-difluoroethyl triflate (**4-Br**).

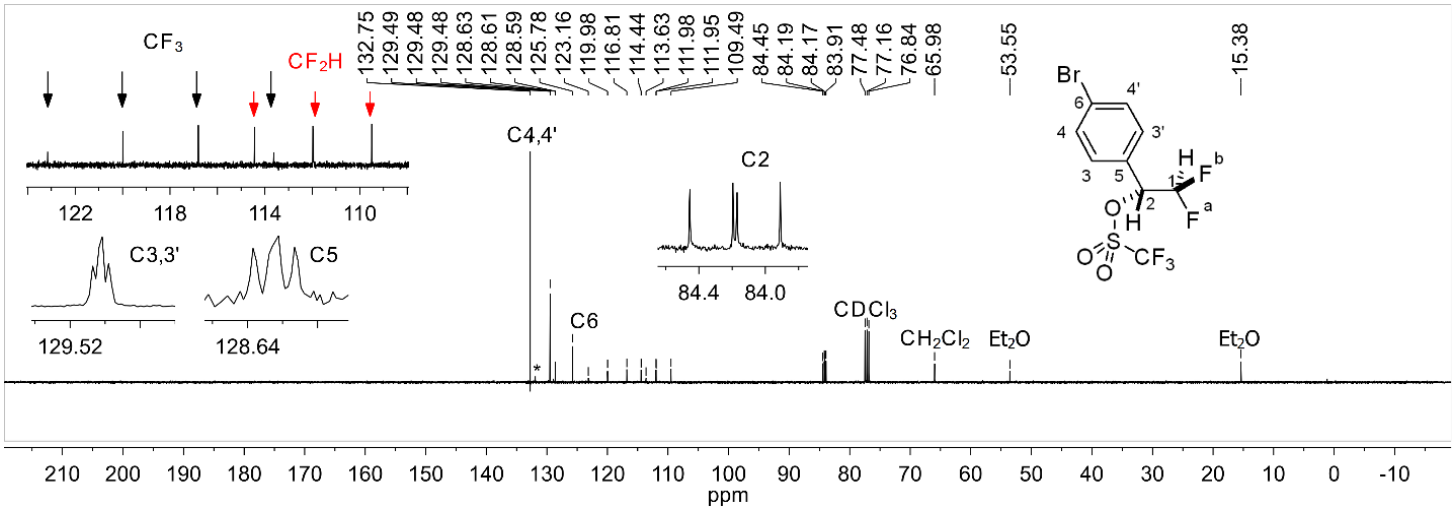


Figure S95. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethyl triflate (**4-Br**).

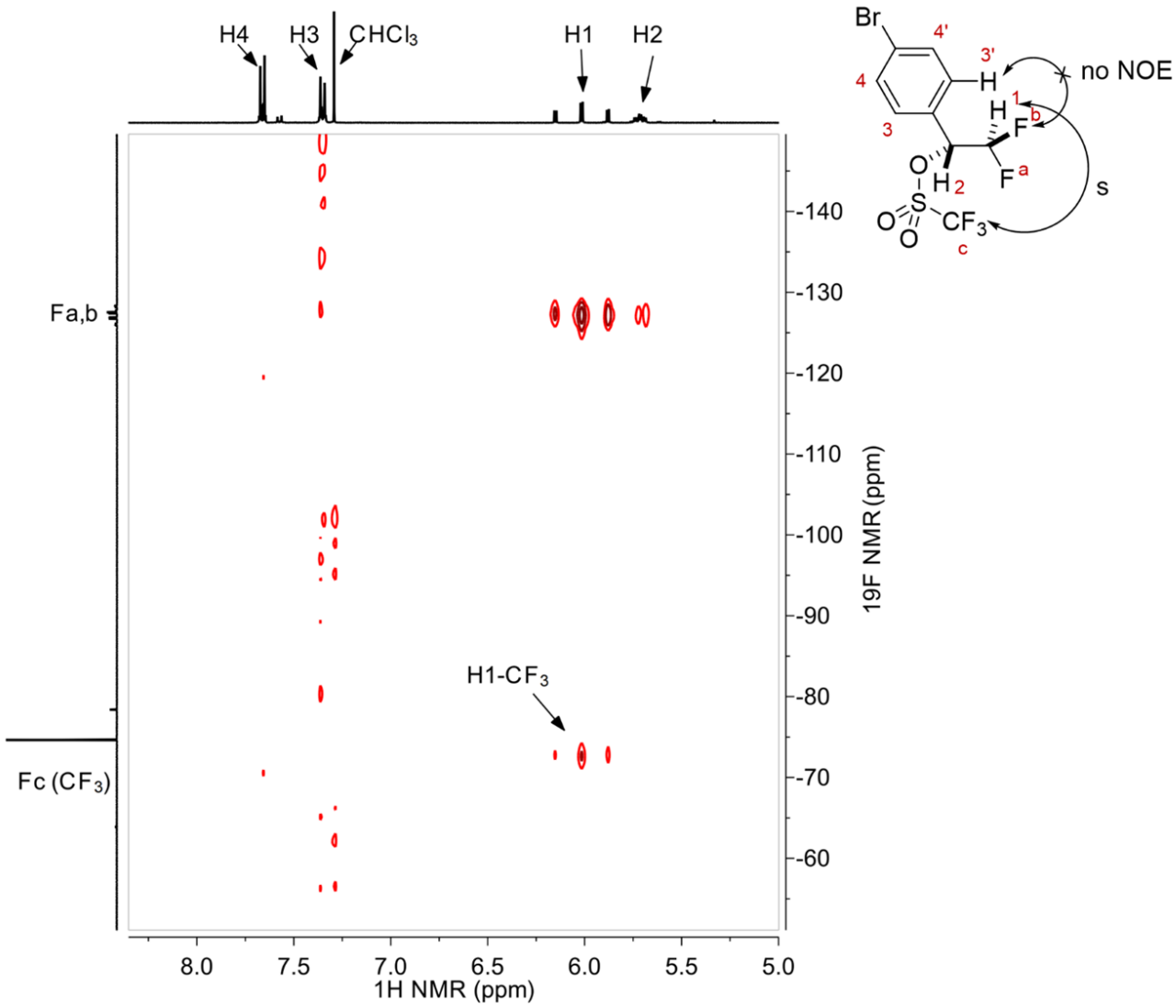


Figure S96. ^{1}H-^{19}F HOESY spectrum of 1-(4-bromophenyl)-2,2-difluoroethyl triflate (**4-Br**).

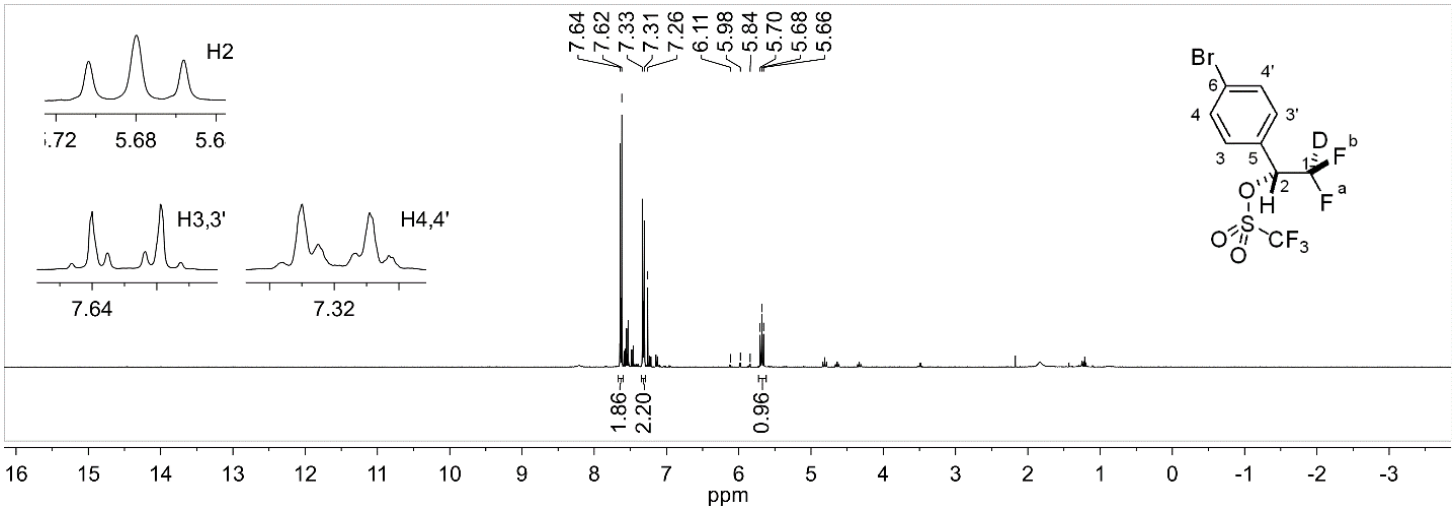


Figure S97. ^{1}H NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethyl-2-deutero triflate (**4-Br-D**).

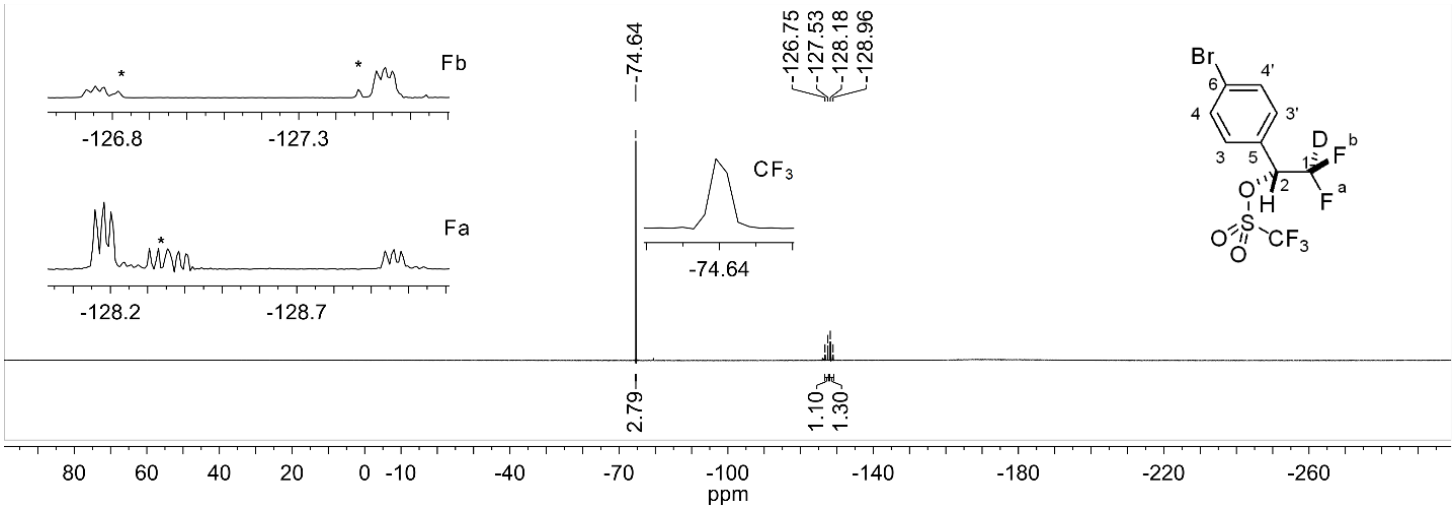


Figure S98. ^{19}F NMR spectrum of 1-(4-bromophenyl)-2,2-difluoroethyl-2-deutero triflate (**4-Br-D**).

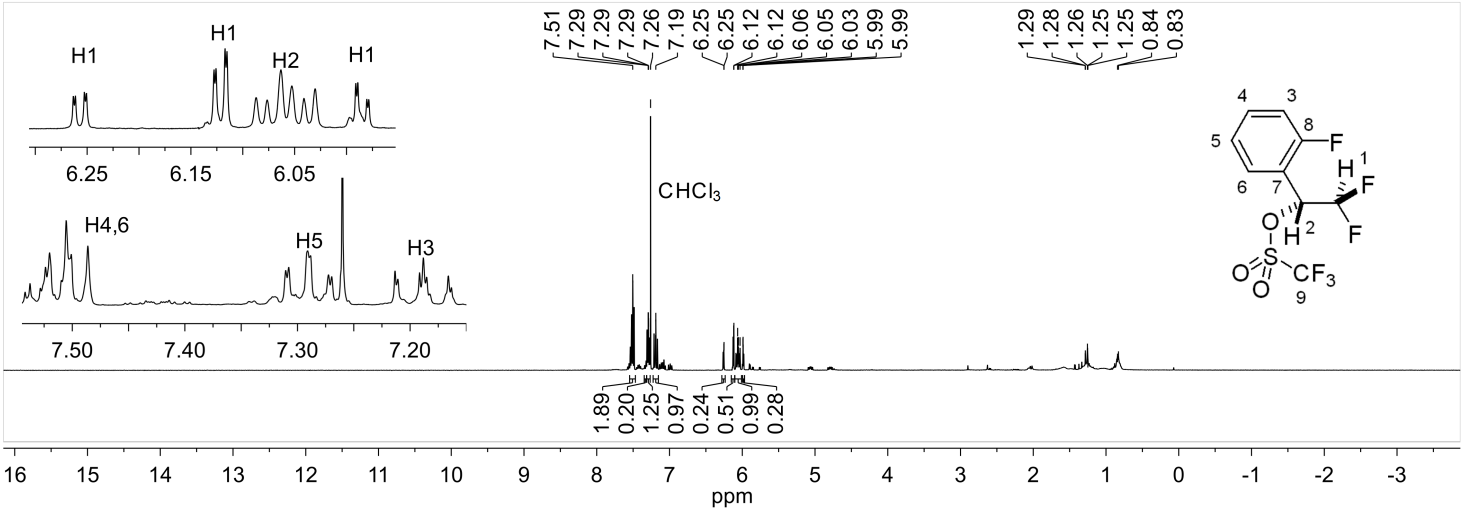


Figure S99. ^{1}H NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**).

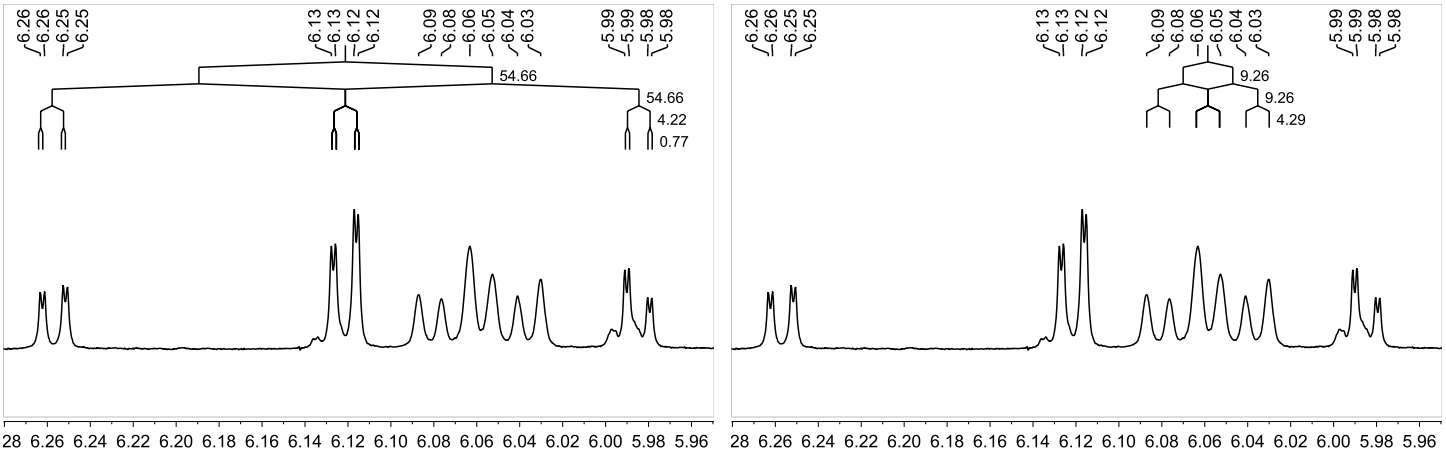


Figure S100. Splitting diagrams for H1 (left) and H2 (right) of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**).

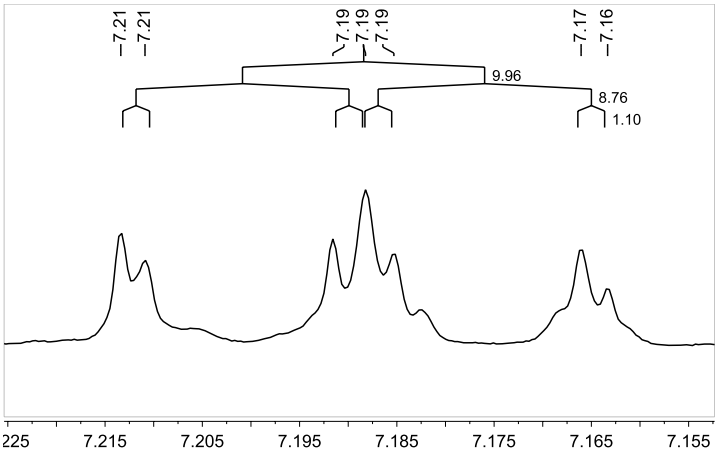


Figure S101. Splitting diagram for H3 of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**).

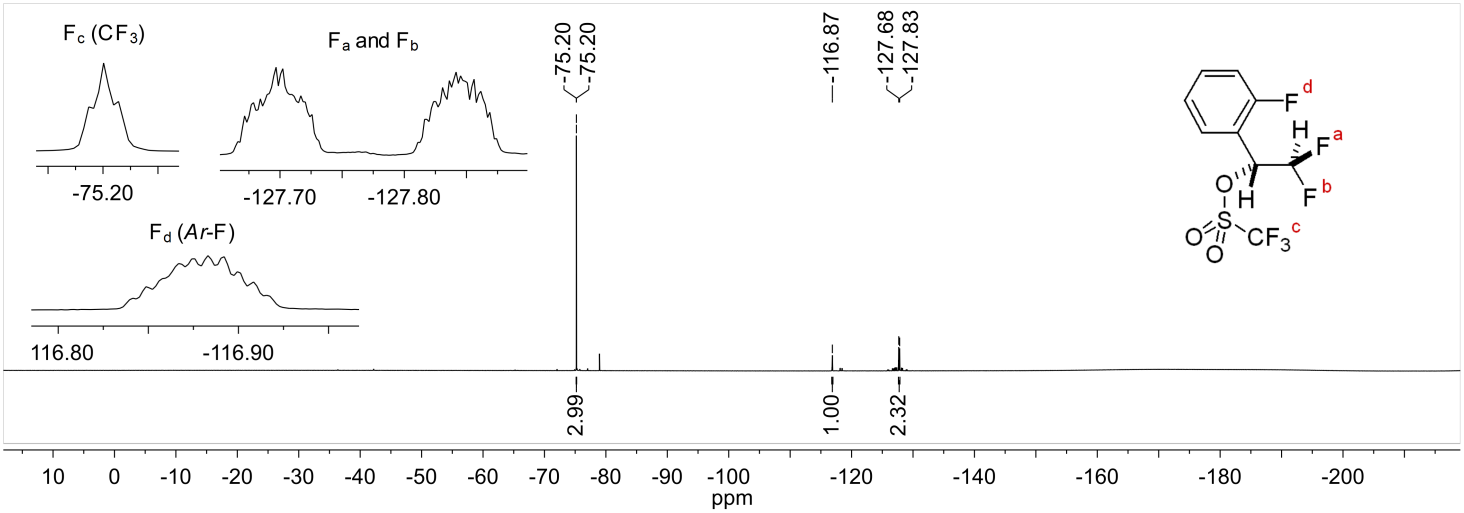


Figure S102. ^{19}F NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**).

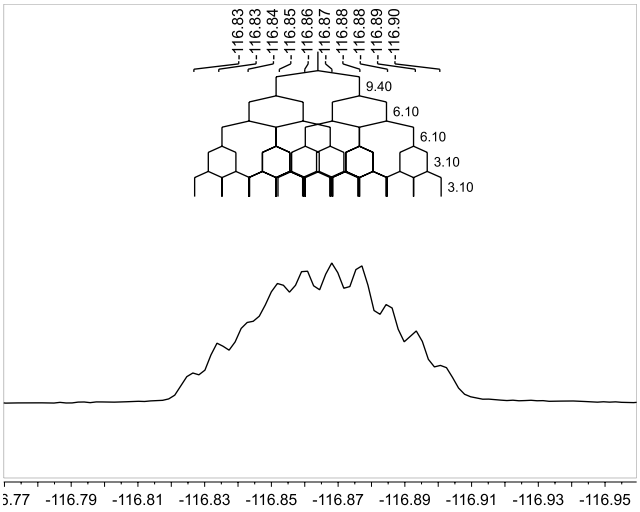


Figure S103. Splitting diagram for Fd of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**) in ^{19}F NMR spectrum.

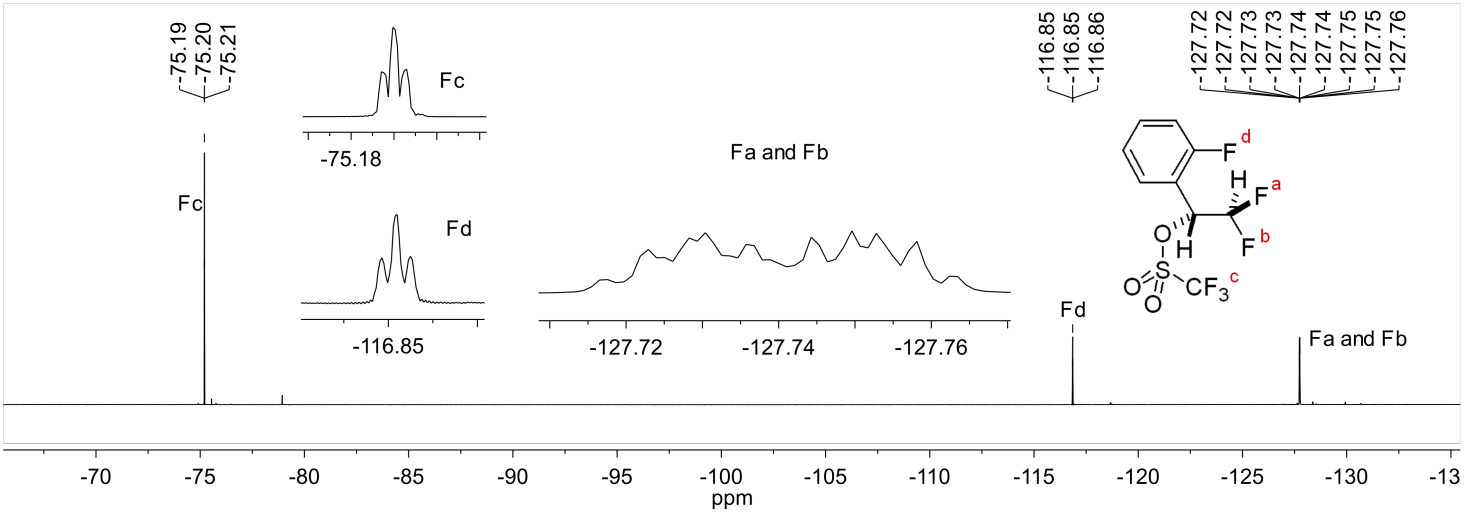


Figure S104. ^{19}F{^{1}H} NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**).

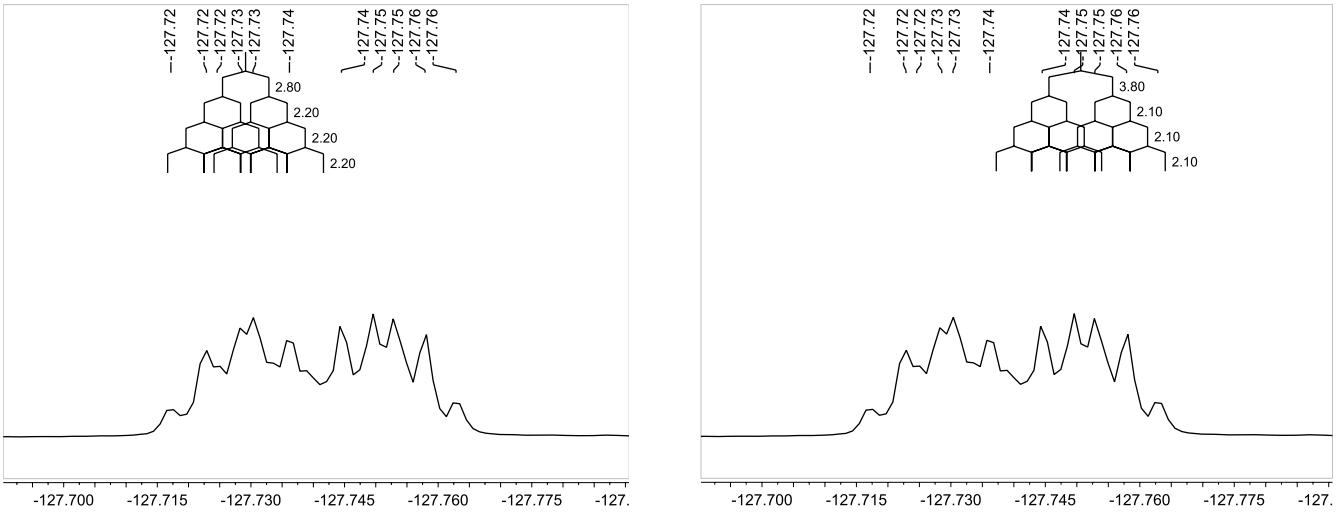


Figure S105. Splitting diagrams for Fa (left) and Fb (right) of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**) in ^{19}F{^{1}H} NMR spectrum.

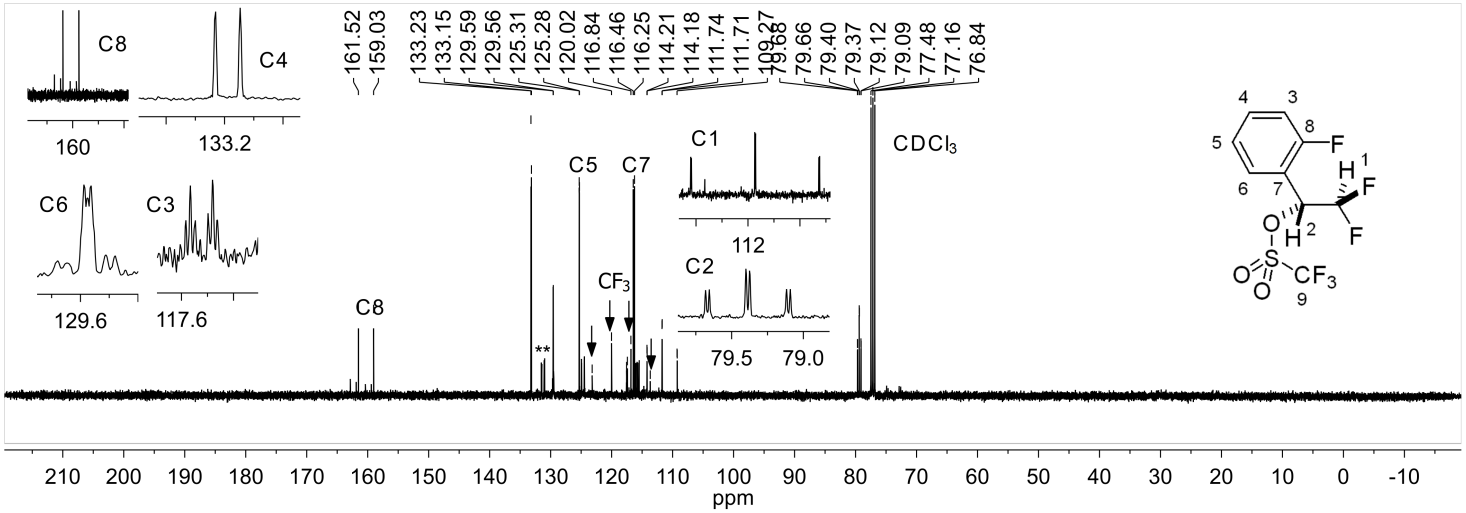


Figure S106. $^{13}C\{^{1}H\}$ NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**).

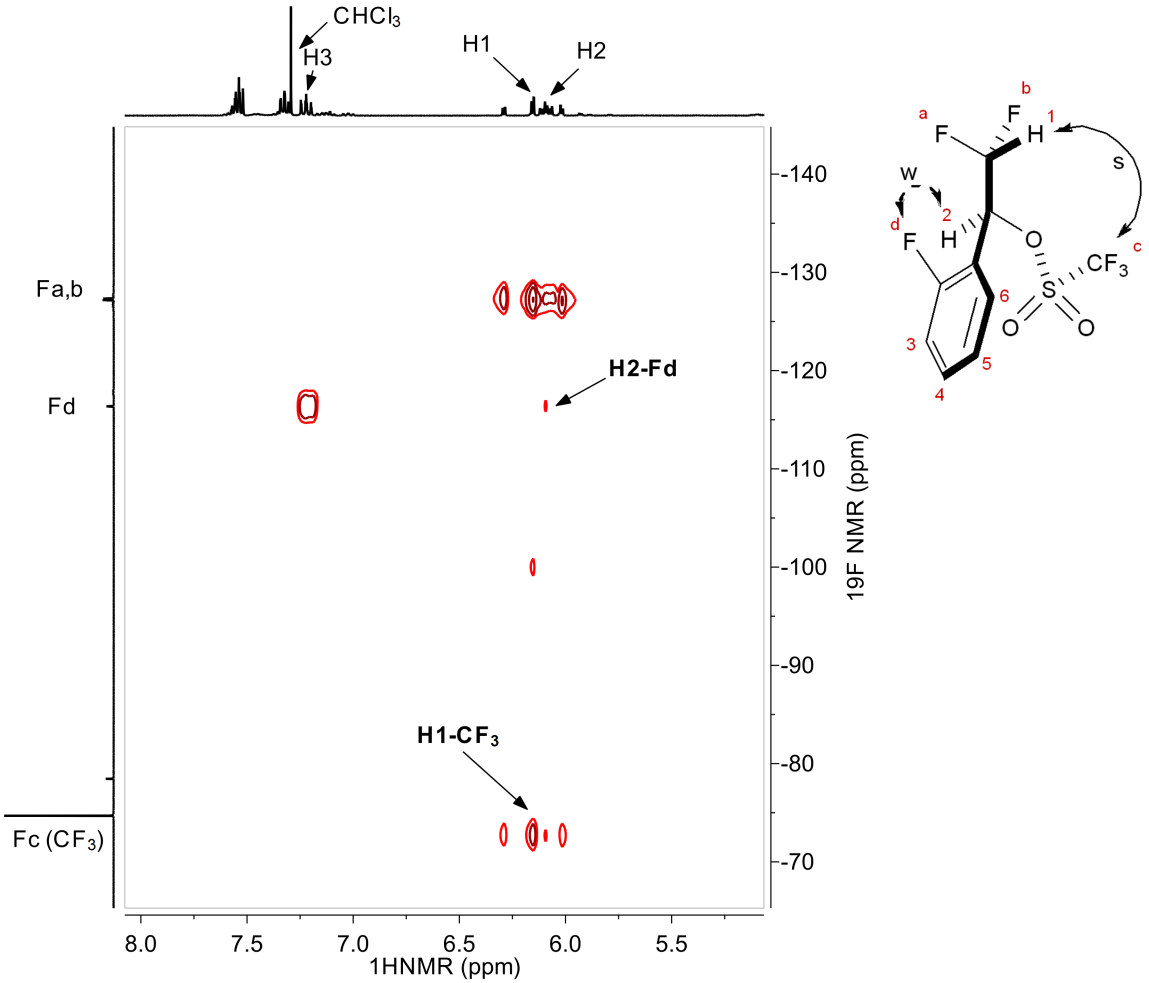


Figure S107. ^{1}H-^{19}F NMR spectrum of 2,2-difluoro-1-(2-fluorophenyl)ethyl triflate (**4-F**).

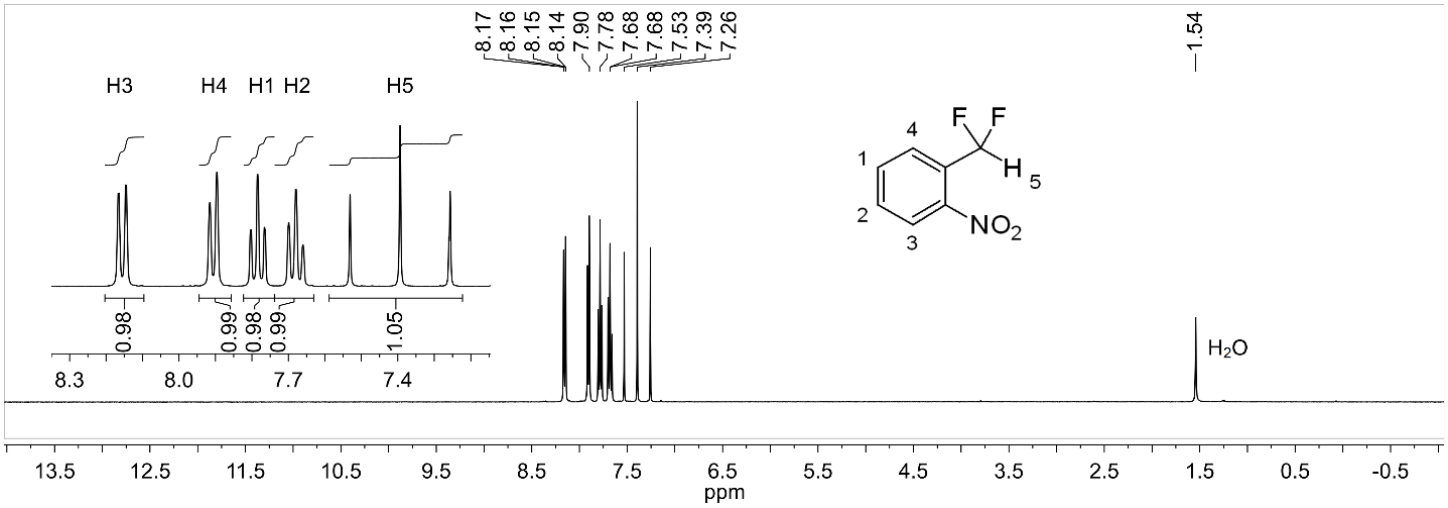


Figure S108. ^{1}H NMR spectrum of *o*-nitro-α,α-difluorotoluene (**1-CF_2H**).

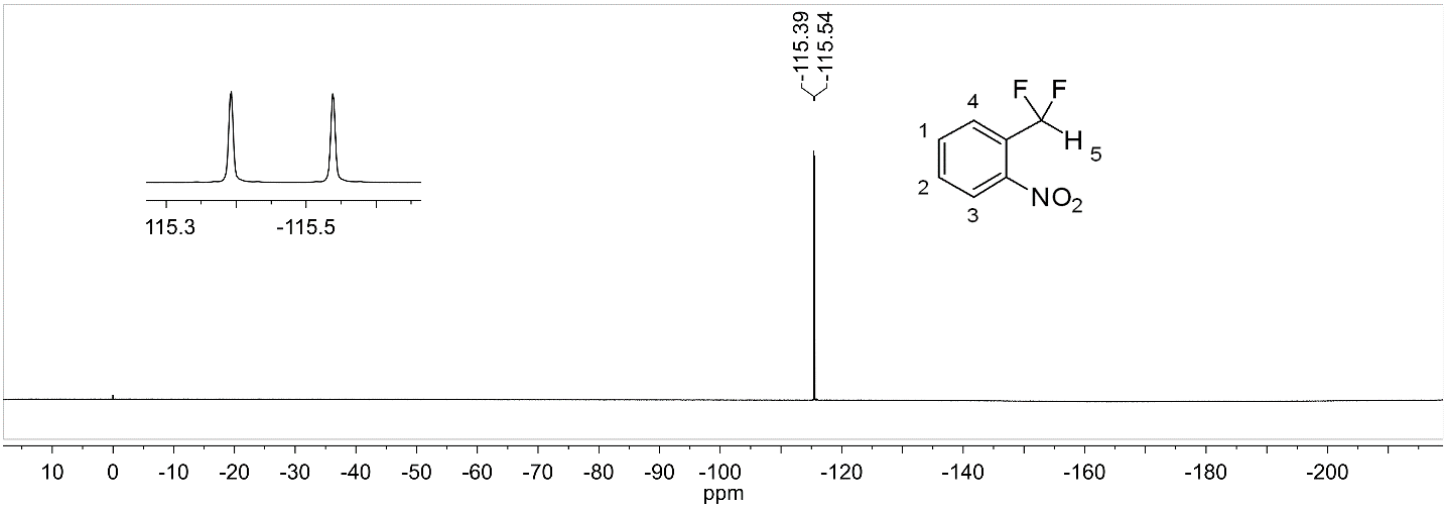


Figure S109. ^{19}F NMR spectrum of *o*-nitro-α,α-difluorotoluene (**1-CF_2H**).

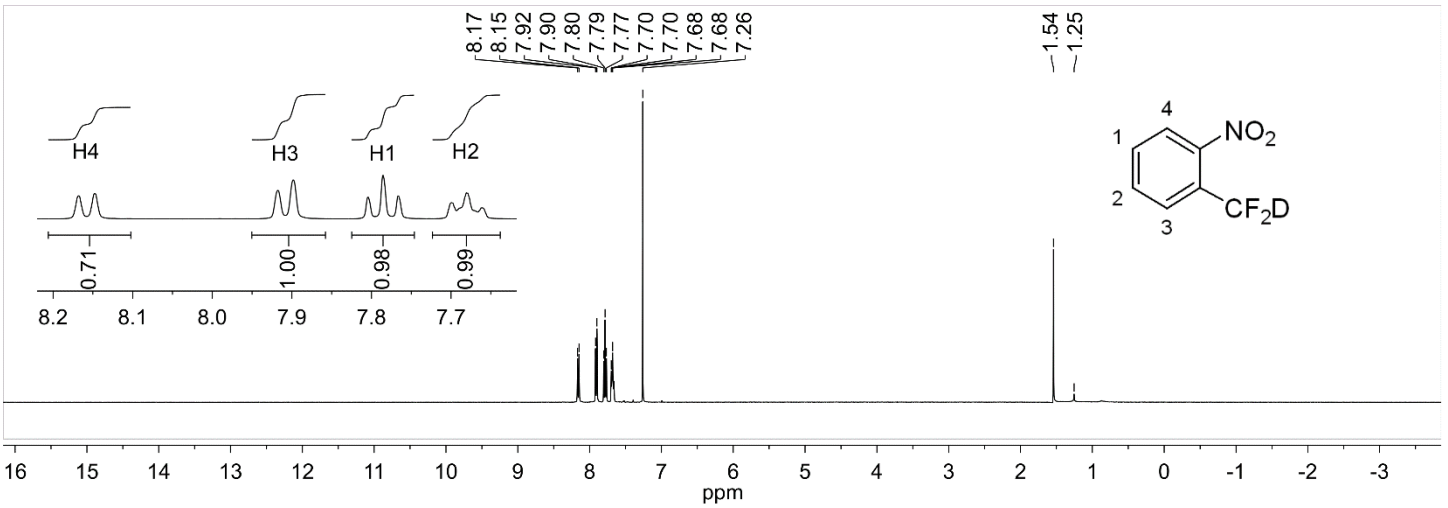


Figure S110. ^{1}H NMR spectrum of *o*-nitro-α-deutero-α,α-difluorotoluene (**1-CF_2D**).

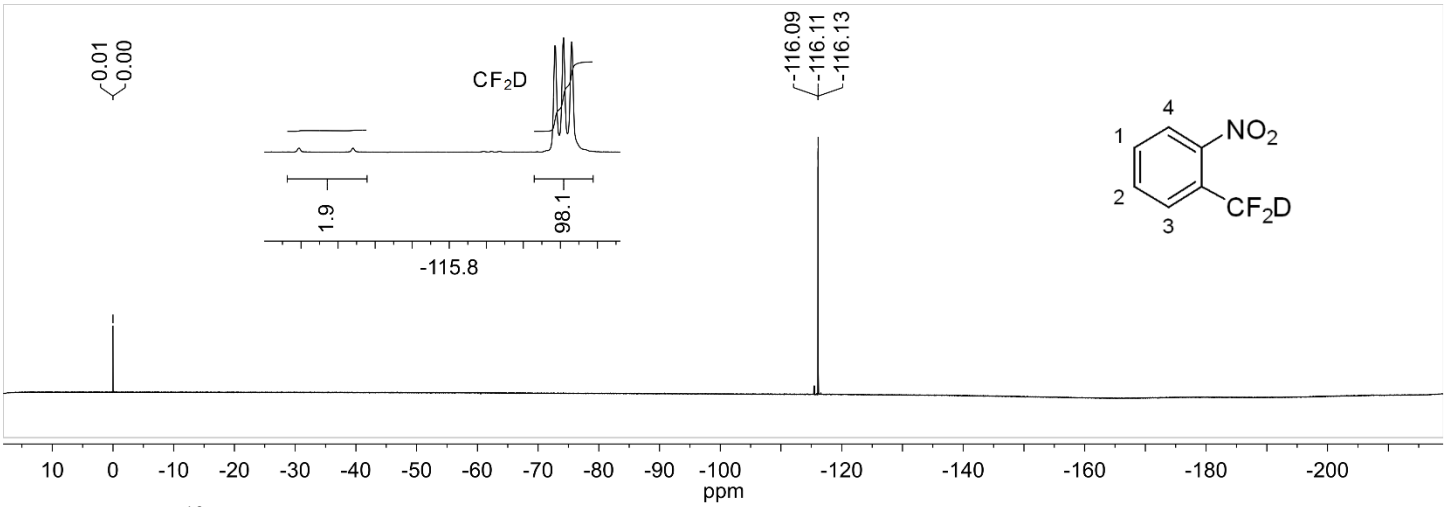


Figure S111. ^{19}F NMR spectrum of *o*-nitro-α-deutero-α,α-difluorotoluene (**1-CF_2D**).

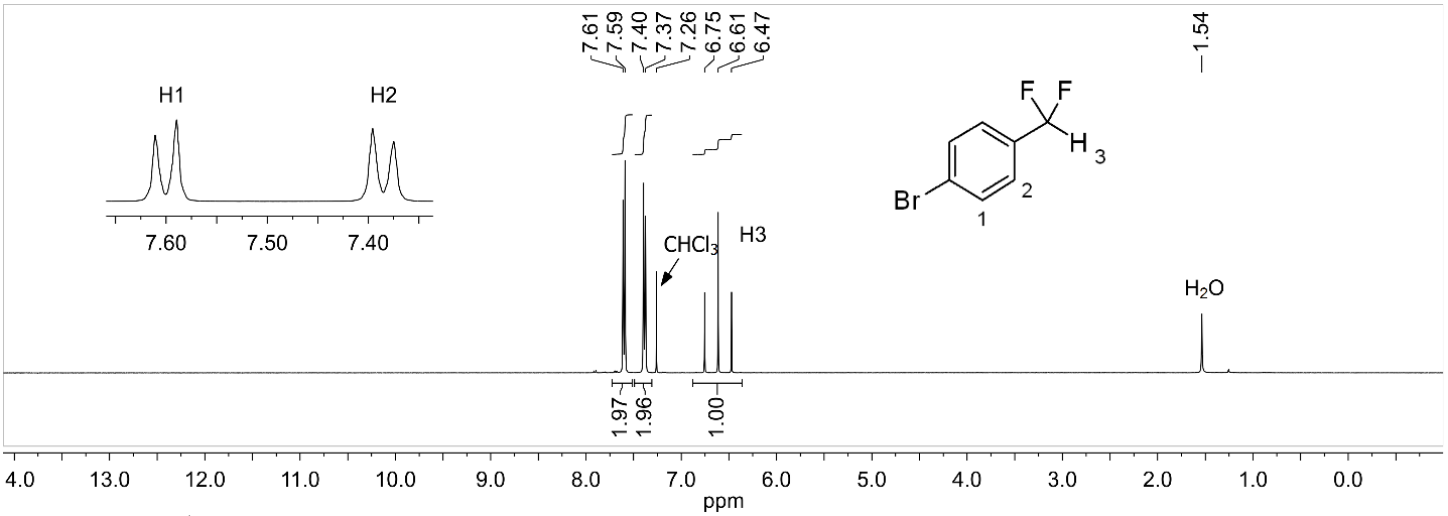


Figure S112. ^{1}H NMR spectrum of *p*-bromo-α,α-difluorotoluene (**2-CF_2H**).

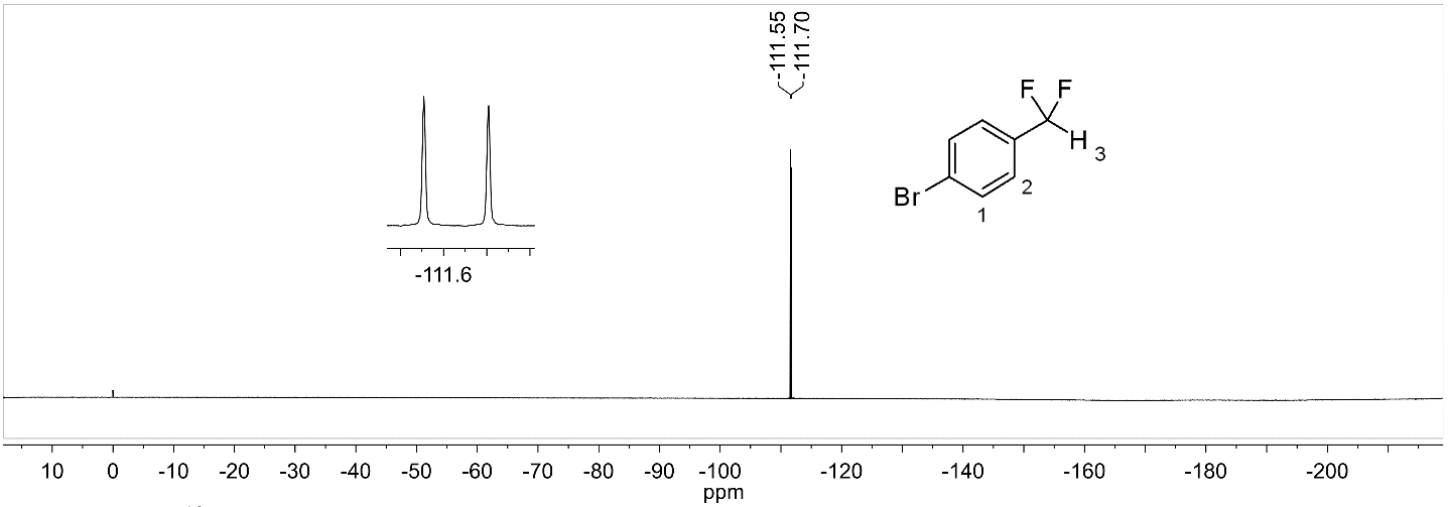


Figure S113. ^{19}F NMR spectrum of *p*-bromo-α,α-difluorotoluene (**2-CF_2H**).

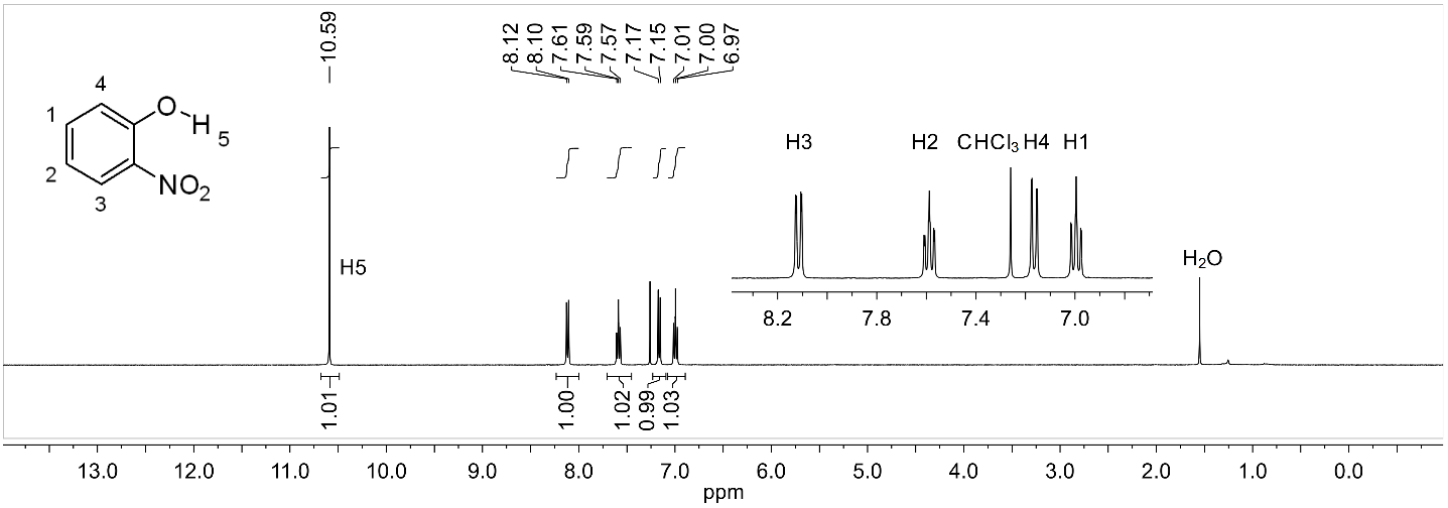


Figure S114. ^{1}H NMR spectrum of *o*-nitrophenol (**1-OH**).

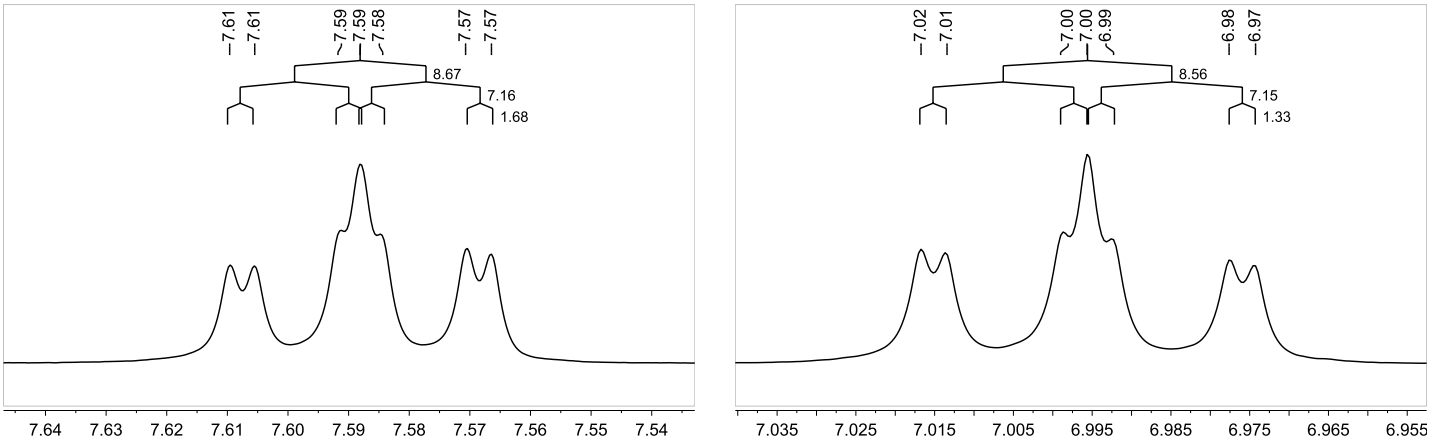


Figure S115. Splitting diagrams for H2 (left) and H1 (right) of *o*-nitrophenol (**1-OH**).

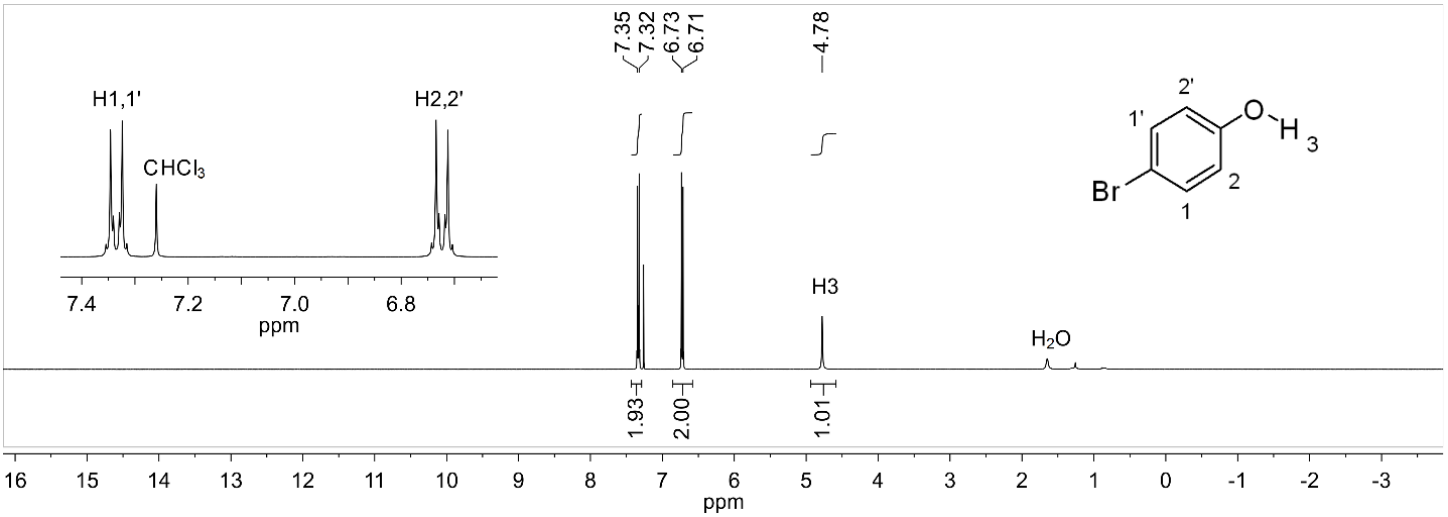


Figure S116. ^{1}H NMR spectrum of *p*-bromophenol (**2-OH**).

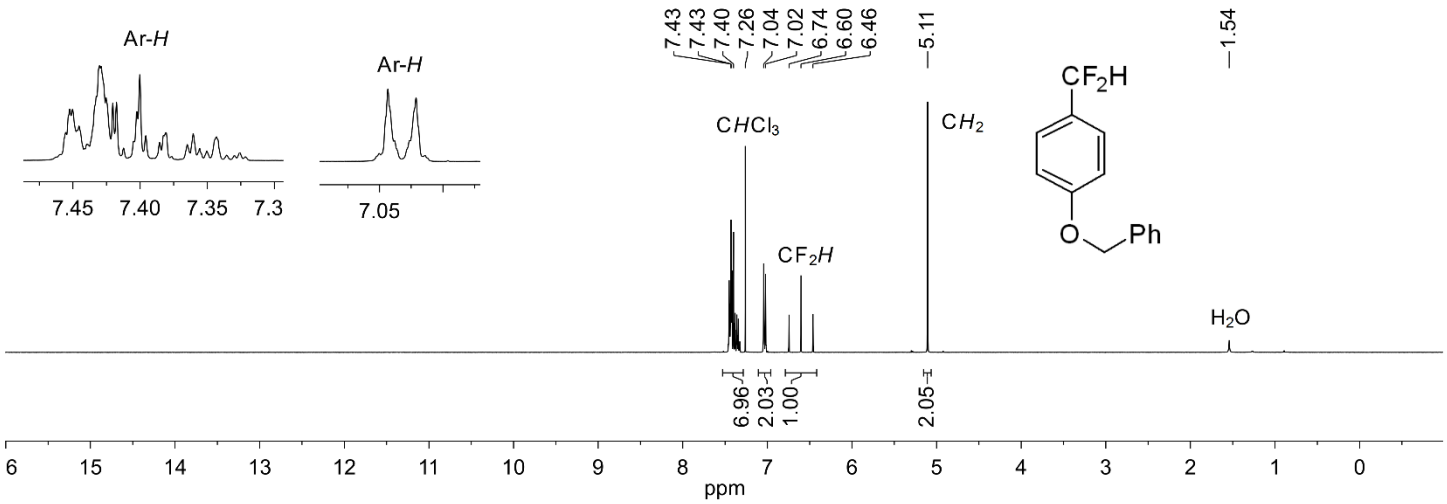


Figure S117. ^{1}H NMR spectrum of 1-benzyloxy-4-(difluoromethyl)benzene (**5-CF_2H**).

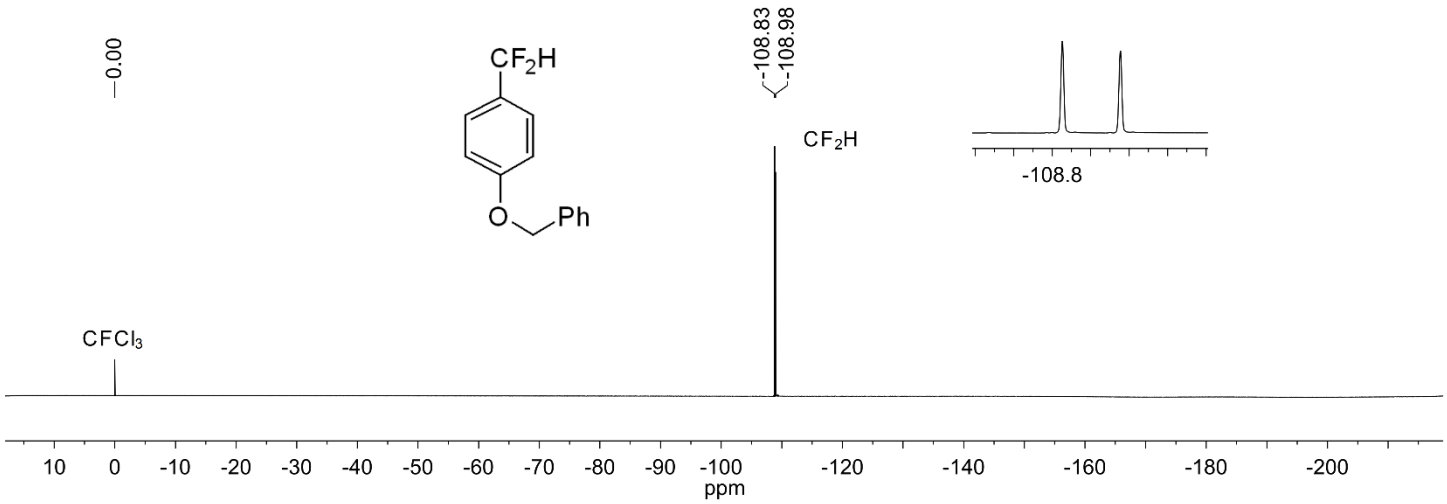


Figure S118. ^{19}F NMR spectrum of 1-benzyloxy-4-(difluoromethyl)benzene (**5-CF_2H**).

8. *o*-Substituent Effects on the ^{1}H NMR Chemical Shift of the CF_2H Group

An analysis of ^{1}H NMR data of α-difluoromethylbenzyl alcohols ($ArCH(OH)CF_2H$) suggests that the deshielding of CF_2H proton is associated with hydrogen bonding acceptors in the *ortho*-position on the phenyl ring. In the absence of hydrogen bonding acceptors in the *ortho*-position, the CF_2H proton peaks appear below 5.80 ppm in $CDCl_3$ (Figure S119, compounds a-c). The CF_2H protons are slightly deshielded when a weak hydrogen bonding acceptor is present in the *ortho*-position (Figure S119, compounds d-f). Strong hydrogen bonding acceptors lead to significant deshielding of the CF_2H proton, indicating the presence of hydrogen bonding interactions (Figure S119, compounds g-h).

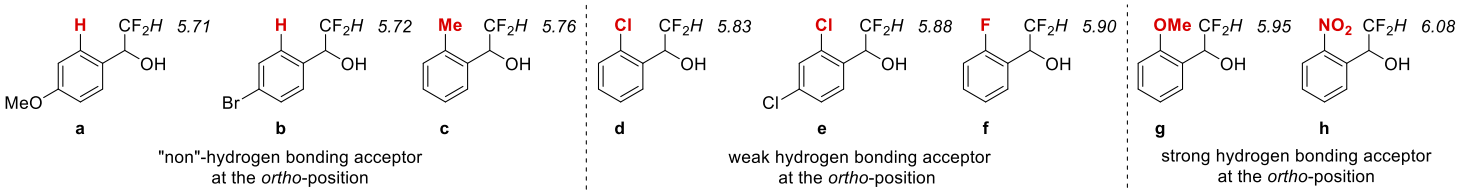


Figure S119. CF_2H proton chemical shifts of various α-difluoromethylbenzyl alcohols ($ArCH(OH)CF_2H$) in $CDCl_3$. Data for compounds a, d, e, and g are from reference [2]. Data for compound c are from reference [28]. Data for the remaining compounds are from this work.

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