Supporting Information
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Supporting Information

for

Synthesis of (E)-1-Benzylolxy-3-fluoro-1,3-butadiene: A novel fluorinated diene for Diels-Alder reactions

Tsuyoshi Hayashi, Yoshinosuke Usuki,* Yosuke Wakamatsu and Hideo Iio

Department of Material Science, Graduate School of Science, Osaka City University
Sugimoto, Sumioshi-ku, Osaka 558-8585, Japan.
Fax: +81 6 6605 2522; E-mail: usuki@sci.osaka-cu.ac.jp

1. General methods S1

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General methods

Solvents and reagents: Dried toluene was used as commercially supplied. Reagents were used as commercially supplied unless otherwise. Chromatography: Flash column chromatography was carried out on a Kanto Chemical silica gel 60N (spherical, neutral, 40-50 µm), and pre-coated Merck silica gel plates (Art5744 Kieselgel 60F254, 0.50 mm) were used for preparative thin-layer chromatography (PTLC). PTLC visualization was accompanied using UV lamp (254 nm) or a charring solution (ethanoic p-anisaldehyde, ethanoic phosphomolybdic acid). NMR Spectra: Unless mentioned otherwise, $^1$H, $^{13}$C and $^{19}$F nuclear magnetic resonance (NMR) spectra were recorded in CDCl$_3$ on an either Bruker DRX-600, JEOL JNM-LA400, JEOL JNM-LA300, Brucker AV-300 spectrometer at ambient temperature. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant in Hz, integration. Coupling constants were determined directly from $^1$H, $^{13}$C and $^{19}$F NMR spectra. Chemical shifts of $^{19}$F NMR were given by δ relative to that of an external trifluoroacetic acid (TFA). MS Spectra: Low resolution mass spectral analyses (LRMS) and high resolution mass spectral analyses (HRMS) were measured on an either JEOL JMS-700T or JEOL JMS-AX500 spectrometer by means of electron ionization (EI), chemical ionization (CI) or fast atom bombardment (FAB). IR Spectra: Infrared (IR) spectra were recorded on a JASCO FT/IR-700.
To a solution of commercially available ethyl 2-(diethoxyphosphoryl)-2-fluoroacetate (1.19 g, 4.91 mmol) in freshly dried THF (22 mL) was added n-BuLi (2.6 M solution in hexane, 1.9 mL, 4.94 mmol) dropwise at 0 °C under Ar. The stirring was continued for 30 min at 0 °C. A solution of benzzyloxyacetaldheyde (0.62 g, 4.13 mmol) in freshly dried THF (9 mL) was added to the Wadsworth–Horner–Emmons reagent, and the mixture was stirred for an additional 30 min at 0 °C. The reaction was quenched with H2O (50 mL), extracted with Et2O (3 × 75 mL), dried over MgSO4 and the solvent was evaporated in vacuo. The crude product was dissolved in dry CH2Cl2 (5 mL) in dry glassware. DIBAL-H (1.0 M in toluene, 12 mL) was added at 0 °C. The mixture was stirred at r.t. overnight before the reaction was quenched with 2M aq. HCl. The aq. layer was extracted with CH2Cl2 (3×50 mL). The combined org extracts was washed with sat. aq. NaHCO3, water (2×50 mL), and brine dried over MgSO4 and evaporated. Product was separated by flash column chromatography (10 % EtOAc in Hexane), yielding 0.614 g (76%, E:Z = 10:1) of a colorless oil.

**4-Benzzyloxy-2-fluoro-but-2-en-1-ol (2)**

\[
\text{EtO}_2\text{CCHFPO(OEt)₂} \xrightarrow{1) \text{n-BuLi / THF, 0 °C}} \text{BnOCHO} \xrightarrow{2) \text{DIBAL / CH₂Cl₂, 0 °C to rt}} 76\%
\]

To a solution of commercially available ethyl 2-(diethoxyphosphoryl)-2-fluoroacetate (1.19 g, 4.91 mmol) in freshly dried THF (22 mL) was added n-BuLi (2.6 M solution in hexane, 1.9 mL, 4.94 mmol) dropwise at 0 °C under Ar. The stirring was continued for 30 min at 0 °C. A solution of benzzyloxyacetaldheyde (0.62 g, 4.13 mmol) in freshly dried THF (9 mL) was added to the Wadsworth–Horner–Emmons reagent, and the mixture was stirred for an additional 30 min at 0 °C. The reaction was quenched with H2O (50 mL), extracted with Et2O (3 × 75 mL), dried over MgSO4 and the solvent was evaporated in vacuo. The crude product was dissolved in dry CH2Cl2 (5 mL) in dry glassware. DIBAL-H (1.0 M in toluene, 12 mL) was added at 0 °C. The mixture was stirred at r.t. overnight before the reaction was quenched with 2M aq. HCl. The aq. layer was extracted with CH2Cl2 (3×50 mL). The combined org extracts was washed with sat. aq. NaHCO3, water (2×50 mL), and brine dried over MgSO4 and evaporated. Product was separated by flash column chromatography (10 % EtOAc in Hexane), yielding 0.614 g (76%, E:Z = 10:1) of a colorless oil.

(E)-2

1H NMR (300 MHz, CDCl3) δ 2.71 (br s, 1H), 4.03 (dd, 4JHF = 1.7 Hz, 3JHH = 7.5 Hz, 2H), 4.17 (d, 3JHF = 20.0 Hz, 2H), 4.50 (s, 2H), 5.56 (dt, 3JHH = 7.5 Hz, 3JHF = 18.9 Hz, 1H), 7.25-7.38 (m, 5H); 13C NMR (100 MHz, CDCl3) δ 57.44 (d, 2JCF = 30.6 Hz, C-1), 63.61 (d, 3JCF = 13.2 Hz, C-4), 72.15, 105.28 (d, 2JCF = 116.2 Hz, C-3), 127.83, 127.88, 128.46, 137.49, 160.64 (d, 1JCF = 256.9 Hz, C-2); 19F NMR (283 MHz, CDCl3) δ -107.04 (dt, 3JHF = 18.9, 20.0 Hz). MS (EI) m/z 196 [M]+; HRMS (EI) Calcd. for C11H12FO2: 196.0900, Found: 196.0895.

(Z)-2

1H NMR (300 MHz, CDCl3) δ 5.11 (dt, 3JHH = 7.7 Hz, 3JHF = 36.2 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 60.55 (d, 2JCF = 30.6 Hz, C-1), 62.28 (d, 3JCF = 5.8 Hz, C-4), 72.29, 103.92 (d, 2JCF = 10.7 Hz, C-3); 19F NMR (283 MHz, CDCl3) δ -116.26 (dt, 3JHF = 36.2, 13.8 Hz).

**4-Benzzyloxy-2-fluoro-but-2-enyl acetate (3)**

\[
\text{2 (E:Z = 10:1)} \xrightarrow{\text{Ac_2O / py, 88%}} \text{3 (E:Z = 10:1)}
\]

2 (0.668 g, 3.4 mmol) was dissolved in dry pyridine (1.1 mL) at 0 °C. Acetic anhydride (0.60 mL, 6.3 mmol) was added slowly at 0 °C. The solution was stirred at r.t. for 1 h and quenched with water. It was diluted with water (30 mL), extracted with Et2O. The combined organic extracts was washed with 0.5M HCl, sat aq NaHCO3, dried over MgSO4, and evaporated under the reduced pressure. The crude product was purified by a flash column...
chromatography (10 % EtOAc in Hexane) to give 3 (0.713 g, 2.994 mmol; yield 88%, E:Z = 10:1).

(E)-3: $^1$H NMR (300 MHz, CDCl$_3$) δ 2.09 (s, 3H), 4.08 (dd, $^4$J$_{HF}$ = 1.8 Hz, $^3$J$_{HH}$ = 7.7 Hz, 2H), 4.51 (s, 2H), 4.69 (d, $^3$J$_{HF}$ = 21.1 Hz, 2H), 5.56 (dt, $^3$J$_{HH}$ = 7.7 Hz, $^3$J$_{HF}$ = 18.9 Hz, 1H), 7.27-7.38 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.61, 58.12 (d, $^2$J$_{CF}$ = 28.9 Hz, C-1), 63.74 (d, $^3$J$_{CF}$ = 11.6 Hz, C-4), 72.24, 108.64 (d, $^2$J$_{CF}$ = 19.8 Hz, C-3), 127.77, 127.83, 128.46, 137.65, 156.97 (d, $^1$J$_{CF}$ = 255.2 Hz, C-2), 170.37; $^{19}$F NMR (283 MHz, CDCl$_3$) δ -106.46 (dt, $^3$J$_{HF}$ = 18.9, 21.1 Hz). IR (CHCl$_3$) 2870, 1741, 1705, 1497, 1454, 1367 cm$^{-1}$. MS (Cl) m/z 239 [M+H]$^+$; HRMS (Cl) Calcd. for C$_{13}$H$_{16}$FO: 239.1083, Found: 239.1112.

(Z)-3 (selected date): $^1$H NMR (300 MHz, CDCl$_3$) δ 2.10 (s, 3H), 4.16 (dd, $^4$J$_{HF}$ = 2.2 Hz, $^3$J$_{HH}$ = 6.8 Hz, 2H), 4.59 (d, $^3$J$_{HF}$ = 15.9 Hz, 2H), 5.20 (dt, $^3$J$_{HH}$ = 7.0 Hz, $^3$J$_{HF}$ = 35.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.61, 15.18, 61.51 (d, $^2$J$_{CF}$ = 32.2 Hz, C-1), 62.26 (d, $^3$J$_{CF}$ = 4.9 Hz, C-4), 72.45, 107.72 (d, $^2$J$_{CF}$ = 11.5 Hz, C-3); $^{19}$F NMR (283 MHz, CDCl$_3$) δ -114.38 (dt, $^3$J$_{HF}$ = 15.9, 35.0 Hz).

(E)-1-benzzyloxy-3-fluoro-1,3-butadiene (I)

Acetate 3 (0.25 g, 1.05 mmol) was placed in a Pyrex tube. After the atmosphere was replaced with argon, tetrakis(triphenylphosphine)palladium (0.012g, 0.010mmol) and hexamethyldisilane (0.461 g, 0.63 mL, 3.15 mmol) were added. Then the tube was sealed and heated at 100 °C for 2h. After cooling to room temperature, the crude product was purified by a flash column chromatography (Hexane) to give 1 (0.077 g, 0.434 mmol, yield 42%).

$^1$H NMR (300 MHz, CDCl$_3$) δ 4.20 (dd, $^2$J$_{HH}$ = 2.9 Hz, $^3$J$_{HF}$ = 50.4 Hz, 1H), 4.43 (dd, $^2$J$_{HH}$ = 2.9 Hz, $^3$J$_{HF}$ = 17.9 Hz, 1H), 4.82 (s, 2H), 5.44 (dd, $^3$J$_{HH}$ = 12.4 Hz, $^3$J$_{HF}$ = 25.3 Hz, 1H), 6.92 (d, $^3$J$_{HH}$ = 12.4 Hz, 1H), 7.32-7.40 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 72.32, 88.74 (d, $^2$J$_{CF}$ = 21.5 Hz, C-2), 99.30 (d, $^2$J$_{CF}$ = 22.3 Hz, C-4), 127.56, 128.26, 128.63, 136.11, 149.67 (d, $^3$J$_{CF}$ = 21.5 Hz, C-1), 161.25 (d, $^1$J$_{CF}$ = 247.8 Hz, C-3); $^{19}$F NMR (283 MHz, CDCl$_3$) δ -111.40 (ddd, $^3$J$_{HF}$ = 17.9, 25.3, 50.4 Hz); IR (CHCl$_3$) 1676, 1654, 1455, 1384, 1288 cm$^{-1}$. MS (EI) m/z 178 [M]$^+$; HRMS (EI) Calcd. for C$_{11}$H$_{11}$FO: 178.0794, Found: 178.0791.

Notes

(1) This compound could be stored in a cold solution for a few days, however, was allowed to decompose in neat liquid.
(2) Large scale preparation of 1 was accomplished with a lower yield (~30%).
General procedure for the Diels-Alder reaction of 1: A mixture of dienophile (0.16 mmol) and 1 (0.16 mmol) in dry toluene (0.6 mL) was heated to reflux in a sealed tube under an argon atmosphere for the time indicated in the text (Bath temperature 130 ºC). No thermal decomposition of 1 was observed during the reaction. After cooling to r.t., solvent was removed under the reduced pressure. The crude product was purified by PTLC.

3-Benzylxoy-5-fluoro-cyclohex-4-ene-1,2-dicarboxylic acid dimethyl ester (4a and 4b): According to general procedure, reaction of 1 (29 mg) with dimethyl fumarate (24 mg), followed by PTLC using hexane/EtOAc (8/2), provided an inseparable mixture of 4a and 4b (44.1 mg, 85%: 52:48) as a clear oil.
4-Benzylxoy-6-fluoro-3a,4,7a-tetrahydro-isobenzofuran-1,3-dione (4c and 4d): According to general procedure, reaction of 1 (22 mg) with maleic anhydride (12 mg), without any further purification, provided a 81:19 mixture of 4c and 4d (30 mg, 80%) as a pale brown oil.

Major isomer

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.59 (ddd, $J = 9.5$ Hz, $J = 10.9$ Hz, $^2J_{HH} = 18.3$ Hz, 1H), 3.03 (ddd, $J = 2.8$ Hz, $J = 6.7$ Hz, $^2J_{HH} = 18.3$ Hz, 1H), 3.20 (dd, $^3J_{HH} = 4.2$ Hz, $^3J_{HH} = 10.1$ Hz, 1H), 3.54 (m, 1H), 4.37 (m, 1H), 4.51 (m, 1H), 4.57 (m, 1H), 5.59 (ddd, $^4J_{HF} = 2.8$ Hz, $^3J_{HH} = 6.4$ Hz, 1H), 7.17 - 7.37 (m, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 21.95 (d, $^2J_{CF} = 28.6$ Hz, C-7), 37.21 (d, $^3J_{CF} = 9.0$ Hz, C-7a), 45.68, 68.73, 70.13, 71.00 (d, $^3J_{CF} = 12.1$ Hz, C-6); 5.59 (ddd, $^4J_{HF} = 13.4$ Hz, 1H), 7.17-7.37 (m, 5H); $^{19}$F NMR (283 MHz, CDCl$_3$) δ -93.87 (m).

Minor isomer (selected date)

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.69 (ddd, $J = 2.2$ Hz, $J = 12.4$ Hz, $^2J_{HH} = 16.8$ Hz, 1H), 2.94 (ddd, $J = 2.6$ Hz, $J = 8.1$ Hz, $^2J_{HH} = 16.8$ Hz, 1H), 4.62 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 24.89 (d, $^2J_{CF} = 28.6$ Hz, C-7), 38.58 (d, $^3J_{CF} = 5.3$ Hz, C-7a), 45.73, 70.86, 71.00 (d, $^2J_{CF} = 12.1$ Hz, C-4), 102.59 (d, $^2J_{CF} = 13.6$ Hz, C-5); 1H NMR (300 MHz, CDCl$_3$) δ -93.87 (m).

3-Benzylxoy-5-fluoro-cyclohex-4-ene-1,2-dicarboxylic acid dimethyl ester (4e and 4f): According to general procedure, reaction of 1 (43 mg) with dimethyl maleate (35 mg), followed by PTLC using hexane/EtOAc (7/3), provided 4f (8.0 mg, 11%) and 4e (4.0 mg, 5%) as colorless oils.

Major isomer

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.55 (dt, $J = 6.1$ Hz, $^2J_{HH} = 18.0$ Hz, 1H), 2.81 (dd, $^3J_{HH} =
10.8 Hz, 2\textit{J}_{HH} = 18.0 Hz, 1H), 3.26 (ddd, 3\textit{J}_{HH} = 3.6 Hz, 3\textit{J}_{HH} = 6.4 Hz, 3\textit{J}_{HH} = 10.8 Hz, 1H), 3.50 (m, 1H), 3.66 (s, 3H), 3.74 (s, 3H), 4.50 (m, 1H), 4.57 (d, A of AB, 2\textit{J}_{HH} = 12.1 Hz, 1H), 4.62 (d, B of AB, 2\textit{J}_{HH} = 12.1 Hz, 1H), 5.41 (dd, 3\textit{J}_{HH} = 5.6 Hz, 3\textit{J}_{HF} = 15.4 Hz, 1H), 7.30-7.36 (m, 5H); 13C NMR (100 MHz, CDCl3) δ 25.33 (d, 2\textit{J}_{CF} = 26.4 Hz, C-6), 36.37 (d, 3\textit{J}_{CF} = 10.7 Hz, C-1), 44.53 (d, 4\textit{J}_{CF} = 2.5 Hz, C-2), 52.09, 52.17, 71.07, 71.74 (d, 3\textit{J}_{CF} = 13.2 Hz, C-3), 101.25 (d, 2\textit{J}_{CF} = 14.8 Hz, C-4), 127.72, 127.86, 128.49, 137.82, 162.72 (d, 1\textit{J}_{CF} = 262.6 Hz, C-5), 170.56, 172.89 (d, 4\textit{J}_{CF} = 2.5 Hz); 19F NMR (283 MHz, CDCl3) δ -96.64 (d, 3\textit{J}_{HF} = 15.4 Hz). IR (CHCl3) 1734, 1702, 1383, 909 cm\textsuperscript{-1}. MS (FAB) m/z 323 (M+H)\textsuperscript{+}; HRMS (FAB) Calcd. for C\textsubscript{17}H\textsubscript{22}FO\textsubscript{4}: 323.1295, Found: 323.1292.

Minor isomer (selected date)

\textsuperscript{1}H NMR (300 MHz, CDCl3) δ 2.44 (dm, 2\textit{J}_{HH} = 14.5 Hz, 1H), 2.98-3.10 (m, 2H), 3.46-3.49 (m, 1H), 3.64 (s, 3H), 3.71 (s, 3H) 4.40 (m, 1H), 4.57 (d, A of AB, 2\textit{J}_{HH} = 11.7 Hz, 1H), 4.74 (d, B of AB, 2\textit{J}_{HH} = 11.7 Hz, 1H), 5.31 (dd, 3\textit{J}_{HH} = 2.1 Hz, 3\textit{J}_{HF} = 15.9 Hz, 1H), 7.26-7.33 (m, 5H); 13C NMR (150 MHz, CDCl3) δ 25.87 (d, 2\textit{J}_{CF} = 27.4 Hz, C-6), 38.88 (d, 3\textit{J}_{CF} = 10.6 Hz, C-1), 43.11, 51.70, 52.20, 71.06, 72.23 (d, 3\textit{J}_{CF} = 11.8 Hz, C-3), 102.57 (d, 2\textit{J}_{CF} = 16.2 Hz, C-4), 127.60, 127.63, 128.29, 137.82, 160.07 (d, 1\textit{J}_{CF} = 261.0 Hz, C-5), 172.05 (d, 4\textit{J}_{CF} = 1.9 Hz), 170.56; 19F NMR (283 MHz, CDCl3) δ -100.54 (d, 3\textit{J}_{HF} = 15.9 Hz).

4,5-Dibenzensulfonyl-3-benzyloxy-1-fluorocyclohexene (4g): According to general procedure, reaction of 1 (21 mg) with \textit{cis}-1,2-bis(phenylsulfonyl)ethylene (36 mg), followed by PTLC using hexane/EtOAc (6/4), provided 4g (40.2 mg, 70%) as a white solid.

\textsuperscript{1}H NMR (600 MHz, CDCl3) δ 2.35 (dt, 2\textit{J}_{HH} = 17.1 Hz, 3\textit{J}_{HH} = 5.8 Hz, 1H), 3.37 (dd, 2\textit{J}_{HH} = 17.1 Hz, 3\textit{J}_{HH} = 11.8 Hz, 1H), 3.94 (dm, 3\textit{J}_{HH} = 11.8 Hz, 1H), 4.21 (brcs, 1H), 4.42 (s, 2H), 4.68 (brcs, 1H), 5.44 (dd, 3\textit{J}_{HH} = 5.4 Hz, 3\textit{J}_{HF} = 14.4 Hz, 1H), 7.14 (m, 2H), 7.32-7.33 (m, 3H), 7.54-7.59 (m, 4H), 7.65-7.70 (m, 2H), 7.83 (d, 3\textit{J}_{HH} = 7.8 Hz, 2H), 7.95 (d, 3\textit{J}_{HH} = 7.2 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 24.30 (d, 2\textit{J}_{CF} = 28.9 Hz, C-6), 58.43 (d, 2\textit{J}_{CF} = 9.1 Hz, C-5), 60.92, 69.88 (d, 3\textit{J}_{CF} = 13.2 Hz, C-3), 71.70, 101.43 (d, 2\textit{J}_{CF} = 15.7 Hz, C-2), 127.84, 128.28, 128.35, 128.68, 128.95, 129.06, 129.42, 134.45, 134.17, 136.60, 138.71, 139.45, 161.40 (d, 1\textit{J}_{CF} = 265.1 Hz, C-1); 19F NMR (283 MHz, CDCl3) δ -95.59 (d, 3\textit{J}_{HF} = 14.4 Hz). IR (CHCl3) 2927, 2917, 1585, 1448, 1329, 1154, 1083 cm\textsuperscript{-1}. MS (FAB) m/z 487 (M+H)\textsuperscript{+}; HRMS (FAB) Calcd. for C\textsubscript{25}H\textsubscript{24}F\textsubscript{2}O\textsubscript{5}S\textsubscript{2}: 487.1049, Found: 487.1051.
4-Benzensulfonyl-3-benzyloxy-1-fluorocyclohexene (4h and 4i): According to general procedure, reaction of 1 (29 mg) with phenyl vinyl sulfone (28 mg), followed by PTLC using hexane/EtOAc (7/3), provided an inseparable mixture of 4h and 4i (36.9 mg, 66%; 7:93) as a clear oil.

Major isomer
$^1$H NMR (600 MHz, CDCl$_3$) δ 2.14 (dm, $^2$J$_{HH}$ = 13.5 Hz, 1H), 2.30 (dm, $^2$J$_{HH}$ = 17.4 Hz, 1H), 2.38 (dm, $^2$J$_{HH}$ = 13.5 Hz, 1H), 2.47 (dm, $^2$J$_{HH}$ = 17.4 Hz, 1H), 3.38 (dt, $^3$J$_{HH}$ = 8.4 Hz, $^3$J$_{HH}$ = 4.2 Hz, 1H), 4.30 (d, A of AB, $^2$J$_{HH}$ = 11.4 Hz, 1H), 4.35 (d, B of AB, $^2$J$_{HH}$ = 11.4 Hz, 1H), 4.56 (dm, $^3$J$_{HH}$ = 4.2 Hz, 1H), 5.34 (dd, $^3$J$_{HH}$ = 3.6 Hz, $^3$J$_{HF}$ = 16.2 Hz, 1H), 7.05-7.07 (m, 2H), 7.23-7.27 (m, 3H), 7.48 (t, $^3$J$_{HH}$ = 7.2 Hz, 2H), 7.59 (t, $^3$J$_{HH}$ = 7.2 Hz, 1H), 7.87 (d, $^2$J$_{HH}$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.21 (d, $^3$J$_{CF}$ = 9.1 Hz, C-5), 23.40 (d, $^2$J$_{CF}$ = 25.6 Hz, C-6), 62.96 (d, $^4$J$_{CF}$ = 1.6 Hz, C-4), 70.51, 70.92 (d, $^3$J$_{CF}$ = 11.5 Hz, C-3), 101.41 (d, $^2$J$_{CF}$ = 16.5 Hz, C-2), 127.58, 127.74, 128.27, 129.10, 133.64, 137.16, 138.94, 162.15 (d, $^1$J$_{CF}$ = 264.3 Hz, C-1); $^{19}$F NMR (283 MHz, CDCl$_3$) δ -97.41 (d, $^3$J$_{HF}$ = 16.2 Hz). IR (CHCl$_3$) 2930, 1704, 1414, 1447, 1307, 1148, 1050 cm$^{-1}$. MS (FAB) m/z 347 (M+H)$^+$; HRMS (FAB) Calcd. for C$_{19}$H$_{20}$F$_3$S : 347.1117, Found: 347.1115.

Minor isomer (selected date)
$^1$H NMR (600 MHz, CDCl$_3$) δ 3.20 (dt, $^3$J$_{HH}$ = 3.3 Hz, $^3$J$_{HH}$ = 12.4 Hz, 1H), 5.46 (dd, $^3$J$_{HH}$ = 5.7 Hz, $^3$J$_{HF}$ = 15.6 Hz, 1H); $^{19}$F NMR (283 MHz, CDCl$_3$) δ -97.41 (dd, $^3$J$_{HF}$ = 3.4, 15.6 Hz).

**Assignment of relative stereochemistry**: The observed $^3$J$_{HH}$ coupling of 4h and 4i between the vinyl hydrogen and the CHOBN proton (5.9 Hz and 3.8 Hz) indicates near co-planarity, which suggests that the benzyloxy group is pseudoaxial. The methine proton in CHSO$_2$Ph of 4h was observed at δ 3.20 (dt). The observed large $^2$J$_{HH}$ (12.4 Hz) suggests that the methine proton in CHSO$_2$Ph is pseudoaxial; the methine proton in CHSO$_2$Ph of 4i was observed at δ 3.38 (dt). The observed $^3$J$_{HH}$ (8.3 Hz and 4.2 Hz) suggests that the methine proton in CHSO$_2$Ph is pseudoequatorial. These results suggests that the exo adduct is the major product 4i.

![Figure S1 Selected $^1$H NMR data of 4h and 4i](S7)
3-Benzylxylo-5-fluoro-cyclohexa-1,4-diene-1,2-dicarboxylic acid dimethyl ester (4j):
According to general procedure, reaction of 1 (24 mg) with dimethyl acetylenedicarboxylate (20 mg), without any further purification, provided the crude product (50.2 mg) as a colorless oil. Yield of 4j (93%) was determined by $^{19}$F NMR spectroscopy. During purification of the PTLC using hexane/CH$_2$Cl$_2$/EtOAc (5/2/1), elimination of BnOH proceeded partially to afford dimethyl 4-fluorophthalate (11.1 mg, 40%).

![Structure of 4j](image)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.05 (dd, $^3$J$_{HF}$ = 6.0 Hz, $^2$J$_{HH}$ = 23.1 Hz, 1H), 3.37 (ddd, $^4$J$_{HH}$ = 1.6 Hz, $^3$J$_{HF}$ = 6.5 Hz, $^2$J$_{HH}$ = 23.1 Hz, 1H), 3.79 (s, 3H), 4.43 (d, A of AB, $^2$J$_{HH}$ = 11.0 Hz, 1H), 4.48 (d, B of AB, $^2$J$_{HH}$ = 11.0 Hz, 1H), 5.27 (m, 1H), 5.46 (dd, $^3$J$_{HH}$ = 3.8 Hz, $^3$J$_{HF}$ = 15.2 Hz, 1H), 7.17-7.37 (m, 5H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 27.81 (d, $^2$J$_{CF}$ = 29.7 Hz, C-6), 65.25, 68.83, 72.74 (d, $^3$J$_{CF}$ = 11.5 Hz, C-3), 100.51 (d, $^2$J$_{CF}$ = 14.8 Hz, C-4), 127.54, 127.93, 128.33, 137.66, 158.72 (d, $^1$J$_{CF}$ = 261.0 Hz, C-5), 165.15, 166.65.

$^{19}$F NMR (283 MHz, CDCl$_3$) $\delta$ -101.73 (dm).

IR (CHCl$_3$) 2928, 1729, 1437, 1119 cm$^{-1}$. MS (FAB) m/z 321 (M+H)$^+$; HRMS (FAB) Calcd. for C$_{17}$H$_{18}$FO$_5$: 321.1138, Found: 321.1120.

3-Benzylxylo-5-fluoro-3,6-dihydro-pyridazine-1,2-dicarboxylic acid diethyl ester (4k):
According to general procedure, reaction of 1 (26 mg) with diethyl azodicarboxylate (66 µl; 40% solution in Toluene), followed by PTLC using hexane/EtOAc (9/1), provided 4k (46.7 mg, 90%) as a colorless oil.

![Structure of 4k](image)

$^1$H NMR (300 MHz, DMSO-d$_6$, 120 °C) $\delta$ 1.05 (t, $^3$J$_{HH}$ = 7.2 Hz, 3H), 1.12 (t, $^3$J$_{HH}$ = 7.2 Hz, 3H), 3.81 (dm, $^2$J$_{HH}$ = 17.1 Hz, 1H), 4.03 (q, $^3$J$_{HH}$ = 7.2 Hz, 2H), 4.09 (q, $^3$J$_{HH}$ = 7.2 Hz, 2H), 4.36 (dd, $^2$J$_{HH}$ = 4.5 Hz, $^2$J$_{HH}$ = 17.1 Hz, 1H), 4.47 (d, A of AB, $^2$J$_{HH}$ = 12.0 Hz, 1H), 4.64 (d, B of AB, $^2$J$_{HH}$ = 12.0 Hz, 1H), 5.49 (dm, $^3$J$_{HH}$ = 15.6 Hz, 1H), 5.73 (m, 1H), 7.11-7.33 (m, 5H);

$^{13}$C NMR (75 MHz, DMSO-d$_6$, 120 °C) $\delta$ 13.94, 13.97, 62.35 (d, $^2$J$_{CF}$ = 23.4 Hz, C-6), 69.62, 79.71 (d, $^3$J$_{CF}$ = 13.6 Hz, C-3), 101.79 (d, $^2$J$_{CF}$ = 13.6 Hz, C-4), 127.35, 127.42, 128.04, 137.77, 154.04, 156.88; $^{19}$F NMR (283 MHz, CDCl$_3$) $\delta$ -111.12 and -112.03 (due to rotamers). IR (CHCl$_3$) 2934, 1708, 1414, 1377, 1348, 1312, 1125 cm$^{-1}$. MS (FAB) m/z 353 (M+H)$^+$; HRMS (FAB) Calcd. for C$_{17}$H$_{18}$FN$_2$O$_5$ : 353.1513, Found: 353.1522.
6-Benzzyloxy-4-fluoro-3,6-dihydro-2H-pyran-2-carboxylic acid n-butyl ester (4l and 4m): According to general procedure, reaction of 1 (26 mg) with n-butyl glyoxylate (21 mg), followed by PTLC using hexane/EtOAc (8/2), provided an inseparable mixture of 4l and 4m (37.9 mg, 84%: 42:58) as a colorless oil.

**Major isomer**

$^1$H NMR (600 MHz, CDCl$_3$) δ 0.95 (t, $^3$J$_{HH}$ = 7.2 Hz, 3H), 1.40 (sextet, $^3$J$_{HH}$ = 7.2 Hz, 2H), 1.67 (m, 2H), 2.45 (ddd, J = 4.2 Hz, J = 8.4 Hz, $^2$J$_{HH}$ = 17.4 Hz, 1H), 2.61 (dm, $^2$J$_{HH}$ = 17.4 Hz, 1H), 4.17-4.25 (m, 2H), 4.62 (d, A of AB, $^2$J$_{HH}$ = 12.0 Hz, 1H), 4.68 (dd, $^3$J$_{HH}$ = 4.2 Hz, $^3$J$_{HH}$ = 11.4 Hz, 1H), 5.29-5.39 (m, 2H), 7.25-7.34 (m, 5H; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.61, 19.00, 28.68 (d, $^2$J$_{CF}$ = 8.3 Hz, C-2), 70.03, 94.56 (d, $^3$J$_{CF}$ = 14.0 Hz, C-6), 102.15 (d, $^2$J$_{CF}$ = 13.2 Hz, C-5), 127.69, 127.98, 128.42, 137.39, 160.04 (d, $^1$J$_{CF}$ = 266.8 Hz, C-4), 169.85; $^{19}$F NMR (283 MHz, CDCl$_3$) δ -100.61 (m). IR (CHCl$_3$) 2935, 1746, 1709, 1425, 1126 cm$^{-1}$. MS (FAB) m/z 309 (M+H)$^+$; HRMS (FAB) Calcd. for C$_{17}$H$_{22}$FO$_4$: 309.1502, Found: 309.1488.

**Minor isomer (selected date)**

$^1$H NMR (600 MHz, CDCl$_3$) δ 0.90 (t, $^3$J$_{HH}$ = 7.2 Hz, 3H), 1.35 (sextet, $^3$J$_{HH}$ = 7.2 Hz, 2H), 1.60 (quintet, $^3$J$_{HH}$ = 6.8 Hz, 2H), 2.55 (dm, $^2$J$_{HH}$ = 17.0 Hz, 1H), 2.73 (dm, $^2$J$_{HH}$ = 17.0 Hz, 1H), 4.02 (dt, $^3$J$_{HH}$ = 6.8 Hz, $^2$J$_{HH}$ = 10.8 Hz, 1H), 4.17-4.25 (m, 1H), 4.46 (m, 1H), 4.65 (d, A of AB, $^2$J$_{HH}$ = 12.0 Hz, 1H), 4.88 (d, B of AB, $^2$J$_{HH}$ = 12.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.58, 18.97, 27.18 (d, $^2$J$_{CF}$ = 24.0 Hz, C-3), 30.36, 65.38, 69.38 (d, $^3$J$_{CF}$ = 9.0 Hz, C-2), 69.66, 95.60 (d, $^3$J$_{CF}$ = 13.2 Hz, C-6), 102.46 (d, $^2$J$_{CF}$ = 13.2 Hz, C-5), 127.64, 127.80, 128.32, 159.53 (d, $^1$J$_{CF}$ = 266.8 Hz, C-4), 169.81; $^{19}$F NMR (283 MHz, CDCl$_3$) δ -99.50 (m).