SUPPORTING INFORMATION FOR:

Photocatalytic alkene reduction by B$_{12}$-TiO$_2$ hybrid catalyst coupled with C-F bond cleavage for gem-difluoroolefin synthesis

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Chemicals

All solvents and chemicals used in this study were of reagent grade and were used without further purification. Deuterium methanol (CH$_3$OD) (99.9 % atom D) was purchased from CEA and was used as received. TiO$_2$ (anatase, AMT-600, surface area=52 m$^2$g$^{-1}$, diameter size=ca. 30 nm) was obtained from Tayca Co., Ltd. Pt-TiO$_2$ (0.15 wt% Pt loaded P-25 TiO$_2$; a mixture of rutile (20%) and anatase (80%), surface area= 50 m$^2$g$^{-1}$) was obtained from NSG Co., Ltd. Aquacyano cobyric acid (Chart S1) was synthesized by a previously reported method.$^{51}$ Heptamethyl cobyritic acid perchlorate (Chart S1) was synthesized by a previously reported method.$^{52,3}$ The substrate, $\alpha$-trifluoromethyl styrene (1) and an authentic sample of 3,3,3-trifluoropropylbenzene (25) were purchased from Wako Chemical Industries, Ltd. The authentic sample of $\alpha$-trifluoromethyl ethylethylbenzene (3) was purchased from Fluorochem. Alfusone$^R$ as an F$^-$ quantification reagent was purchased from DOJINDO.

![Chemical structures](chart_s1.png)

Cyanoaquac cobyric acid  Heptamethyl cobyritic acid perchlorate

Chart S1.

Measurements

The NMR spectra were recorded by Bruker Avance 500 and 300 spectrometers at the Center of Advanced Instrumental Analysis of Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. The GC-
mass spectra were obtained using a Shimadzu GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μm). The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer at room temperature. The diffuse reflectance (DR) UV-vis reflectance spectra were measured by a Hitachi U-3300 spectrophotometer equipped with a Φ 60 integrating sphere at room temperature under nitrogen. The ESR spectra were obtained using a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter at room temperature. The cyclic voltammograms (CV) were obtained using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with 3-mm diameter glassy carbon wires as the working and platinum counter electrodes was used. An Ag/AgCl (3.0 M NaCl) electrode served as the reference. The $E_{1/2}$ value of the ferrocene–ferrocenium ($Fc/Fc^+$) was 0.45 V vs. Ag/AgCl with this setup.
**Fig S1.** Diffuse reflectance (DR) UV-VIS spectral change of the B$_{12}$-TiO$_2$ during UV light irradiation in the absence (a) and in the presence of (b) 1 in MeOH under N$_2$. 
Fig. S2. CVs of B$_{12}$, heptamethyl cobyrinate perchlorate (1mM), in CH$_3$CN containing of 0.1 M $n$-Bu$_4$NClO$_4$ under N$_2$ (a) and in the presence of 0.2 M of 1 (b). CV of 1 (c).
**Fig. S3.** UV-VIS spectrum for F⁻ quantification after catalytic reaction of entry 1 in Table 1.

(a)

![UV-VIS spectrum](image)

(b)

**Fig. S4.** GS-MS of products from 1 in CH₃OD, gem-difluoroolefin (2-d₁) (a) and reduced product (3-d₂) (b).
**Fig. S5.** ESR spectra observed during the UV light irradiation of the B\textsubscript{12}-TiO\textsubscript{2} without 1; [DMPO]=1 M, 2 mg of B\textsubscript{12}-TiO\textsubscript{2} under N\textsubscript{2} at room temperature in MeOH.
**General procedure for catalytic reaction by the B$_{12}$-TiO$_2$**

A mixture of an alkene (1) (4.1 mg, 4 mM) and B$_{12}$-TiO$_2$ (anatase, AMT-600, 10 mg, B$_{12}$=1.60x10$^{-5}$ M) was stirred in 6 mL of CH$_3$OH under nitrogen. After the solution was stirred for 24 hours during irradiation by 365 nm UV light (black light, 10 cm distance), the B$_{12}$-TiO$_2$ was removed by filtration. The resulting solution was analyzed by GC-MS and yields of the products were calculated by comparison to the ratio of the peak area using diphenyl as an internal standard.

**F$^-$ Quantification experiment**

First, a 5% Alfusone$^R$ aqueous solution and 0.001 mg F$^-$/mL sodium fluoride aqueous solution were prepared. The 5% Alfusone$^R$ aqueous solution (5 mL), acetone (20 mL) and 0.001 mg F$^-$/mL sodium fluoride aqueous solution (0 mL, 1 mL, 2 mL, 3 mL, 4 mL, 5 mL) were mixed and diluted to 50 mL by water. After 1 hour, the UV-vis absorbance was measured at 620 nm to make the calibration curve. F$^-$ generated from the catalytic reaction was then quantified by the same method according to the calibration curve.

**ESR spin-trapping experiment**

The ESR spectra for the DMPO spin-adducts were observed after 1 hour of UV-light irradiation of B$_{12}$-TiO$_2$ (2 mg) in the presence of 1 (9.4 mM) and DMPO (1.0 M) in 2 mL of MeOH or MeOD under nitrogen at room temperature. The settings for the ESR measurements were a frequency of 9.78 GHz, power of 1.0 mW, a center field of 3515 G, a sweep width of 150 G, a modulation amplitude of 5.0 G, a time constant of 40 ms, and a sweep time of 20 s.

**DR-UV-VIS measurement**

The DR-UV-VIS spectral change for the B$_{12}$-TiO$_2$ with substrate 1 (0.06 M) during UV-light irradiation was observed from the B$_{12}$-TiO$_2$ (4mg) suspended methanol (5mL) solution under nitrogen at room temperature.
Preparation of α-(tri/difluoromethyl) styrenes

The compounds were prepared according to a previously described procedure. To a diethyl ether solution (5 mL) of Ph₃PCH₃I (1.055 mmol), t-BuONa (1.055 mmol) was added at 0°C. The reaction mixture was stirred for 30 min at room temperature, then cooled to -78°C. To the mixture was slowly added a diethyl ether solution (2 mL) of tri/difluoroacetophenones (0.9589 mmol) at -78°C over 10 min. The mixture was gradually warmed to room temperature and stirred for 11h, then saturated aqueous NH₄Cl was added. The organic materials were extracted three times with Et₂O. The combined extracts were washed with brine and dried over anhydrous Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) and further distillation under reduced pressure to give the products.

α-Trifluoromethyl-p-methyl styrene (4)

For the preparation of α-trifluoromethyl-p-methyl styrene, 4'-methyl-2,2,2-trifluoroacetopheneone was used as the reactant. Colorless liquid, yield (26%); ¹H NMR (500 MHz, CDCl₃): δ 7.36 and 7.20 (A₂B₂, J=10 Hz, 4H), 5.91 (s, 1H), 5.74 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 138.85 (q, J=30 Hz), 138.98, 130.84, 129.27, 127.27, 122.37 (q, J=272.5 Hz), 119.56 (q, J=6.25 Hz), 21.26. ¹⁹F NMR (282 MHz, CDCl₃): δ -65.98; GC-MS: M⁺=186.

α-Trifluoromethyl-p-chloro styrene (13)

For the preparation of α-trifluoromethyl-p-chloro styrene, 4'-chloro-2,2,2-trifluoroacetopheneone was used as the reactant. Colorless liquid, yield (65%); ¹H NMR (500 MHz, CDCl₃): δ 7.40-7.37 (m, 4H), 5.98 (s, 1H), 5.77 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 138.05 (q, J=30 Hz), 135.24, 132.11,
128.86, 128.80, 120.90 (q, $J=$272.5 Hz), 120.81 (q, $J=$ 5Hz). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -66.13; GC-MS: $M^+$=206.

\textit{α-Trifluoromethyl-}p\textit{-fluoro styrene (10)}

For the preparation of α-trifluoromethyl-p-fluoro styrene, 4’-fluoro-2,2,2-trifluoroacetopheneone was used as reactant. Colorless liquid, yield (20%); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.44 and 7.07 (A$_2$B$_2$, $J=5$ Hz, 4H), 5.95 (s, 1H), 5.73 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 164.21, 162.23, 138.34 (q, $J=30$ Hz), 129.42 (d, $J=8.75$Hz), 124.32 (q, $J=272.5$Hz), 120.50 (q, $J=6.25$Hz), 115.71(d, $J=22.5$Hz); GC-MS: $M^+$=190.

\textit{α-Trifluoromethyl-}p\textit{-bromo styrene (16)}

For the preparation of α-trifluoromethyl-p-bromo styrene, 4’-bromo-2,2,2-trifluoroacetopheneone was used as reactant. Colorless liquid, yield (44%); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.53 and 7.33 (A$_2$B$_2$, $J=10$ Hz, 4H), 5.98 (s, 1H), 5.77 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 138.36(q, $J=30$Hz), 132.59, 131.84, 129.06, 124.18(q, $J=272.5$Hz), 123.43, 120.90 (q, $J=6.25$Hz). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -66.12; GC-MS: $M^+$=250.

\textit{α-Trifluoromethyl-}p\textit{-methoxy styrene (7)}

For the preparation of α-trifluoromethyl-p-methoxy styrene, 4’-methoxy-2,2,2-trifluoroacetopheneone was used as reactant. Colorless liquid, yield (33%); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.40 and 6.91 (A$_2$B$_2$, $J=5$Hz, 4H), 5.87 (d, $J=5$Hz, 1H), 5.70 (d, $J=5$Hz, 1H). 3.83 (s, 3H) $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 160.21, 138.59(q, $J=30$Hz), 128.67, 126.09, 124.58(q, $J=272.5$Hz), 118.85 (q, $J=5$Hz), 114.00, 55.33. $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -66.03; GC-MS: $M^+$=202.
**α-Difluoromethyl styrene (19)**

For the preparation of α-difluoromethyl styrene, 2,2-difluoroacetophenone was used as the reactant.

Colorless liquid, yield (60%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.49-7.37 (m, 5H), 6.40 (t, \(J=55\) Hz, 1H), 5.73 (t, \(J=5\) Hz, 1H), 5.67 (t, \(J=2.5\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 142.13 (t, \(J=20\) Hz), 134.83, 128.64, 128.59, 126.99, 118.84 (t, \(J=10\) Hz), 115.40 (t, \(J=237.5\) Hz). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -114.49 (d, \(J=54\) Hz); GC-MS: \(M^+=154\).

### [Preparation of authentic samples of products]

**Preparation of β, β-difluoro-α-methyl styrenes**

The compounds were prepared according to a procedure analogous to that previously described.\(^5\) To a stirred hot (180° bath) solution of 0.012 mol of the ketone, 0.0132 mol of tributylphosphine and 2mL of N-methylpyrrolidone, was added dropwise from an equilibrating dropping funnel over a period of about 30 min, a warm (60°) solution of 0.024 mol of sodium chlorodifluoroacetate in 10mL N-methylpyrrolidone. The flask contents were distilled at 85°C, and the fractional distillations were further purified by silica gel column chromatography to give the corresponding products.

**β, β-Difluoro-α-methyl styrene (2)**

For preparation of the β, β-difluoro-α-methyl styrenes, acetophenone was used as the reactant.

Colorless liquid, yield (10%); \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO): \(\delta\) 7.46-7.31 (m, 5H), 2.00 (t, \(J=5\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 153.52 (dd, \(J=284.4, 287.5\) Hz), 134.97 (t, \(J=3.75\) Hz), 128.39, 127.53 (t, \(J=3.75\)Hz), 127.09, 87.51(dd, \(J=15, 22.5\) Hz),
For preparation of the 4-methyl-\(\beta\), \(\beta\)-difluoro-\(\alpha\)-methyl styrene, \(p\)-acetyltoluene was used as the reactant. Colorless liquid, yield (28%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.26-7.16 (m, 4H), 2.35 (s, 3H), 1.95 (t, \(J=5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 153.41 (dd, \(J=287.5, 287.5\) Hz), 136.82, 131.97 (t, 3.75 Hz), 129.08, 127.38 (t, 3.75Hz), 87.29 (dd, \(J=21.25, 22.5\) Hz), 21.08, 13.28; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): -92.29 (dd, \(J=46.53, 2.82\) Hz), -90.75 (dd, \(J=46.53, 2.82\) Hz); GC-MS: \(M^+=154\).

For preparation of the 4-chloro-\(\beta\), \(\beta\)-difluoro-\(\alpha\)-methyl styrene, \(p\)-chloroacetophenone was used as the reactant. Colorless liquid, yield (16%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.33-7.28 (m, 4H), 1.95 (t, \(J=2.5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 153.54 (dd, \(J=285, 290\) Hz), 133.37 (t, \(J=3.75\) Hz), 132.93, 128.80 (t, \(J=3.75\) Hz), 128.59, 86.78 (dd, \(J=14, 22.5\) Hz), 13.15; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): -90.75 (dq, \(J=42.3, 2.82\)Hz), -91.2 (dq, \(J=42.3, 2.82\) Hz); GC-MS: \(M^+=188\).

For the preparation of 4-fluoro-\(\beta\), \(\beta\)-difluoro-\(\alpha\)-methyl styrene, \(p\)-fluoroacetophenone was used as reactant. Colorless liquid, yield (15%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.36 and 7.07 (A\(_2\)B\(_2\), \(J=5\)Hz, 4H), 1.98 (t, \(J=5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 162.76, 160.80, 129.18 (t, \(J=7.5\) Hz), 115.41, 115.24, 86.82 (dd, \(J=15, 23.75\) Hz), 13.15; GC-MS:
Preparation of (tri or difluoro-1-methylethyl)benzenes

α-(Tri or difluoromethyl) styrenes (0.49 mmol), Pd-C (30 mg), MeOH (10 mL) and THF (5 mL) were placed in a reactor. After degassing, H₂ gas filled the reactor. The solution was then stirred at room temperature for 3 hours. The solution was purified by filtration and the solvent was removed under reduced pressure.

4-Methyl-(2,2,2-trifluoro-1-methylethyl)benzene (6)

For preparation of the 4-methyl-(2,2,2-trifluoro-1-methylethyl)benzene, 4-methyl-1-(trifluoromethyl)vinylbenzene was used as the reactant. Colorless liquid, yield (92%); ¹H NMR (500 MHz, CDCl₃): δ 7.21 and 7.17 (A₂B₂, J=7.5 Hz, 4H), 3.44-3.37 (m, 1H), 2.35 (s, 3H), 1.48 (d, J=10 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 137.82, 133.53 (d, 1.25 Hz), 129.31, 128.37, 126.17, 43.75 (q, 27.5 Hz), 21.06, 14.64 (q, 2.5 Hz); ¹⁹F NMR (282 MHz, CDCl₃): -72.85 (d, 11.28 Hz); GC-MS: M⁺=188.

4-Chloro-(2,2,2-trifluoro-1-methylethyl)benzene (15)

For preparation of the 4-chloro-(2,2,2-trifluoro-1-methylethyl)benzene, 4-chloro-1-(trifluoromethyl)vinylbenzene was used as the reactant. Colorless liquid, yield (90%); ¹H NMR (500 MHz, (CD₂)₂CO): δ 7.46-7.42 (m, 4H), 3.77-3.72 (m, 1H), 1.50 (d, J= 5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 134.85 (d, 2.5Hz), 134.07, 129.85, 128.82, 127.98, 43.53 (q, 27.5 Hz), 14.52 (q, 2.5 Hz); ¹⁹F NMR (282 MHz, CDCl₃): -72.90 (d, 11.28 Hz); GC-MS: M⁺=206.

4-Fluoro-(2,2,2-trifluoro-1-methylethyl)benzene (12)
For the preparation of 4-fluoro-(2,2,2-trifluoro-1-methylethyl)benzene, 4-fluoro-1-(trifluoromethyl)vinylbenzene was used as reactant. Colorless liquid, yield (60%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.29 and 7.04 (A\(_2\)B\(_2\), \(J=5\) Hz, 4H), 3.45-3.38 (m, 1H), 1.50(d, \(J=5\)Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 163.56, 161.60, 130.15, 128.12(q, \(J=277.5\)Hz), 115.63(d, \(J=22.5\)Hz), 43.67(q, \(J=27.5\)Hz), 14.68; \(^19\)F NMR (282 MHz, CDCl\(_3\)): -115.48, -73.04; GC-MS: M\(^+\)=192.

4-Methoxy-(2,2,2-trifluoro-1-methylethyl)benzene (9)

For the preparation of 4-methoxy-(2,2,2-trifluoro-1-methylethyl)benzene, 4-methoxy-1-(trifluoromethyl)vinylbenzene was used as reactant. Colorless liquid, yield (99%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.24 and 6.89 (A\(_2\)B\(_2\), \(J=5\) Hz, 4H), 3.41-3.36 (m, 1H), 1.49(d, \(J=10\)Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 159.44, 129.56, 128.54, 128.40(q, \(J=277.5\) Hz), 114.05, 55.29, 43.53(q, \(J=2.5\)Hz), 14.65; GC-MS: M\(^+\)=204.

2,2-Difluoro-1-methylethylbenzene (22)

For preparation of the (2,2-difluoro-1-methylethyl)benzene, (3,3-difluoroprop-1-en-2yl)benzene was used as the reactant. Colorless liquid, yield (80%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.36-7.27 (m, 5H), 5.81 (td, \(J=55\)Hz, 5 Hz 1H), 3.17 (m, 1H), 1.40 (d, \(J=5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 138.69 (t, \(J=3.75\) Hz), 128.67, 128.24, 127.51, 118.28 (t, \(J=242.5\) Hz), 43.98(t, \(J=20.63\) Hz), 13.73 (t, \(J=5\) Hz); \(^19\)F NMR (282 MHz, CDCl\(_3\)): -124.43 (ddq, \(J=666.93\) Hz, 138.18 Hz, 19.74 Hz); GC-MS: M\(^+\)=156.

Preparation of \(\beta\)-fluoro-\(\alpha\)-methylstyrenes (E/Z) (20/21)

\[
\begin{array}{c}
\text{\(\text{C}_{6}\text{H}_{5}\text{C}^\text{F}_2\)} \\
\text{\(\text{C}_{6}\text{H}_{5}\text{C}^\text{F}_2\)}
\end{array}
\xrightarrow{\text{SBAH, 0°C}}
\begin{array}{c}
\text{\(\text{C}_{6}\text{H}_{5}\text{CH}^\text{F}\)} \\
\text{\(\text{C}_{6}\text{H}_{5}\text{CH}^\text{H}\)}
\end{array}
\]
The compounds were prepared according to a procedure analogous to that previously described.\textsuperscript{S6} A mixture of (2) (1.3 mmol), a benzene solution of 70% sodium bis(2-methoxyethoxy)aluminum (70% SBAH)(0.6 mL), and dry benzene(3 mL) was stirred at -5~0°C for 1 hour. The mixture was then poured into ice-water and acidified with concentrated hydrochloric acid until the pH of the solution was 6. The organic layer was washed with saturated aqueous NaCl, and dried by Na\textsubscript{2}SO\textsubscript{4}. The products were obtained after evaporation. Yield: 60% as colorless oil (E/Z mixture with ratio 2.8). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.5-7.28 (m, 7H), 6.98-6.57 (m, 1H), 2.05-1.91(m, 4H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 147.04, 145.24, 144.99, 130.47 (dq, 37.5, 1.25 Hz), 132.58 (dq, 37.5, 1.25 Hz), 128.56, 128.23, 127.78, 127.73, 127.41,125.96, 126.93, 16.03 (d, \( J=6.25 \) Hz), 12.26 (d, \( J=5 \) Hz); \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}): -130.47(dq, \( J=84.6, \) 2.82 Hz), -132.60(dq, \( J=87.42, \) 2.82 Hz); GC-MS: M\textsuperscript{+}=136.

\textbf{Preparation of \( \beta \)-trifluoromethyl styrene (24)}

\[
\begin{array}{c}
\text{\textsuperscript{Br}C_6H_5} + \text{\textsuperscript{F}_3\text{C}C_2\text{CH}_2\text{COOH}} \xrightarrow{\text{Pd(OAc)}_2(0.4 \text{ equiv})} \text{CuO(1 equiv)} \\
\text{K}_{2}\text{CO}_3(4 \text{ equiv}) \xrightarrow{\text{NMP, 130°C,15h, N}_2} \text{\textsuperscript{CF}_3C_\text{6}H_4} \text{= (24)}
\end{array}
\]

The compound was prepared according to a procedure analogous to that previously described.\textsuperscript{S7} A 100-mL pressure tube was charged with bromobenzene (10 mmol), 3,3,3-trifluoromethyl acryl acid (20 mmol), palladium acetate (4 mmol), copper oxide (10mmol), and potassium carbonate (40 mmol), then 1-methyl-2-pyrrolidinone (NMP) (1.5 mL) was added, and the mixture was stirred at 130 °C for 15 hours under an nitrogen atmosphere. After cooling, the reaction mixture was diluted with ethyl acetate, filtered through celite and the filtrate was washed with water. The aqueous layer was extracted with ethyl acetate (3 times), the organic layers were washed with water, and brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under vacuum. The residue was purified by column chromatography with dichloromethane. Yield: 68% as brown liquid; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.39-7.31 (m, 5H), 7.10-7.07 (m, 1H), 6.16-6.11 (m, 1H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 137.70 (q, \( J=7.5 \) Hz), 133.52, 130.02, 128.96, 127.55, 115.87 (q, \( J=33.75 \) Hz); \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}): -63.34 (dd, \( J=5.64, 2.82 \) Hz); GC-MS: M\textsuperscript{+}=172.
Preparation of 4-bromo-β,β-difluoro-α-methyl styrene, 4-methoxy-β, β-difluoro-α-methylstyrene and 4-bromo-(2,2,2-trifluoro-1-methylethyl)benzene

The compounds were prepared by referring to literature\textsuperscript{S8} and purified by GPC.

**4-Bromo-β,β-difluoro-α-methyl styrene (17)**
Colorless liquid, yield (46%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.48 and 7.24 (A\(_2\)B\(_2\), \(J=10\) Hz, 4H), 1.95 (t, \(J=5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 153.46, 133.88(t, \(J=4\) Hz), 131.56, 129.13 (t, \(J=4\) Hz), 121.02, 86.92 (dd, \(J=13.75, 23.75\) Hz), 13.09; GC-MS: M\(^+=\)234.

**4-Methoxy-β,β-difluoro-α-methyl styrene (8)**
Colorless liquid, yield (46%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.30 and 6.90 (A\(_2\)B\(_2\), \(J=10\) Hz, 4H), 3.81 (s, 3H), 1.94 (t, \(J=5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 158.63, 153.33(t, \(J=286.25\) Hz), 128.63(t, \(J=4\) Hz), 127.22(t, \(J=24\) Hz), 113.89, 87.00(dd, \(J=15, 21.88\) Hz), 55.30, 13.37; GC-MS: M\(^+=\)184.

**4-Bromo-(2,2,2-trifluoro-1-methylethyl)benzene (18)**
Colorless liquid, yield (17%); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.50 and 7.20 (A\(_2\)B\(_2\), \(J=10\) Hz, 4H), 3.43-3.37 (m, 1H), 1.50(d, \(J=10\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 135.46, 131.83, 130.19, 127.94, 122.23, 43.70, 14.52; GC-MS: M\(^+=\)252.
Preparation of 1-aryl-1-methyl-2,2-dichloro-3,3-difluorocyclopropanes (26, 27, 28)

The compounds were prepared according to a procedure analogous to that previously described.88

2,2-Dichloro-3,3-difluoro-1-methyl-1-phenylcyclopropane (26)
Colorless liquid, yield (98%); 1H NMR (500 MHz, CDCl₃): δ 7.26~7.29 (m, 5H), 1.66 (t, J=2.5Hz, 3H); 13C NMR (125 MHz, CDCl₃): δ 135.33, 133.08, 128.86, 128.72, 108.98 (t, 303 Hz), 64.09, 42.69, 20.75; GC-MS: M⁺=236.

2,2-Dichloro-3,3-difluoro-1-methyl-1-p-methylphenylcyclopropane (27)
Colorless liquid, yield (97%); 1H NMR (500 MHz, CDCl₃): δ 7.21~7.17 (m, 4H), 2.35 (s, 3H), 1.64 (s, 3H); 13C NMR (125 MHz, CDCl₃): δ 137.91, 132.33, 129.42, 128.70, 109.09 (t, 303 Hz), 74.84, 42.49, 21.18, 20.83; GC-MS: M⁺=254.

2,2-Difluoro-3,3-difluoro-1-methyl-1-p-chlorophenylcyclopropane (28)
Colorless liquid, yield (81%); 1H NMR (500 MHz, CDCl₃): δ 7.38 and 7.23 (A₂B₂, J=5 Hz, 4H), 1.65 (s, 3H); 13C NMR (125 MHz, CDCl₃): δ 134.27, 133.70, 130.27, 129.07, 108.77 (t, 303 Hz), 63.81 (t, 13.75 Hz), 42.02, 20.53; GC-MS: [M-Cl⁺]=235.
Theoretical calculations.

Geometry optimizations were performed using the hybrid (Hartree-Fock/DFT) B3LYP functional\textsuperscript{9,10} combined with the 6-31G** basis set.\textsuperscript{11} The RB3LYP functional was used for the closed-shell molecules. Solvent effects are estimated for methanol by using the PCM method. The Gaussian 09 program\textsuperscript{12} was used for all calculations.

DFT calculations also demonstrate that MeOH plays a role of proton source in the protonation of CB\textsuperscript{-} (Fig. S45(b)). In the first step CB\textsuperscript{-} and MeOH form CB–MeOH with a binding energy of 12.0 kcal/mol. The hydroxy group of methanol is anchored to the anionic carbon of the CB\textsuperscript{-} moiety through a hydrogen bond of 1.924 Å. TS\textsuperscript{2} is a transition state, which connects CB–MeOH and 3-MeO\textsuperscript{-}. Computed activation energy of TS\textsuperscript{2} is only 5.5 kcal/mol relative to CB–MeOH, and the relative energy of 3-MeO\textsuperscript{-} is -7.8 kcal/mol. Thus, computed results suggest that the protonation of CB\textsuperscript{-} is likely to occur in MeOH. In TS\textsuperscript{2} the O-H bond and the C-H bond were computed to be 1.229 Å and 1.393 Å, respectively, which is consistent with a transition structure leading to the cleavage of an O-H bond and the formation of a C-H bond. After formation of the C-H bond the two C-C bonds are increased to 1.523 Å (C-C\textsubscript{F}) and 1.523 Å (C-C\textsubscript{Ph}).

References


Fig. S6  $^1$H NMR spectrum of $\alpha$-trifluoromethyl-$p$-methyl styrene (4).
**Fig. S7** $^{13}$C NMR spectrum of $\alpha$-trifluoromethyl-$p$-methyl styrene (4).

**Fig. S8** $^{19}$F NMR spectrum of $\alpha$-trifluoromethyl-$p$-methyl styrene (4).
Fig. S9. $^1$H NMR spectrum of $\alpha$-trifluoromethyl-$p$-chloro styrene (13).
**Fig. S10.** $^{13}$C NMR spectrum of $\alpha$-trifluoromethyl-$p$-chloro styrene (13).

**Fig. S11.** $^{19}$F NMR spectrum of $\alpha$-trifluoromethyl-$p$-chloro styrene (13).
Fig. S12. $^1$H NMR spectrum of $\alpha$-trifluoromethyl-$p$-fluoro styrene (10).

Fig. S13. $^{13}$C NMR spectrum of $\alpha$-trifluoromethyl-$p$-fluoro styrene (10).
Fig. S14. ¹H NMR spectrum of α-trifluoromethyl-\(p\)-bromo styrene (16).

Fig. S15. ¹³C NMR spectrum of α-trifluoromethyl-\(p\)-bromo styrene (16).
Fig. S16. $^{19}$F NMR spectrum of $\alpha$-trifluoromethyl-$p$-bromo styrene (16).

Fig. S17. $^1$H NMR spectrum of $\alpha$-trifluoromethyl-$p$-methoxy styrene (7).
**Fig. S18.** $^{13}$C NMR spectrum of $\alpha$-trifluoromethyl-$p$-methoxy styrene (7).

**Fig. S19.** $^{19}$F NMR spectrum of $\alpha$-trifluoromethyl-$p$-methoxy styrene (7).
Fig. S20. $^1$H NMR spectrum of $\alpha$-difluoromethyl styrene (19).
Fig. S21. $^{13}$C NMR spectrum of $\alpha$-difluoromethyl styrene (19).
Fig. S22. $^{19}$F NMR spectrum of $\alpha$-difluoromethy styrene (19).
Fig. S23. $^1$H NMR spectrum of β, β-difluoro-α-methyl styrene (2).
Fig. S24. $^{13}$C NMR spectrum of $\beta, \beta$-difluoro-$\alpha$-methyl styrene (2).
Fig. S25. $^{19}$F NMR spectrum of $\beta, \beta$-difluoro-$\alpha$-methyl styrene (2).

Fig. S26. $^1$H NMR spectrum of 1-(1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (5).
Fig. S27. $^{13}$C NMR spectrum of 1-(1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (5).
Fig. S28. $^{13}$C NMR spectrum of 1-(1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (5).

Fig. S29. $^1$H NMR spectrum of 1,1-difluoro-2-(4'-chlorophenyl)propene (14).
Fig. S30. $^{13}$C NMR spectrum of 1,1-difluoro-2-(4'-chlorophenyl)propene (14).
Fig. S31. $^{19}$F NMR spectrum of 1,1-difluoro-2-(4'-chlorophenyl)propene (14).

Fig. S32. $^1$H NMR spectrum of 4-fluoro-β,β-difluoro-α-methyl styrene (11).
Fig. S33. $^{13}$C NMR spectrum of 4-fluoro-β,β-difluoro-α-methyl styrene (11).

Fig. S34. $^1$H NMR spectrum of 4-bromo-β,β-difluoro-α-methyl styrene (17).
Fig. S35. $^{13}$C NMR spectrum of 4-bromo-β,β-difluoro-α-methyl styrene (17).

Fig. S36. $^1$H NMR spectrum of 4-methoxy-β,β-difluoro-α-methyl styrene (8).
Fig. S37. $^{13}$C NMR spectrum of 4-methoxy-β,β-difluoro-α-methyl styrene (8).

Fig. S38. $^1$H NMR spectrum of 4-methyl-(2,2,2-trifluoro-1-methylethyl)benzene (6).
137.82, 133.53, 128.37, 129.31

44.18, 43.96, 43.75, 43.53

21.06, 14.66

Solvent

TMS
Fig. S39. $^{13}\text{C}$ NMR spectrum of 4-methyl-(2,2,2-trifluoro-1-methylethyl)benzene (6).
S40. $^{19}$F NMR spectrum of 4-methyl-(2,2,2-trifluoro-1-methylethyl)benzene (6).

Fig. S41. $^1$H NMR spectrum of 4-chloro-(2,2,2-trifluoro-1-methylethyl)benzene (15).
Fig. S42. $^{13}$C NMR spectrum of 4-chloro-(2,2,2-trifluoro-1-methylethyl)benzene (15).
Fig. S43. $^{19}$F NMR spectrum of 4-chloro-(2,2,2-trifluoro-1-methylehtyl)benzene (15).

Fig. S44. $^1$H NMR spectrum of 4-fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene (12).
**Fig. S45.** $^{13}$C NMR spectrum of 4-fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene (12).

**Fig. S46.** $^{19}$F NMR spectrum of 4-fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene (12).
**Fig. S47.** $^1$H NMR spectrum of 4-bromo-(2,2,2-trifluoro-1-methylethyl)benzene (18).

**Fig. S48.** $^{13}$C NMR spectrum of 4-bromo-(2,2,2-trifluoro-1-methylethyl)benzene (18).
Fig. S49. $^1$H NMR spectrum of 4-methoxy-(2,2,2-trifluoro-1-methylethyl)benzene (9).

Fig. S50. $^{13}$C NMR spectrum of 4-methoxy-(2,2,2-trifluoro-1-methylethyl)benzene (9).
Fig. S51. $^1$H NMR spectrum of 2,2-difluoro-1-methylehtylbenzene (22).
Chemical Shift (ppm)

-138.69, 128.24, 127.51, 120.22, 118.28, 116.34

Solvent

TMS

44.14, 43.98, 43.81, 13.77, 13.73

Chemical Shift (ppm)
Fig. S52. $^{13}$C NMR spectrum of 2,2-difluoro-1-methylehtylbenzene (22).

Fig. S53. $^{19}$F NMR spectrum of 2,2-difluoro-1-methylehtylbenzene (22).
Fig. S54. $^1$H NMR spectrum of $\beta$-fluoro-$\alpha$-methyl styrenes (E/Z) (20/21).
Fig. S55. $^{13}$C NMR spectrum of $\beta$-fluoro-$\alpha$-methyl styrenes ($E/Z$) (20/21).
Fig. S56. $^{19}$F NMR spectrum of $\beta$-fluoro-$\alpha$-methyl styrenes ($E/Z$) (20/21).
Fig. S57. $^1$H NMR spectrum of $\beta$-trifluoromethyl styrene (24).
\[ ^{13}C \text{ NMR} \]

Chemical Shift (ppm)

Solvent

H\(_2\)O

137.75
137.70
130.02
128.96
116.35
115.59
115.59
115.86
116.13
127.55
116.35
Fig. S58. $^{13}$C NMR spectrum of $\beta$-trifluoromethyl styrene (24).
Fig. S59. $^{19}$F NMR spectrum of $\beta$-trifluoromethyl styrene (24).
TMS

Solvent

Chemical Shift (ppm)

4.90

7.33

7.26

7.29

3.00

1.54

1.67

1.66

H₂O

TMS
Fig. S60. $^1$H NMR spectrum of 26.

Fig. S61. $^{13}$C NMR spectrum of 26.
Fig. S62. $^1$H NMR spectrum of 27.

Fig. S63. $^{13}$C NMR spectrum of 27.
Fig. S64. $^1$H NMR spectrum of 28.

Fig. S65. $^{13}$C NMR spectrum of 28.
Fig. S66. Optimized structures and computed energy diagrams for (a) β-fluorine elimination and (b) protonation in carbanion intermediate (CB'). Units are in kcal/mol and angstrom.