Supporting Information

Boron-trihalide-promoted Regioselective Ring-opening Reactions of \(\text{gem}\)-Difluorocyclopropyl Ketones

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General Information
Reagents and solvents were purchased from commercial sources and used as received. Tetramethylsilane or residual proton signals were used as internal standards for $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra. Data for $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

General Procedure for the Synthesis of Aryl vinyl ketones:
Into the solution of paraformaldehyde (0.3 mol) and TAMA ($N$-methylanilinium trifluoroacetate, 50 mmol) in THF (50 mL) was added aryl methyl ketone (50 mmol) under N$_2$ atmosphere. The mixture was refluxed for 10 h. After being cooled to room temperature, the solvent was removed by concentration. The residue was dissolved with ethyl acetate. Hydrochloric acid solution was added to neutralize the mixture. The organic solution was separated and dried over Na$_2$SO$_4$. The solvent was removed by concentration, and the residue was subjected to silica-gel column chromatography with hexane/ethyl acetate to afford the aryl vinyl ketones product.

1-phenylprop-2-en-1-one$^1$

![5a](image)

Colorless liquid (55%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.95 (d, $J = 7.7$ Hz, 2 H), 7.58 (t, $J = 7.4$ Hz, 1 H), 7.48 (t, $J = 7.7$ Hz, 2 H), 7.16 (dd, $J = 17.1$, 10.7 Hz, 1 H), 6.44 (d, $J = 17.1$ Hz, 1 H), 5.94 (d, $J = 10.6$ Hz, 1 H) ppm.

1-(p-tolyl)prop-2-en-1-one$^1$

![5b](image)

Colorless liquid (42%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.87 (d, $J = 8.3$ Hz, 2 H), 7.28 (d, $J = 8.3$ Hz, 2 H), 7.17 (dd, $J = 17.1$, 10.5 Hz, 1 H), 6.43 (dd, $J = 17.1$, 1.7 Hz, 1 H), 5.90 (dd, $J = 10.5$, 1.7 Hz, 1 H).
Hz, 1 H), 2.42 (s, 3 H) ppm.

1-(4-methoxyphenyl)prop-2-en-1-one

Colorless liquid (40%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.97 (d, $J = 8.9$ Hz, 2 H), 7.18 (dd, $J = 17.1$, 10.5 Hz, 1 H), 6.96 (d, $J = 8.9$ Hz, 2 H), 6.43 (dd, $J = 17.1$, 1.5 Hz, 1 H), 5.88 (dd, $J = 10.5$ Hz, $J = 1.5$ Hz, 1 H), 3.88 (s, 3 H) ppm.

1-(3-methoxyphenyl)prop-2-en-1-one

Colorless liquid (71%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.56-7.47 (m, 2 H), 7.39 (t, $J = 7.8$ Hz, 1 H), 7.19-7.10 (m, 2 H), 6.44 (d, $J = 17.0$ Hz, 1 H), 5.93 (d, $J = 10.5$ Hz, 1 H), 3.87 (s, 3 H) ppm.

1-(4-fluorophenyl)prop-2-en-1-one

Colorless liquid (37%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.99 (m, 2 H), 7.14 (m, 3 H), 6.44 (dd, $J = 17.0$ Hz, $J = 1.5$ Hz, 1 H), 5.94 (dd, $J = 10.6$, 1.5 Hz, 1 H) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$): δ = -105.55 - -105.64 (m, 1 F) ppm.

1-(4-chlorophenyl)prop-2-en-1-one
Colorless liquid (72%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J = 8.4$ Hz, 2 H), 7.46 (d, $J = 8.4$ Hz, 2 H), 7.12 (dd, $J = 17.1$, 10.5 Hz, 1 H), 6.45 (dd, $J = 17.1$, 1.1 Hz, 1 H), 5.96 (dd, $J = 10.5$ Hz, $J = 1.1$ Hz, 1 H) ppm.

1-(4-bromophenyl)prop-2-en-1-one$^1$

Colorless liquid (59%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.82$ (d, $J = 8.5$ Hz, 2 H), 7.63 (d, $J = 8.5$ Hz, 2 H), 7.11 (dd, $J = 17.2$, 10.5 Hz, 1 H), 6.45 (d, $J = 17.2$ Hz, 1 H), 5.96 (d, $J = 10.5$ Hz, 1 H) ppm.

1-(3-chlorophenyl)prop-2-en-1-one$^2$

Colorless liquid (32%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.92$ (t, $J = 1.4$ Hz, 1 H), 7.82 (d, $J = 7.9$ Hz, 1 H), 7.55 (d, $J = 7.9$ Hz, 1 H), 7.43 (t, $J = 7.9$ Hz, 1 H), 7.11 (dd, $J = 17.3$, 10.6 Hz, 1 H), 6.46 (dd, $J = 17.2$, 1.7 Hz, 1 H), 5.98 (dd, $J = 10.6$, 1.7 Hz, 1 H) ppm.

1-(3-bromophenyl)prop-2-en-1-one$^1$
Colorless liquid (51%). $^1$H NMR (300 MHz, CDCl₃): $\delta$ 8.07 (t, $J = 1.8$ Hz, 1 H), 7.86 (dt, $J = 7.9$, 1.2 Hz, 1 H), 7.73-7.69 (m, 1 H), 7.37 (t, $J = 7.9$ Hz, 1 H), 7.11 (dd, $J = 17.3$, 10.5 Hz, 1 H), 6.46 (dd, $J = 17.3$, 1.5 Hz, 1 H), 5.98 (dd, $J = 10.5$, 1.5 Hz, 1 H) ppm.

1-(4-nitrophenyl)prop-2-en-1-one

![Structure](5j)

White solid (27%) $^1$H NMR (300 MHz, CDCl₃): $\delta$ 8.34 (d, $J = 8.7$ Hz, 2 H), 8.08 (d, $J = 8.7$ Hz, 2 H), 7.13 (dd, $J = 17.2$, 10.5 Hz, 1 H), 6.49 (d, $J = 17.2$ Hz, 1 H), 6.08 (d, $J = 10.5$ Hz, 1 H) ppm.

1-(naphthalen-2-yl)prop-2-en-1-one

![Structure](5k)

White solid (45%) $^1$H NMR (300 MHz, CDCl₃): $\delta$ 8.47 (s, 1 H), 8.05 (dd, $J = 8.6$, 1.5 Hz, 1 H), 7.99-7.88 (m, 3 H), 7.65-7.54 (m, 2 H), 7.33 (dd, $J = 17.2$, 10.5 Hz, 1 H), 6.51 (dd, $J = 17.2$, 1.5 Hz, 1 H), 5.99 (dd, $J = 10.5$, 1.5 Hz, 1 H) ppm.

1-cyclohexylprop-2-en-1-one

![Structure](5l)

Colorless liquid (16%) $^1$H NMR (400 MHz, CDCl₃) $\delta$ = 6.41 (dd, $J = 17.5$, 10.5 Hz, 1 H), 6.24 (dd, $J = 17.5$, 1.4 Hz, 1 H), 5.76 – 5.71 (m, 1 H), 2.60 (ddd, $J = 11.3$ Hz, $J = 7.3$ Hz, 1 H), 1.86 – 1.74 (m, 4 H), 1.68 (d, $J = 10.5$ Hz, 1 H), 1.42 – 1.17 (m, 5 H) ppm.

**General Procedure for the Synthesis of gem-Difluorocyclopropyl Ketones:**

Into the mixture of aryl vinyl ketones (20 mmol) and anhydrous sodium fluoride (2 mmol) was added m-xylene (1 mL) under N₂. The mixture was heated to 110°C and stirred for 5 min. TFDA
(FSO₂CF₂CO₂SiMe₃, 40 mmol) was added dropwise in 30 min. Then the mixture was stirred for further 30 min at 110°C. When the substrate was completely conversed detected by TLC, the mixture was cooled to room temperature. After removal of the solvent under reduced pressure, the residue was subjected to column chromatography to afford the pure product (Hexane : Et₂O = 20 : 1).

(2,2-difluorocyclopropyl)(phenyl)methanone⁶

![Image of molecule 1a]

Colorless liquid (77%). ¹H NMR (300 MHz, CDCl₃): δ 8.01 (d, J = 7.3 Hz, 2 H), 7.63 (t, J = 7.3 Hz, 1 H), 7.52 (t, J = 7.3 Hz, 2 H), 3.39 (m, 1 H), 2.43 (m, 1 H), 1.81 (m, 1 H) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ: -124.16 (dtd, J = 149.0, 13.0, 6.0 Hz, 1 F), -140.04 (ddd, J = 149.0, 12.2, 4.8 Hz, 1 F) ppm;

(2,2-difluorocyclopropyl)(p-tolyl)methanone⁷

![Image of molecule 1b]

White solid (38%) ¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H), 3.37 (m, 1 H), 2.41 (m, 1 H), 2.44 (s, 3 H), 1.78 (m, 1 H) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ = -124.18 (dtd, J = 149.0, 12.4, 5.9 Hz 1 F), -140.13 (ddd, J = 149.0, 12.1, 4.7 Hz, 1 F) ppm

(2,2-difluorocyclopropyl)(4-methoxyphenyl)methanone⁷

![Image of molecule 1c]

Slightly yellow liquid (41%) ¹H NMR (300 MHz, CDCl₃): δ 8.00 (d, J = 8.7 Hz, 2 H), 6.98 (d, J = 8.7 Hz, 2 H), 3.89 (s, 3 H), 3.34 (m, 1 H), 2.40 (m, 1 H), 1.77 (m, 1 H) ppm; ¹⁹F NMR (282 MHz,
CDCl₃): δ = -124.39 (dtd, J = 149.0, 13.0, 5.8 Hz, 1 F), -140.35 (ddd, J = 149.0, 12.2, 4.6 Hz, 1 F) ppm

(2,2-difluorocyclopropyl)(3-methoxyphenyl)methanone⁷

Colorless liquid (71%) ¹H NMR (300 MHz, CDCl₃): δ 7.60 (d, J = 7.9 Hz, 1 H), 7.52 (s, 1 H), 7.43 (t, J = 7.9 Hz, 1 H), 7.17 (dd, J = 7.9, 2.6 Hz, 1 H), 3.87 (s, 3 H), 3.38 (m, 1 H), 2.43 (m, 1 H), 1.81 (m, 1 H) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ = -124.73 (dm, J = 148.0 Hz, 1 F), -140.65 (dm, J = 148.0 Hz, 1 F) ppm

(2,2-difluorocyclopropyl)(4-fluorophenyl)methanone⁷

Colorless liquid (28%) ¹H NMR (300 MHz, CDCl₃): δ 8.08-8.02 (m, 2 H), 7.23-7.16 (m, 2 H), 3.35 (m, 1 H), 2.43 (m, 1 H), 1.82 (m, 1 H) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ = -103.89 (m, 1 F), -124.28 (dtd, J = 148.5, 12.7, 5.9 Hz, 1 F), -140.07 (ddm, J = 148.5, 12.0 Hz, 1 F) ppm

(4-chlorophenyl)(2,2-difluorocyclopropyl)methanone⁶

Slightly yellow solid (22%) ¹H NMR (300 MHz, CDCl₃): δ 7.95 (d, J = 8.4 Hz, 2 H), 7.49 (d, J = 8.4 Hz, 2 H), 3.34(m, 1 H), 2.43 (m, 1 H), 1.82 (m, 1 H) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ -124.07 (dtd, J = 149.0, 12.3, 5.7 Hz, 1 F), -139.90 (ddd, J = 149.0, 12.2, 4.9 Hz, 1 F) ppm

(4-bromophenyl)(2,2-difluorocyclopropyl)methanone
White solid (m.p. 67-69°C, 32%) $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.8$ Hz, 2 H), 7.66 (d, $J = 8.8$ Hz, 2 H), 3.35 (m, 1 H), 2.43 (m, 1 H), 1.84 (m, 1 H) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -124.56 (dt, $J = 148.3$, 12.3, 5.9 Hz, 1 F), -140.36 (ddd, $J = 148.3$, 12.1, 4.7 Hz, 1 F) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 189.5, 135.7, 132.3, 129.9, 129.1, 111.5 (t, $J = 287.6$ Hz), 29.7 (dd, $J = 11.7$, 9.6 Hz), 15.8 (dd, $J = 11.0$, 8.8 Hz) ppm; EI-MS (m/z, %): 183 (100), 185 (92.6), 76 (54.0), 155 (50.2), 157 (49.6), 75 (47.3), 50 (44.1), 133 (39.2). IR (KBr): 3117, 3095, 3075, 3060, 1671, 1582, 1453, 1400, 1381, 1319, 1247, 1180, 1008, 846, 703, 658, 515, 479 cm$^{-1}$. HRMS for C$_{10}$H$_7$OF$_2$Br: 259.9648; Found: 259.9649.

(3-chlorophenyl)(2,2-difluorocyclopropyl)methanone

White solid (70%) $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.97 (t, $J = 1.8$ Hz, 1 H), 7.89 (dt, $J = 7.9$, 1.8 Hz, 1 H), 7.60 (dt, $J = 7.9$, 1.8 Hz, 1 H), 7.47 (t, $J = 7.9$ Hz, 1 H), 3.36 (m, 1 H), 2.45 (m, 1 H), 1.84 (m, 1 H) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -124.52$ (dm, $J = 148.4$ Hz, 1 F), -140.36 (dm, $J = 148.1$ Hz, 1 F) ppm.

(3-bromophenyl)(2,2-difluorocyclopropyl)methanone

White solid (m.p. 32-33°C, 62%) $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.12 (s, 1 H), 7.93 (d, $J = 7.9$ Hz, 1 H), 7.75 (d, $J = 7.9$ Hz, 1 H), 7.41 (t, $J = 7.9$ Hz, 1 H), 3.37 (m, 1 H), 2.44 (m, 1 H), 1.85 (m, 1 H) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -124.48$ (dt, $J = 148.5$, 12.2, 6.0 Hz, 1 F), -140.28 (ddd, $J = 148.5$, 12.1, 4.8 Hz, 1 F) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.3, 138.7, 136.6,
131.4, 130.4, 127.0, 123.2, 111.5 (dd, \( J = 288.4, 286.9 \) Hz), 29.8 (dd, \( J = 11.7, 10.3 \) Hz), 15.9 (dd, \( J = 11.0, 8.8 \) Hz) ppm; EI-MS (m/z, %): 183 (100), 185 (99), 155 (48.6), 157 (47.7), 133 (28.6), 76 (28.0), 181 (26.6), 75 (22.9). IR (KBr): 3116, 3062, 3026, 1669, 1566, 1459, 1374, 1316, 1247, 1203, 1055, 1008, 929, 919, 908, 817, 773, 704, 679, 667, 478 cm\(^{-1}\). HRMS for C\(_{10}\)H\(_7\)OF\(_2\)Br: 259.9648; Found: 259.9651.

(2,2-difluorocyclopropyl)(4-nitrophenyl)methanone

\[
\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{image}
\caption{1j}
\end{figure}
\]

White solid (m.p. 62-64°C, 44%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 8.38 (d, \( J = 8.5 \) Hz, 2 H), 8.18 (d, \( J = 8.5 \) Hz, 2 H), 3.44 (m, 1 H), 2.50 (m, 1 H), 1.94 (m, 1 H) ppm; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \( \delta \) = -123.66 (dt, \( J = 148.1, 12.2, 6.0 \) Hz, 1 F), -139.32 (ddd, \( J = 148.1, 12.0, 4.7 \) Hz, 1 F) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 189.3, 150.7, 141.3, 129.4, 124.1, 111.4 (t, \( J = 288.5 \) Hz), 30.2 (dd, \( J = 11.8, 10.3 \) Hz), 16.3 (dd, \( J = 11.4, 9.1 \) Hz) ppm; EI-MS (m/z, %): 150 (100), 104 (58.4), 76 (54.2), 133 (41.3), 50 (37.8), 51 (26.3), 75 (25.6), 77 (25.5). IR (KBr): 3113, 3087, 3052, 1677, 1607, 1451, 1413, 1321, 1298, 1208, 1052, 963, 923, 856, 729, 703, 685, 479 cm\(^{-1}\). HRMS for C\(_{10}\)H\(_7\)NO\(_3\)F\(_2\): 227.0394; Found: 227.0397.

(2,2-difluorocyclopropyl)(naphthalen-2-yl)methanone

\[
\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{image}
\caption{1k}
\end{figure}
\]

White solid (m.p. 91-93 °C, 57%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 8.52 (s, 1 H), 8.07-7.98 (m, 2 H), 7.91 (t, \( J = 8.8 \) Hz, 2 H), 7.65-7.55 (m, 2 H), 3.56 (m, 1 H), 2.49 (m, 1 H), 1.86 (m, 1 H) ppm; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \( \delta \) = -124.51 (dt, \( J = 148.1, 12.5, 5.9 \) Hz, 1 F), -140.43 (ddd, \( J = 148.1, 12.3, 5.1 \) Hz, 1 F) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 190.4, 135.9, 134.5, 132.5, 130.5, 129.7, 128.9, 128.8, 127.9, 127.1, 123.8, 111.7 (dd, \( J = 288.1, 286.6 \) Hz), 29.84 (dd, \( J = 11.8, 9.6 \) Hz), 15.76 (dd, \( J = 11.0, 9.0 \) Hz) ppm; EI-MS (m/z, %): 127 (100), 155 (75.2), 232 (46.3), 128
Colorless liquid (21%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 2.79$ (ddd, $J = 14.0$, 10.3, 8.0 Hz, 1H), 2.47 (tt, $J = 11.1$, 3.4 Hz, 1H), 2.18 (m, 1H), 2.02 – 1.95 (m, 1H), 1.87 (dd, $J = 10.0$, 4.4, 1H), 1.83 – 1.75 (m, 2H), 1.73 – 1.57 (m, 2H), 1.45 – 1.16 (m, 5H), $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -124.7$ – -125.2 (m, 1 F), -139.9 – -140.4 (m, 1 F) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 203.36$, 111.38 (dd, $J = 288.0$, 285.3 Hz), 51.65, 31.02 (dd, $J = 12.0$, 9.0 Hz), 27.85, 27.52, 25.68, 25.50, 25.22, 15.54 (dd, $J = 11.1$, 9.0 Hz ). IR (KBr): 2933, 2857, 1709, 1451, 1374, 1317, 1241, 1044, 1022, 1005, 955, 911, 893, 669; GC-MS : 108.1; HRMS: 108.1014; Found:108.1013.

**General procedure for the ring-opening of gem-difluorocyclopropyl ketones promoted by boron trifluoride:**

Into the solution of gem-difluorocyclopropyl ketone (0.2 mmol) in CHCl$_3$ (1 mL) was added BF$_3$•Et$_2$O (0.4 mmol). The mixture was stirred at 60 °C until the reaction was complete determined by $^{19}$F NMR. After being cooled to room temperature, saturated NaHCO$_3$ solution was added to quench the reaction. After extraction with CH$_2$Cl$_2$ (10 mL x 3), the organic solution was dried over Na$_2$SO$_4$. The solvent was removed by concentration, and the residue was subjected to column chromatography to afford the $\beta$-trifluoromethyl ketones.

4,4,4-trifluoro-1-phenylbutan-1-one

White solid (95%) $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.98$ (d, $J = 7.3$ Hz, 2 H), 7.61 (t, $J = 7.3$ Hz, 1 H), 7.49 (t, $J = 7.3$ Hz, 2 H), 3.27 (t, $J = 7.7$ Hz, 2 H), 2.68-2.52 (m, 2 H) ppm; $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -66.39$ (t, $J = 10.3$ Hz, 3 F) ppm.
4,4,4-Trifluoro-1-(p-tolyl)butan-1-one.

\[
\begin{align*}
\text{O} & \quad \text{CF}_3 \\
\text{2b}
\end{align*}
\]

White solid (m.p. 83-84°C, 85%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.87 (d, \(J = 8.1\) Hz, 2 H), 7.28 (d, \(J = 8.1\) Hz, 2 H), 3.23 (t, \(J = 7.5\) Hz, 2 H), 2.66-2.50 (m, 2 H), 2.42 (s, 3 H) ppm.; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): δ -66.21 (t, \(J = 10.3\) Hz, 3 F) ppm.; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): δ 195.9, 144.5, 133.8, 129.5, 128.1, 127.2 (q, \(J = 275.9\) Hz), 31.05 (t, \(J = 2.9\) Hz), 28.42 (q, \(J = 29.3\) Hz), 21.63 ppm.; EI-MS (m/z, %): 119 (100), 91 (37.2), 65 (11.6), 120 (9.03), 89 (7.71), 77 (6.04), 216 (5.99), 90 (5.20).; IR(KBr): 3115, 2994, 1680, 1609, 1439, 1337, 1309, 1259, 1227, 1147, 1098, 983, 976, 824, 781, 641, 570, 459 cm\(^{-1}\).; HRMS for C\(_{11}\)H\(_{11}\)OF\(_3\): 216.0762; Found: 216.0760.

4,4,4-Trifluoro-1-(4-methoxyphenyl)butan-1-one.

\[
\begin{align*}
\text{O} & \quad \text{CF}_3 \\
\text{MeO} & \\
\text{2c}
\end{align*}
\]

White solid (m.p. 65-67°C, 76%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.95 (d, \(J = 8.8\) Hz, 2 H), 6.95 (d, \(J = 8.8\) Hz, 2 H), 3.88 (s, 3 H), 3.21 (t, \(J = 7.6\) Hz, 2 H), 2.66-2.50 (m, 2 H) ppm; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): δ -66.80 (t, \(J = 11.9\) Hz, 3 F); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): δ 194.8, 163.9, 130.3, 129.3, 127.3 (q, \(J = 275.9\) Hz), 113.9, 55.5, 30.78 (d, \(J = 2.9\) Hz), 28.47 (q, \(J = 30\) Hz) ppm.

4,4,4-Trifluoro-1-(3-methoxyphenyl)butan-1-one.

\[
\begin{align*}
\text{O} & \quad \text{CF}_3 \\
\text{OMe} & \\
\text{2d}
\end{align*}
\]

Colorless liquid (84%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ 7.54 (d, \(J = 7.8\) Hz, 1 H), 7.48 (s, 1 H), 7.39 (t, \(J = 7.8\) Hz, 1 H), 7.14 (d, \(J = 7.8\) Hz, 1 H), 3.86 (s, 3 H), 3.24 (t, \(J = 7.5\) Hz, 2 H), 2.66-2.50 (m, 2 H) ppm; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): δ -66.14 (t, \(J = 10.3\) Hz, 3 F) ppm; \(^{13}\)C
NMR (CDCl3, 100 MHz): δ 196.2, 160.0, 137.5, 129.8, 127.2 (q, J = 275.9 Hz), 120.6, 120.0, 112.4, 55.45, 31.31 (q, J = 2.2 Hz), 28.40 (q, J = 30.1 Hz) ppm; EI-MS (m/z, %): 135 (100), 232 (36.33), 107 (28.69), 77 (17.48), 92 (11.55), 136 (9.33), 64 (4.73), 233 (4.61); IR (KBr): 3078, 3008, 2963, 2840, 1682, 1600, 1585, 1487, 1447, 1388, 1365, 1259, 1146, 1099, 1070, 977, 874, 778, 686, 619, 556 cm⁻¹; HRMS for C11H11O2F3: 232.0711; Found: 232.0712.

4,4,4-Trifluoro-1-(4-fluorophenyl)butan-1-one.

Slightly yellow liquid (95%) ¹H NMR (300 MHz, CDCl₃): δ 8.02 (dd, J = 8.8 Hz, J = 5.2 Hz, 2 H), 7.17 (t, J = 8.8 Hz, 2 H), 3.25 (t, J = 7.3 Hz, 2H), 2.68-2.52 (m, 2 H) ppm.; ¹⁹F NMR (282 MHz, CDCl₃): δ -66.85 (t, J = 9.9 Hz, 3 F), -104.57 (m, 1 F) ppm.; ¹³C NMR (CDCl₃, 100 MHz): δ 194.7, 166.1 (d, J = 255.3 Hz), 132.6 (d, J = 3 Hz), 130.7 (d, J = 9.5 Hz), 127.1 (q, J = 275.9 Hz), 115.9 (d, J = 22Hz), 31.14 (d, J = 2.2 Hz), 28.35 (q, J = 30.1 Hz) ppm.; EI-MS (m/z, %): 123 (100), 95 (37.0), 75 (11.7), 124 (9.68), 220 (4.75), 69 (4.07), 201 (3.85), 96 (3.18); IR (KBr): 3077, 2964, 2924, 1693, 1600, 1511, 1447, 1413, 1333, 1262, 1226, 1154, 1101, 980, 843, 642, 590, 569, 492, 418 cm⁻¹; HRMS for C₁₀H₈OF₄: 220.0511; Found: 220.0510.

1-(4-Chlorophenyl)-4,4,4-trifluorobutan-1-one.

White solid (m.p. 68-70°C, 75%) ¹H NMR (300 MHz, CDCl₃): δ 7.92 (d, J = 8.5 Hz, 2 H), 7.47 (d, J = 8.5 Hz, 2 H), 3.23 (t, J = 7.5 Hz, 2 H), 2.64-2.55 (m, 2 H) ppm; ¹⁹F NMR (282 MHz, CDCl₃): δ -66.19 (t, J = 10.3 Hz, 3 F) ppm; ¹³C NMR (CDCl₃, 100MHz): δ 195.1, 140.2, 134.5, 129.4, 129.1, 127.1 (q, J = 275.8 Hz), 31.22 (d, J = 2.2 Hz), 28.31 (q, J = 30.0 Hz) ppm; EI (m/z, %): 139 (100), 141 (35.1), 111 (31.7), 75 (14.7), 113 (10.5), 140 (9.39), 236 (6.36), 76 (4.40); IR(KBr): 1686, 1651, 1593, 1489, 1441, 1403, 1335, 1260, 1144, 1096, 979, 840, 827, 782, 629, 526 cm⁻¹; HRMS for C₁₀H₈OF₃Cl: 236.0216; Found: 236.0218.
1-(4-Bromophenyl)-4,4,4-trifluorobutan-1-one.

White solid (m.p. 82-84°C, 93%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.83 (d, \(J = 8.7\) Hz, 2 H), 7.63 (d, \(J = 8.7\) Hz, 2 H), 3.22 (t, \(J = 7.5\) Hz, 2H), 2.67-2.51 (m, 2 H) ppm; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -66.21 (t, \(J = 10.3\) Hz, 3 F) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 195.3, 134.9, 132.1, 129.5, 128.9, 127.1 (q, \(J = 275.8\) Hz), 31.20 (d, \(J = 2.9\) Hz), 28.29 (q, \(J = 29.3\) Hz) ppm; EI-MS (m/z, %): 183 (100), 185 (82.34), 157 (32.36), 155 (31.20), 76 (26.45), 75 (21.29), 50 (17.32), 193 (16.11); IR (KBr): 2966.3, 2922.8, 1686.4, 1588.6, 1560.8, 1388.4, 1259.3, 1010.9, 780.7, 626.4 cm\(^{-1}\). HRMS for C\(_{10}\)H\(_8\)OF\(_3\)Br: 279.9711; Found: 279.9715.

1-(3-Chlorophenyl)-4,4,4-trifluorobutan-1-one.

Slightly yellow liquid (70%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.94 (t, \(J = 1.8\) Hz, 1 H), 7.85 (dt, \(J = 7.9\) Hz, \(J = 1.8\)Hz, 1 H), 7.58 (dm, \(J = 7.9\) Hz, 1 H), 7.44 (t, \(J = 7.9\) Hz, 1 H), 3.25 (t, \(J = 7.6\) Hz, 2 H), 2.68-2.52 (m, 2 H) ppm; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -66.82 (t, \(J = 9.9\) Hz, 3 F) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 195.1, 137.6, 135.2, 133.6, 130.1, 128.2, 127.0 (q, \(J = 275.8\) Hz), 126.1, 31.38 (q, \(J = 2.9\) Hz), 28.26 (q, \(J = 30.1\) Hz) ppm; EI-MS (m/z, %): 139 (100), 141 (35.4), 111 (35.0), 75 (13.8), 113 (11.7), 236 (9.94), 140 (9.37), 76 (4.71); IR (KBr): 3071, 2963, 2923, 1573, 1473, 1451, 1422, 1389, 1322, 1272, 1224, 1145, 1001, 999, 978, 977, 903, 805, 776, 720, 681, 660, 620, 570 cm\(^{-1}\). HRMS for C\(_{10}\)H\(_8\)OF\(_3\)Cl: 236.0216; Found: 236.0215.

1-(3-Bromophenyl)-4,4,4-trifluorobutan-1-one.\(^{10}\)
Slightly yellow liquid (89%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.09 (s, 1 H), 7.89 (d, \(J = 7.9\) Hz, 1 H), 7.73 (d, \(J = 7.9\) Hz, 1 H), 7.38 (t, \(J = 7.9\) Hz, 1 H), 3.24 (t, \(J = 7.3\) Hz, 2 H), 2.67-2.51 (m, 2 H) ppm; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -66.28 (t, \(J = 10.4\) Hz, 3 F) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) = 195.0, 137.8, 136.5, 131.2, 130.4, 127.0 (q, \(J = 275.9\) Hz), 126.5, 31.36 (q, \(J = 2.9\) Hz), 28.27 (q, \(J = 29.3\) Hz) ppm; EI-MS (m/z, %): 183 (100), 185 (93.62), 76 (41.18), 155 (38.88), 157 (37.76), 75 (33.12), 50 (28.50), 77 (19.49); IR (KBr): 3067.6, 2962.0, 2922.0, 1696.5, 1568.2, 1388.5, 1331.1, 1100.2, 976.4, 774.1, 679.9 cm\(^{-1}\). HRMS for C\(_{10}\)H\(_8\)OF\(_3\)Br: 279.9711; Found: 279.9716.

4,4,4-Trifluoro-1-(4-nitrophenyl)butan-1-one.

White solid (m.p. 69-71°C, 77%) \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.36 (d, \(J = 8.5\) Hz, 2 H), 8.16 (d, \(J = 8.5\) Hz, 2 H), 3.34 (t, \(J = 7.3\) Hz, 2 H), 2.72-2.56 (m, 2 H) ppm.; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) -66.82 (t, \(J = 11.9\) Hz, 3 F); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 194.8, 150.7, 140.4, 129.1, 126.9 (q, \(J = 275.8\) Hz), 124.0, 31.88 (d, \(J = 2.9\) Hz), 28.20 (q, \(J = 30.1\) Hz) ppm.; EI-MS (m/z, %): 150 (100), 104 (23.8), 76 (14.2), 92 (10.8), 77 (8.60), 151 (8.34), 50 (7.03), 75 (6.17); IR (KBr): 3114, 2931, 1691, 1604, 1513, 1444, 1337, 1264, 1225, 1151, 1095, 978, 966, 781, 744, 688, 628, 571, 507 cm\(^{-1}\); HRMS for C\(_{10}\)H\(_8\)N\(_2\)O\(_3\)F\(_3\): 247.0456; Found: 247.0452.

4,4,4-Trifluoro-1-(naphthalen-2-yl)butan-1-one.
White solid (m.p. 92-94°C, 83%) $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.45 (s, 1 H), 8.02-7.95 (m, 2 H), 7.91-7.86 (m, 2 H), 7.64-7.54 (m, 2 H), 3.38 (t, $J = 7.9$ Hz, 2 H), 2.72-2.56 (m, 2 H) ppm. $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -66.66 (t, $J = 10.0$ Hz, 3 F) ppm.; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 196.2, 135.8, 133.5, 132.5, 129.8, 129.6, 128.8, 128.7, 127.9, 127.3 (q, $J = 275.1$ Hz), 127.0, 123.6, 31.28 (d, $J = 2.9$ Hz), 28.50 (q, $J = 29.4$ Hz) ppm; EI-MS (m/z, %): 155 (100), 127 (72.5), 252 (26.6), 126 (16.8), 156 (13.1), 77 (11.1), 128 (8.71), 101 (4.94); IR (KBr): 2964, 1683, 1626, 1436, 1420, 1358, 1323, 1262, 1225, 1138, 979, 918, 869, 748, 643, 563, 485, 461 cm$^{-1}$; HRMS for C$_{14}$H$_{11}$OF$_3$: 252.0762; Found: 252.0768.

1-Cyclohexyl-4,4,4-trifluorobutan-1-one

Slightly yellow liquid (74%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 2.71 – 2.66 (m, 2H), 2.44 – 2.30 (m, 3H), 1.88 – 1.73 (m, 4H), 1.70 – 1.62 (m, 1H), 1.40 – 1.15 (m, 5H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -66.72 (t, $J = 10.9$ Hz, 3F). $^{13}$C NMR (101MHz, CDCl$_3$) $\delta$ = 210.09, 126.97 (q, $J = 275.7$ Hz), 50.68, 32.69 (dd, $J = 5.0, 2.4$ Hz), 28.32, 27.82 (dd, $J = 59.4, 29.7$ Hz), 25.63, 25.44. IR (KBr): 2934, 2858, 1714, 1450, 1374, 1326, 1257, 1221, 1141, 997, 969, 624; GC-Ms: 208.1. HRMS: 208.1076; Found: 208.1075.

**General Procedure for the ring-opening of gem-difluorocyclopropyl ketones promoted by boron trichloride:**

Into the solution of gem-difluorocyclopropyl ketone (0.2 mmol) in CHCl$_3$ (1.0 mL) was added BCl$_3$ (0.4 mL, 1 M in CH$_2$Cl$_2$) slowly at room temperature. The mixture was stirred at the same temperature until the reaction was complete determined by $^{19}$F NMR. Saturated NaHCO$_3$ solution was added to quench the reaction. After extraction with CH$_2$Cl$_2$ (10 mL x 3), the organic solution was dried over Na$_2$SO$_4$. The solvent was removed by concentration, and the residue was subjected to column chromatography to afford the β-chlorodifluoromethyl ketones.

4-Chloro-4,4-difluoro-1-phenylbutan-1-one$^{11}$
Colorless liquid (63%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.00 – 7.96 (m, 2H), 7.63 – 7.58 (m, 1H), 7.51 – 7.46 (m, 2H), 3.34 – 3.29 (m, 2H), 2.86 – 2.75 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -51.05 (t, $J$ = 12.9 Hz, 2F).

4-Chloro-4,4-difluoro-1-(p-tolyl)butan-1-one

Yellow liquid (82%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.01 (dd, $J$ = 8.2, 5.6 Hz, 2H), 7.16 (t, $J$ = 8.2, 2H), 3.32 – 3.24 (m, 2H), 2.86-2.72 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -51.12 (t, $J$ = 12.8 Hz, 2F), -104.20 – -104.30 (m, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 194.69, 165.97 (d, $J$ = 255.7 Hz), 132.53 (d, $J$ = 3.1Hz), 130.67 (d, $J$ = 9.4 Hz), 129.55 (t, $J$ = 291.1 Hz), 115.89 (d, $J$ = 22.0 Hz), 36.24 (t, $J$ = 25.2 Hz), 32.44 (t, $J$ = 2.7 Hz). IR (KBr): 2962, 1692, 1601, 1508, 1436, 1412, 1317, 1231, 1208, 1184, 1158, 1102, 1047, 997, 931, 842, 815, 669, 604, 562, 522, 490; GC-MS: 236.0. HRMS: 236.0214; Found: 236.0216.

4-Chloro-1-(4-chlorophenyl)-4,4-difluorobutan-1-one.
Yellow solid (m.p. 52-54 °C, 77%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.90 (d, $J$ = 8.2 Hz, 2H), 7.31 (d, $J$ = 8.2 Hz, 2H), 3.34 – 3.27 (m, 2H), 2.86-2.78 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -51.00 (t, $J$ = 12.9 Hz, 2F). $^{13}$C NMR (101MHz, CDCl$_3$) $\delta$ = 195.09, 140.08, 134.37, 129.51 (t, $J$ = 291.2 Hz), 129.40, 129.07, 36.19 (t, $J$ = 25.2 Hz), 32.52 (t, $J$ = 2.8 Hz). IR (KBr): 2959, 2925, 1692, 1591, 1572, 1489, 1435, 1401, 1315, 1299, 1209, 1185, 1094, 1047, 1014, 994, 932, 838, 785, 757, 662, 560, 530, 463; GC-MS: 252.0; HRMS: 251.9919; Found:251.9920.

1-(4-Bromophenyl)-4-chloro-4,4-difluorobutan-1-one.

Yellow solid (m.p. 46-48 °C, 80%). $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.84 (d, $J$ = 8.0 Hz, 2H), 7.63 (d, $J$ = 8.0 Hz, 2H), 3.31 – 3.23 (m, 2H), 2.86 – 2.72 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -51.12 (t, $J$ = 12.8 Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 195.25, 134.77, 132.37 (t, $J$ = 281.1 Hz), 132.07, 129.49, 128.84, 36.15 (t, $J$ = 25.2 Hz), 32.47 (t, $J$ = 2.8 Hz); IR (KBr): 3088, 3062, 2959, 2924, 2855, 2361, 1690, 1586, 1568, 1485, 1398, 1314, 1207, 1070, 1010, 986, 931, 803, 782, 748, 659, 568, 522, 456; GC-MS: 298.0; HRMS: 295.9414; Found:295.9415.

4-Chloro-1-(3-chlorophenyl)-4,4-difluorobutan-1-one.

Yellow liquid (82%) $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.93 – 7.90 (m, 1H), 7.83 (d, $J$ = 7.8, 1H), 7.57 – 7.52 (m, 1H), 7.44 – 7.38 (m, 1H), 3.29 – 3.23 (m, 2H), 2.84 – 2.71 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -51.15 (t, $J$ = 12.8 Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 195.01, 137.52, 135.09, 133.47, 130.06, 129.42 (t, $J$ = 291.3 Hz), 128.07, 126.04, 36.10 (t, $J$ = 25.3 Hz), 32.63 (t, $J$ = 2.8 Hz); IR (KBr): 3069, 2960, 2926, 2855, 1696, 1573, 1473, 1421, 1313, 1207, 1185, 1106, 1047, 938, 904, 778, 728, 698, 681, 670, 570, 558; GC-MS:252.0; HRMS: 251.9918; Found: 251.9920.

1-(3-Bromophenyl)-4-chloro-4,4-difluorobutan-1-one.
4-Chloro-4,4-difluoro-1-(4-nitrophenyl)butan-1-one.

4-Chloro-4,4-difluoro-1-(naphthalen-2-yl)butan-1-one.
4-Chloro-1-cyclohexyl-4,4-difluorobutan-1-one.

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\text{CF}_2\text{Cl}
\]

Slightly yellow liquid (49%) \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) \( \delta = 2.79-2.68 \) (m, 2H), 2.64 – 2.52 (m, 2H), 2.42-2.32 (m, 1H), 1.89 – 1.73 (m, 4H), 1.71 – 1.63 (m, 1H), 1.42 – 1.12 (m, 5H). \( ^{19}\text{F NMR (376 MHz, CDCl}_3 \) \( \delta = -51.19 \) (m, 2F). \( ^{13}\text{C NMR (101MHz, CDCl}_3 \) \( \delta = 210.14, 129.53 \) (t, \( J = 291.2 \) Hz), 50.74, 35.81 (t, \( J = 25.0 \) Hz), 34.07 (t, \( J = 2.5 \) Hz), 28.35, 25.64, 25.46. IR (KBr): 2933, 2857, 1713, 1451, 1316, 1294, 1207, 1189, 1102, 1027, 998, 936, 887, 659; GC -MS: 224.1; HRMS: 224.0776; Found: 224.0779.

**General Procedure for the ring-opening of \( \text{gem-difluorocyclopropyl ketones} \) promoted by boron tribromide:**

Into the solution of \( \text{gem-difluorocyclopropyl ketone} \) (0.2 mmol) in CHCl\(_3\) (1.0 mL) was added \( \text{BBr}_3 \) (1 mL, 0.4 M in CH\(_2\)Cl\(_2\)) slowly at -78 °C. The mixture was stirred at the same temperature until the reaction was complete determined by \( ^{19}\text{F NMR} \). After being warmed to room temperature, saturated NaHCO\(_3\) solution was added to quench the reaction. After extraction with CH\(_2\)Cl\(_2\) (10 mL x 3), the organic solution was dried over Na\(_2\)SO\(_4\). The solvent was removed by concentration, and the residue was subjected to silica-gel column chromatography to afford the \( \beta\)-bromodifluoromethyl ketones.

4-Bromo-4,4-difluoro-1-phenylbutan-1-one.

\[
\text{O} \quad \text{CF}_2\text{Br}
\]

Yellow liquid (57%) \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) \( \delta = 8.00 – 7.96 \) (m, 2H), 7.63 – 7.57 (m, 1H), 7.52-7.45 (m, 1H), 3.34-3.28 (m, 2H), 2.92-2.80 (m, 2H). \( ^{19}\text{F NMR (376MHz, CDCl}_3 \) \( \delta = -44.03 \) (t, \( J = 13.6 \) Hz, 2F). \( ^{13}\text{C NMR (101MHz,CDCl}_3 \) \( \delta = 196.15, 136.07, 133.59, 128.75, 128.01, 122.43 \) (t, \( J = 304.7 \) Hz), 38.69 (t, \( J = 22.6 \) Hz), 33.14 (t, \( J = 2.8 \) Hz). IR (KBr): 3063, 2956, 2935,
1690, 1598, 1450, 1321, 1205, 1102, 1041, 917, 747, 689, 627, 554; GC-MS: 262.0; HRMS: 261.9808; Found: 261.9805.

4-Bromo-4,4-difluoro-1-(p-tolyl)butan-1-one.

4-Bromo-4,4-difluoro-1-(4-fluorophenyl)butan-1-one.

4-Bromo-1-(4-chlorophenyl)-4,4-difluorobutan-1-one.

Electronic Supplementary Material (ESI) for Chemical Communications
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Yellow solid (m.p. 58-60 °C, 71%). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.87 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 3.27 - 3.20 (m, 2H), 2.87 – 2.74 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ = -44.16 (t, $J = 13.5$ Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 194.92, 140.09, 134.37, 129.41, 129.08, 122.25 (t, $J = 304.6$ Hz), 38.59 (t, $J = 22.7$ Hz), 33.13 (t, $J = 2.8$ Hz). IR (KBr): 2935, 1693, 1591, 1488, 1433, 1401, 1314, 1298, 1209, 1176, 1094, 989, 920, 834, 803, 750, 528, 463; GC-MS: 298.0; HRMS: 295.9412; Found: 295.9415.

4-Bromo-1-(4-bromophenyl)-4,4-difluorobutan-1-one.

Yellow solid (m.p. 57-59 °C, 74%). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.85 – 7.81 (m, 2H), 7.64 – 7.59 (m, 2H), 3.30 – 3.24 (m, 2H), 2.91 – 2.78 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ = -44.14 (t, $J = 13.5$ Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 195.11, 134.77, 132.07, 129.50, 128.84, 122.24 (t, $J = 304.7$ Hz), 38.57 (t, $J = 22.7$ Hz), 33.11 (t, $J = 2.8$ Hz). IR (KBr): 2960, 2919, 1693, 1586, 1568, 1484, 1433, 1399, 1315, 1299, 1206, 1176, 1101, 1070, 1041, 1011, 987, 920, 836, 801, 782, 741, 628, 557, 520, 455; GC-MS: 341.9; HRMS: 339.8909; Found: 339.8910.

4-Bromo-1-(3-chlorophenyl)-4,4-difluorobutan-1-one.

Yellow liquid (58%) $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.95-7.92 (m, 1H), 7.89-7.82 (m, 1H), 7.59-7.53 (m, 1H), 7.46-7.42 (m, 1H), 3.33-3.26 (m, 2H), 2.92 – 2.79 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ = -44.20 (t, $J = 13.5$ Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 194.88, 137.55, 135.13, 133.52, 130.09, 128.10, 126.09, 122.16 (t, $J = 301.5$ Hz), 38.53 (t, $J = 22.7$ Hz), 33.27 (t, $J = 2.9$ Hz). IR (KBr): 3069, 2920, 1694, 1573, 1422, 1313, 1206, 1178, 1104, 1041, 998, 973, 920, 777, 721, 680, 628, 555, 525, 471; GC-MS: 298.0; HRMS: 295.9412; Found: 295.9415.

4-Bromo-1-(3-bromophenyl)-4,4-difluorobutan-1-one.

Yellow solid (m.p. 58-60 °C, 71%). $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.87 (d, $J = 8.3$ Hz, 2H), 7.41 (d, $J = 8.3$ Hz, 2H), 3.27 – 3.20 (m, 2H), 2.87 – 2.74 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ = -44.16 (t, $J = 13.5$ Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 194.92, 140.09, 134.37, 129.41, 129.08, 122.25 (t, $J = 304.6$ Hz), 38.59 (t, $J = 22.7$ Hz), 33.13 (t, $J = 2.8$ Hz). IR (KBr): 2935, 1693, 1591, 1488, 1433, 1401, 1314, 1298, 1209, 1176, 1094, 989, 920, 834, 803, 750, 528, 463; GC-MS: 298.0; HRMS: 295.9412; Found: 295.9415.
Yellow liquid (61%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.11 - 8.08$ (m, 1H), 7.92-7.88 (m, 1H), 7.74 – 7.70 (m, 1H), 7.41-7.35(m, 1H), 3.31 – 3.26 (m, 2H), 2.92 – 2.80 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -44.20$ (t, $J = 13.5$Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 194.81$, 137.73, 136.45, 131.06, 130.35, 126.54, 123.13, 122.17 (t, $J = 304.7$ Hz), 38.53 (t, $J = 22.7$ Hz), 33.26 (t, $J = 2.8$ Hz). IR (KBr): 3066, 2933, 1694, 1567, 1471, 1420, 1313, 1205, 1177, 1104, 1069, 1041, 996, 918, 775, 704, 679, 654, 627, 555; GC-MS: 341.9. HRMS: 339.8912; Found: 339.8910.

4-Bromo-4,4-difluoro-1-(4-nitrophenyl)butan-1-one.

Yellow solid (m.p. 65-67 °C, 54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.36 - 8.32$ (m, 2H), 8.17 – 8.12 (m, 2H), 3.42-3.36 (m, 2H), 2.96 – 2.83 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -44.38$ (t, $J = 13.5$ Hz, 2F). $^{13}$C NMR (101MHz, CDCl$_3$) $\delta = 194.68$, 150.58, 140.36, 129.10, 124.00, 121.94 (t, $J = 303.9$ Hz), 38.42 (t, $J = 22.9$ Hz), 33.75 (t, $J = 2.8$ Hz). IR (KBr): 3112, 3081, 2922, 2859, 1698, 1604, 1531, 1433, 1409, 1348, 1317, 1207, 1102, 1042, 990, 922, 857, 743, 687, 630, 559, 549, 509; GC-MS: 307.0; HRMS: 306.9651; Found: 306.9656.

4-Bromo-4,4-difluoro-1-(naphthalen-2-yl)butan-1-one.

Yellow solid (m.p. 76-78 °C, 57%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.48$ (s, 1H), 8.03 (dd, $J = 8.7$, 1.6 Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.90 (t, $J = 8.2$ Hz, 2H), 7.65 – 7.55 (m, 2H), 3.47 – 3.41 (m, 2H), 2.99 – 2.87 (m, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -43.93$ (t, $J = 13.6$ Hz, 2F). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 196.06$, 135.74, 133.38, 132.40, 129.83, 129.59, 128.76, 128.65, 127.81, 126.97, 123.53, 122.50 (t, $J = 304.7$ Hz), 38.82 (t, $J = 22.6$ Hz), 33.19 (t, $J = 2.7$Hz). IR
(KBr): 3061, 2958, 2934, 1689, 1628, 1596, 1470, 1377, 1352, 1310, 1174, 1101, 1041, 989, 944, 914, 862, 823, 747, 708, 638, 625, 595, 550, 476; GC-MS: 312.0; HRMS: 311.9963; Found: 311.9961.

4-Bromo-1-cyclohexyl-4,4-difluorobutan-1-one.

Faint yellow liquid (65%) 1H NMR (400 MHz, CDCl<sub>3</sub>) δ = 2.78 – 2.71 (m, 2H), 2.71 – 2.58 (m, 2H), 2.36 (ddd, J = 11.2, 7.3, 3.3 Hz, 1H), 1.90 – 1.72 (m, 4H), 1.72 – 1.61 (m, 1H), 1.40 – 1.12 (m, 5H). 19F NMR (376 MHz, CDCl<sub>3</sub>) δ = -44.14 (t, J = 13.4 Hz, 2F). 13C NMR (101 MHz, CDCl<sub>3</sub>) δ = 210.00, 122.35 (t, J = 304.7 Hz), 50.74, 38.21 (t, J = 22.5 Hz), 34.70 (t, J = 2.6 Hz), 28.35, 25.64, 25.47. IR (KBr): 2933, 2856, 1713, 1450, 1315, 1204, 1102, 996, 923, 887, 669, 628, 550; GC-MS: 268.1. HRMS: 268.0276; Found: 268.0274.

References:
$^1$H NMR, $^{19}$F NMR and $^{13}$C NMR Spectra

$^1$H NMR spectrum of compound of 5a

$^1$H NMR spectrum of compound of 5b
$^1$H NMR spectrum of compound of 5c

$^1$H NMR spectrum of compound of 5d
$^1$H NMR spectrum of compound of 5e

$^{19}$F NMR spectrum of compound of 5e
$^1$H NMR spectrum of compound of 5f

$^1$H NMR spectrum of compound of 5g
$^1$H NMR spectrum of compound of 5h

$^1$H NMR spectrum of compound of 5i
$^1$H NMR spectrum of compound of 5j

$^1$H NMR spectrum of compound of 5k
$^1$H NMR spectrum of compound of 51

$^1$H NMR spectrum of compound of 1a
$^{19}$F NMR spectrum of compound of 1a

$^1$H NMR spectrum of compound of 1b
$^{19}$F NMR spectrum of compound 1b

$^1$H NMR spectrum of compound 1c
$^{19}\text{F NMR spectrum of compound of 1c}$

$^{1}\text{H NMR spectrum of compound of 1d}$
$^{19}$F NMR spectrum of compound of 1d

$^1$H NMR spectrum of compound of 1e
$^{19}$F NMR spectrum of compound of 1e

$^1$H NMR spectrum of compound 1f
$^{19}$F NMR spectrum of compound of 1f

$^1$H NMR spectrum of compound of 1g
$^{19}$F NMR spectrum of compound of 1g

$^{1}$H NMR spectrum of compound of 1h
$^{19}$F NMR spectrum of compound of 1h

$^1$H NMR spectrum of compound of 1i
$^{19}$F NMR spectrum of compound of 1i

$^1$H NMR spectrum of compound 1j
$^{19}$F NMR spectrum of compound of 1j

$^1$H NMR spectrum of compound of 1k
$^{19}\text{F}$ NMR spectrum of compound of 1k

$^{1}\text{H}$ NMR spectrum of compound of 1l

$^{19}\text{F}$ NMR spectrum of compound of 1l
$^{13}$C NMR spectrum of compound of 11
$^1$H NMR spectrum of compound of 2a

$^{19}$F NMR spectrum of compound of 2a
$^{13}$C NMR spectrum of compound of 2b

$^1$H NMR spectrum of compound of 2c
$^{19}$F NMR spectrum of compound of 2c

$^{13}$C NMR spectrum of compound of 2c
$^1$H NMR spectrum of compound of 2d

$^{19}$F NMR spectrum of compound of 2d
$^{13}$C NMR spectrum of compound of 2d

$^1$H NMR spectrum of compound of 2e
$^{19}$F NMR spectrum of compound of 2e

$^{13}$C NMR spectrum of compound of 2e
$^1$H NMR spectrum of compound of 2f

$^{19}$F NMR spectrum of compound of 2f
$^{13}$C NMR spectrum of compound of 2f

$^1$H NMR spectrum of compound of 2g
$^{19}$F NMR spectrum of compound of 2g

$^{13}$C NMR spectrum of compound of 2g
$^1$H NMR spectrum of compound of 2h

$^{19}$F NMR spectrum of compound of 2h
$^{13}$C NMR spectrum of compound of 2h

$^1$H NMR spectrum of compound of 2i
$^{19}$F NMR spectrum of compound of $2i$

$^{13}$C NMR spectrum of compound of $2i$
$^{1}H$ NMR spectrum of compound of 2j

$^{19}F$ NMR spectrum of compound of 2j
$^{13}$C NMR spectrum of compound of 2j

$^1$H NMR spectrum of compound of 2k
$^{19}$F NMR spectrum of compound of $2k$

$^{13}$C NMR spectrum of compound of $2k$
$^1$H NMR spectrum of compound of 2I

$^{19}$F NMR spectrum of compound of 2I
$^{13}$C NMR spectrum of compound of 21

$^1$H NMR spectrum of compound of 3a
$^{19}$F NMR spectrum of compound of 3a

$^1$H NMR spectrum of compound of 3b
$^{19}$F NMR spectrum of compound of 3b

$^1$H NMR spectrum of compound of 3c
$^{19}$F NMR spectrum of compound of 3c

$^{13}$C NMR spectrum of compound of 3c
$^1$H NMR spectrum of compound of 3d

$^{19}$F NMR spectrum of compound of 3d
$^{13}$C NMR spectrum of compound of 3d

$^1$H NMR spectrum of compound of 3e
$^1^9$F NMR spectrum of compound of 3e

$^{1^3}$C NMR spectrum of compound of 3e
$^1$H NMR spectrum of compound of 3f

$^{19}$F NMR spectrum of compound of 3f
$^{13}$C NMR spectrum of compound of 3f

$^1$H NMR spectrum of compound of 3g
$^{19}F$ NMR spectrum of compound of 3g

$^{13}C$ NMR spectrum of compound of 3g
$^1$H NMR spectrum of compound of 3h

$^{19}$F NMR spectrum of compound of 3h
$^{13}$C NMR spectrum of compound of 3h

$^1$H NMR spectrum of compound of 3i
$^{19}$F NMR spectrum of compound of 3i

$^{13}$C NMR spectrum of compound of 3i
$^1$H NMR spectrum of compound of 3j

$^{19}$F NMR spectrum of compound of 3j
$^{13}$C NMR spectrum of compound of $3j$

$^1$H NMR spectrum of compound of $4a$
$^{19}$F NMR spectrum of compound of 4a

$^{13}$C NMR spectrum of compound of 4a
$^1$H NMR spectrum of compound of 4b

$^{19}$F NMR spectrum of compound of 4b
$^{13}$C NMR spectrum of compound of 4b

$^1$H NMR spectrum of compound of 4c
$^{19}$F NMR spectrum of compound of 4c

$^{13}$C NMR spectrum of compound of 4c
$^1$H NMR spectrum of compound of 4d

$^{19}$F NMR spectrum of compound of 4d
$^{13}$C NMR spectrum of compound of 4d

$^{1}$H NMR spectrum of compound of 4e
$^{19}$F NMR spectrum of compound of 4e

$^{13}$C NMR spectrum of compound of 4e
$^1$H NMR spectrum of compound of 4f

$^{19}$F NMR spectrum of compound of 4f
\(^{13}\)C NMR spectrum of compound of 4f

\(^1\)H NMR spectrum of compound of 4g
$^{19}\text{F} \text{ NMR spectrum of compound of } 4\text{g}$

$^{13}\text{C} \text{ NMR spectrum of compound of } 4\text{g}$
$^1$H NMR spectrum of compound of 4h

$^{19}$F NMR spectrum of compound of 4h
$^{13}$C NMR spectrum of compound of 4h

$^1$H NMR spectrum of compound of 4i
$^{19}$F NMR spectrum of compound of 4i

$^{13}$C NMR spectrum of compound of 4i
$^1$H NMR spectrum of compound of 4j

$^{19}$F NMR spectrum of compound of 4j
$^{13}$C NMR spectrum of compound of 4j