Supporting Information

Photoinduced radical-initiated carboxylative cyclization of allyl amines with carbon dioxide

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General Considerations

All reactions were carried out with standard Schlenk techniques. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 °C) and ethyl acetate. Photoreactions were carried out using a Xe lamp (CEL-HXF300, Radiant output 300W, visible output 5000 Lu, color temperature 5600K). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 400 MHz spectrometer at 20 °C. All $^1$H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for CDCl$_3$ (7.26 ppm), DMSO-$d_6$ (2.50 ppm), CD$_3$CN (1.94 ppm) with $^1$H decoupling. Coupling constants, $J$, are reported in hertz (Hz). Multiplets were assigned as singlet (s), doublet (d), triplet (t), doublet of doublet (dd) and multiplet (m). $^{13}$C NMR was recorded at 101 MHz relative to CDCl$_3$ (77.16 ppm), DMSO-$d_6$ (39.52 ppm), CD$_3$CN (118.26 ppm). FT-IR was recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a RTX-5MS capillary column at an ionization voltage of 70 eV. The data are given as mass units per charge (m/z). Electrospray ionization mass spectra (ESI-MS) were recorded with an Agilent 6520 Q-TOF mass spectrometer. High resolution mass spectrometry was conducted using a Varian 7.0 T FTICR-MS by ESI technique.

Materials

Anhydrous DMSO and DMF were purchased from J&K chemical Co.. Anhydrous CH$_3$CN, THF and anhydrous CHCl$_3$ were purified according to Purification of Common Laboratory Chemicals. Unless otherwise noted, carbon dioxide (99.999%) was used. Allyl amines 1a – 1b, 1d – 1i were synthesized as previously described.$^{1,2}$ Other allyl amines/alcohols and chemicals were obtained from TCI, Aladdin or Alfa Aesar and used as received. The [TBDH]$^+$I$^-$ was synthesized via the neutralization of TBD and anhydrous hydriodic acid according to the reported procedures.$^3$

General Procedure for Synthesis of Allyl Amines

(1) A general procedure for synthesis of allyl amines 1a – 1b, 1e – 1i

\[
\text{Br} + \text{RNH}_2 \xrightarrow{\text{KI, DMSO, rt}} \text{N}^\text{H}_R
\]

To a solution of corresponding amine (25.1 mmol) and KI (21.0 mg, 0.125 mmol) in DMSO (15 mL) was added dropwise 3-bromopropene or 3-bromo-2-methylprop-1-ene (12.7 mmol) via a
syringe at 0 °C. After stirring for 18 h at room temperature, to the reaction mixture was added 1M aqueous NaHCO$_3$ (30 mL), and the aqueous layer was extracted with Et$_2$O (5 × 15 mL). The combined organic layer was washed with brine (15 mL), dried over anhydrous MgSO$_4$ and filtered. The solution was concentrated in vacuo followed by silica gel flash column chromatography (elucent; petroleum ether/ethyl acetate = 4/1 to 1/1) to provide the corresponding allyl amines (yield 47% ~ 75%).

(2) A general procedure for synthesis of allyl amine 1d

3-Bromopropene (1.09 g, 0.75 mL, 9 mmol) was added dropwise over 3 min to stirred and cooled (0 °C) n-butylamine (4.6 mL, 90 mmol). The resulting mixture was stirred and heated under reflux for 20 h, and then cooled to 0 °C. Concentrated hydrochloric acid was added dropwise to it over 5 min until pH 1 was attained. Water (25 mL) was added to the resulting suspension, which was then washed with diethyl ether (2 × 25 mL). The remaining aqueous solution was cooled to 0 °C and then brought to pH 10 by slow addition of potassium hydroxide pellets. The liberated amine was extracted into diethyl ether (3 × 25 mL). The combined organic phases were dried, filtered and the solvent removed under reduced pressure at 2 °C to leave a pale yellow liquid. The liquid was further purified by Kugelrohr distillation to yield the N-(tert-butyl)prop-2-en-1-amine (0.43 g, 38%) as a colourless oil.

N-benzylprop-2-en-1-amine 1a: yield 75%; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, $J = 4.4$ Hz, 4H), 7.28 – 7.23 (m, 1H), 5.94 (dt, $J = 16.3$, 6.0 Hz, 1H), 5.20 (dd, $J = 17.2$, 1.6 Hz, 1H), 5.12 (dd, $J = 10.3$, 1.4 Hz, 1H), 3.80 (s, 2H), 3.28 (dt, $J = 5.9$, 1.2 Hz, 2H), 1.54 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.3, 136.9, 128.4, 128.2, 127.0, 116.0, 53.3, 51.8; MS (ESI): calcd. for C$_{10}$H$_{14}$N$^+$ [M + H]$^+$ = 148.11, found 148.07.

N-allylcyclohexanamine 1b: yield 47%; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 5.90 (ddt, $J = 16.6$, 10.4, 6.1 Hz, 1H), 5.14 (d, $J = 18.0$ Hz, 1H), 5.06 (d, $J = 10.2$ Hz, 1H), 3.26 (d, $J = 6.0$ Hz, 2H), 2.44 (tt, $J = 10.4$, 3.7 Hz, 1H), 1.87 (d, $J = 10.4$ Hz, 2H), 1.72 – 1.61 (m, 5H), 1.25 – 1.18 (m, 2H), 1.09 – 1.04 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.9, 116.0, 57.9, 56.2, 49.4, 33.4,
N-(tert-butyl)prop-2-en-1-amine 1d: yield 38%; colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.89 (dq, $J = 11.0, 6.0$ Hz, 1H), 5.15 (d, $J = 17.2$ Hz, 1H), 5.06 (d, $J = 10.2$ Hz, 1H), 3.23 (d, $J = 5.8$ Hz, 2H), 2.59 (t, $J = 7.1$ Hz, 2H), 1.50 – 1.42 (m, 2H), 1.37 – 1.24 (m, 3H), 0.90 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.2, 115.7, 52.7, 49.3, 32.4, 20.6, 14.1; MS (ESI): calcd. for C$_{9}$H$_{18}$N$^{+}$ [M + H]$^{+}$ = 140.14, found 140.13.

N-(4-fluorobenzyl)prop-2-en-1-amine 1e: yield 70%; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.26 (m, 2H), 7.00 (t, $J = 8.6$ Hz, 2H), 5.92 (dq, $J = 10.6, 6.0$ Hz, 1H), 5.19 (d, $J = 17.2$ Hz, 1H), 5.11 (d, $J = 10.2$ Hz, 1H), 3.75 (s, 2H), 3.25 (d, $J = 5.9$ Hz, 2H), 1.50 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.9 (d, $J = 244.5$ Hz), 136.7, 136.0 (d, $J = 3.1$ Hz), 129.8 (d, $J = 7.9$ Hz), 116.2, 115.2 (d, $J = 21.2$ Hz), 52.5, 51.8; MS (ESI): calcd. for C$_{10}$H$_{13}$FN$^{+}$ [M + H]$^{+}$ = 166.21, found 166.07.

N-(4-chlorobenzyl)prop-2-en-1-amine 1f: yield 72%; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.24 (m, 1H), 5.91 (ddt, $J = 16.3, 10.3, 6.0$ Hz, 1H), 5.12 (dd, $J = 10.2, 1.2$ Hz, 1H), 3.75 (s, 1H), 3.25 (d, $J = 6.0$ Hz, 2H), 1.45 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.8, 136.7, 132.7, 129.6, 128.6, 116.3, 52.5, 51.8; MS (ESI): calcd. for C$_{10}$H$_{13}$ClN$^{+}$ [M + H]$^{+}$ = 182.07, found 182.00.

N-(4-bromobenzyl)prop-2-en-1-amine 1g: yield 70%; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 8.3$ Hz, 2H), 7.20 (d, $J = 8.2$ Hz, 2H), 5.91 (ddt, $J = 16.3, 10.3, 6.0$ Hz, 1H), 5.18 (dd, $J = 17.2, 1.6$ Hz, 1H), 5.11 (dd, $J = 10.2, 1.3$ Hz, 1H), 3.73 (s, 2H), 1.54 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.3, 136.7, 131.5, 130.0, 120.8, 116.3, 52.6, 51.7; MS (ESI): calcd. for C$_{10}$H$_{13}$BrN$^{+}$ [M + H]$^{+}$ = 226.02, 228.02, found 226.00, 228.00.

N-(4-methoxybenzyl)prop-2-en-1-amine 1h: yield 69%; yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J = 7.5$ Hz, 2H), 6.88 (d, $J = 7.3$ Hz, 2H), 5.95 (dq, $J = 11.1, 6.0$ Hz, 1H), 5.17 (dd, $J = 33.1, 13.7$ Hz, 2H), 3.81 (s, 3H), 3.74 (s, 2H), 3.28 (d, $J = 5.9$ Hz, 2H),
1.53 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.6, 136.9, 132.4, 129.4, 116.0, 113.8, 55.3, 52.7, 51.7; MS (ESI): calcd. for C$_{11}$H$_{16}$NO$^+$ [M + H]$^+$ = 178.12, found 178.00.

$N$-(benzo[d][1,3]dioxol-5-ylmethyl)prop-2-en-1-amine 1i: yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.85 (s, 1H), 6.79 – 6.74 (m, 2H), 5.96 – 5.89 (m, 3H), 5.20 (dd, $J$ = 17.2, 1.5 Hz, 1H), 5.13 (dd, $J$ = 10.2, 1.1 Hz, 1H), 3.72 (s, 2H), 3.27 (d, $J$ = 6.0 Hz, 2H), 2.52 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.7, 146.7, 136.0, 133.3, 121.5, 116.7, 108.1, 108.9, 100.9, 52.7, 51.3; MS (ESI): calcd. for C$_{11}$H$_{14}$NO$_2^+$ [M + H]$^+$ = 192.10, 192.01

The Procedure for Synthesis of [TBDH]$^+$I$^-$

In a 25 mL round bottom flask, anhydrous hydriodic acid (55% w/w, 1.2 mL, 5 mmol HI,) was dropped into the solution of TBD (0.6950 g, 5 mmol) in 5 mL water at 0 °C within 20 minutes. After the addition, the reaction mixture was stirred for an addition period of 2 hours at room temperature to ensure the reaction had proceeded to completion. The solution was concentrated in vacuo and the small amount of water was removed by heating the residue at 80 °C in high vacuum until the weight of the residue remained constant. The white crystalline [TBDH]$^+$I$^-$ was obtained in 99% yield (1.3216 g). Melting point: 106 – 108 °C; IR (KBr) v 3310, 3282, 3220, 3040, 2871, 1638, 1534, 1375, 1065 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.36 (s, 2H), 3.28 (t, $J$ = 6 Hz, 4H), 3.19 – 3.16 (m, 4H), 1.89 – 1.83 (m, 4H), $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 150.5, 46.2, 37.5, 20.2.

General procedure for photoinduced radical-initiated carboxylative cyclization of allyl amines/alcohols with CO$_2$

TBD (0.1044 g, 0.75 mmol) was charged to the tube in a 100 mL steel autoclave. Then the autoclave was subjected to three cycles of pressurization and depressurization with CO$_2$. In CO$_2$ atmosphere, allyl amines/alcohol (0.5 mmol), MeCN/DMSO (2 mL) was added and the mixture was stirred for 2 h. Then perfluoroalkyl iodide (1 mmol) was added and the contents was stirred for appropriate time under a 300 W Xe lamp (420 – 700nm). Thereafter, the autoclave was cooled to room
temperature and carefully depressurized. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1) to provide the corresponding products (yield 47% ~ 99%).

3,4,6,7,8,9-Hexahydro-2H-pyrimido[1,2-a]pyrimidin-1-ium

allyl(benzyl)carbamate (E), 1H NMR (400 MHz, CD3CN) δ 11.32 (s, 2H), 7.56 – 6.88 (m, 5H), 5.98 – 5.60 (m, 1H), 5.00 (d, J = 12.3 Hz, 2H), 4.39 (s, 2H), 3.76 (d, J = 5.4 Hz, 2H), 3.22 (t, J = 5.7 Hz, 4H), 3.13 (t, J = 5.3 Hz, 4H), 1.90 – 1.82 (m, 4H); 13C NMR (101 MHz, DMSO-d6) δ 164.4, 152.7, 142.2, 137.5, 129.0, 128.3, 127.1, 115.2, 49.6, 49.2, 47.3, 38.2, 21.7.

3-Benzyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxazolidin-2-one (2a): 1H NMR (400 MHz, CDCl3) δ 7.40-7.26 (m, 5H), 4.95-4.80 (m, 1H), 4.49 (d, J = 14.8 Hz, 1H), 4.38 (d, J = 14.8 Hz, 1H), 3.63 (t, J = 8.7 Hz, 1H), 3.19 (dd, J = 9.0, 7.5 Hz, 1H), 2.75-2.61 (m, 1H), 2.39 (ddd, J = 24.2, 16.5, 7.2 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 157.04, 135.33, 129.13, 128.39, 128.34, 66.94 (t, J = 3.3 Hz), 49.71, 48.49, 36.15 (t, J = 21.0 Hz), (carbon peaks of –C4F9 are omitted due to complicated C-F splitting); 19F NMR (377 MHz, CDCl3) δ -81.0 (t, J = 9.1 Hz, 3F), -112.7 – -112.8 (m, 2F), -124.5 (m, 2F), -126.0 (t, J = 12.4 Hz, 2F); HRMS (ESI): C15H13F9NO2+ for [M + H]+ calculated 410.0797, found 410.0797.

3-Cyclohexyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxazolidin-2-one (2b): 1H NMR (400 MHz, CDCl3) δ 4.86 (qd, J = 7.4, 5.5 Hz, 1H), 3.74 – 3.65 (m, 2H), 3.28 (dd, J = 8.9, 7.3 Hz, 1H), 2.76 – 2.61 (m, 1H), 2.42 (ddd, J = 24.1, 17.3, 7.4 Hz, 1H), 1.81 – 1.80 (m, 4H), 1.69 – 1.66 (m, 1H), 1.41 – 1.28 (m, 4H), 1.12 – 1.03 (m, 1H); 13C NMR (101 MHz, DMSO-d6) δ 155.9, 155.9, 66.8, 52.1, 45.4, 34.7 (t, J = 20.2 Hz), 29.9, 29.5, 25.0 (m), (carbon peaks of –C4F9 are omitted due to complicated C-F splitting); 19F NMR (377 MHz, CDCl3) δ -81.0 (t, J = 9.1 Hz, 3F), -112.7 – -112.8 (m, 2F), -124.5 (s, 2F), -126.0 (t, J = 12.4 Hz, 2F); HRMS (ESI): C14H17F9NO2+ for
[M + H]$^+$ calculated 402.1110, found 402.1106.

3-Methyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxazolidin-2-one (2c):

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{CH}_3
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.89 − 4.82 (m, 1H), 3.76 (t, $J = 8.7$ Hz, 1H), 3.33 (t, $J = 8.1$ Hz, 1H), 2.87 (s, 3H), 2.67 (ddd, $J = 38.1$, 15.7, 5.6 Hz, 1H), 2.43 (ddd, $J = 36.1$, 15.4, 6.8 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.3, 66.6, 52.4, 36.1 (t, $J = 20.9$ Hz), 31.0, (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.1 (t, $J = 9.5$ Hz, 3F), -112.7 – -113.2 (m, 2F), -124.4 – -124.7 (m, 2F), -125.9 – -126.2 (m, 2F); HRMS (ESI): C$_{8}$H$_{9}$F$_{9}$NO$_2^+$ for [M + H]$^+$ calculated 334.0484, found 334.0492.

3-(Tert-butyl)-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxazolidin-2-one (2d):

\[
\begin{align*}
\text{O} & \quad \text{N} \quad \text{tBu}
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.96 − 4.86 (m, 1H), 3.79 (t, $J = 8.6$ Hz, 1H), 3.36 − 3.19 (m, 3H), 2.70 (td, $J = 20.5$, 4.9 Hz, 1H), 2.46 (qd, $J = 16.6$, 7.0 Hz, 1H), 1.58 – 1.51 (m, 2H), 1.40 – 1.31 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.0, 66.7, 50.3, 44.0, 36.2 (t, $J = 21.0$ Hz), 29.4, 19.9, 13.7, (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -81.2 (t, $J = 9.1$ Hz, 3F), -112.8 – -112.9 (m, 2F), -124.5 (s, 2F), -126.0 (t, $J = 12.4$ Hz, 2F); HRMS (ESI): C$_{12}$H$_{15}$F$_{9}$NO$_2^+$ for [M + H]$^+$ calculated 376.0954, found 376.0952.

3-(4-Fluorobenzyl)-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxazolidin-2-one (2e):

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{C}_4\text{F}_9
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 − 7.26 (m, 2H), 7.09 – 7.03 (m, 2H), 4.89 (dt, $J = 14.2$, 7.2 Hz, 1H), 4.47 (d, $J = 14.9$ Hz, 1H), 4.36 (d, $J = 14.9$ Hz, 1H), 3.64 (t, $J = 8.7$ Hz, 1H), 3.20 (dd, $J = 8.9$, 7.5 Hz, 1H), 2.76 – 2.61 (m, 1H), 2.41 (ddd, $J = 36.2$, 15.7, 7.0 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.7 (d, $J = 247.0$ Hz), 157.0, 131.2 (d, $J = 2.9$ Hz), 130.10 (d, $J = 8.1$ Hz), 116.02 (d, $J = 21.7$ Hz), 67.0, 49.6, 47.8, 36.1 (t, $J = 20.9$ Hz), (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -81.1 (t, $J = 9.5$ Hz, 3F), -112.7 – -112.9 (m, 2F), -113.7 – -113.8 (m, 1F), -124.4 – -124.5 (m, 2F), -126.0
(t, J = 11.9 Hz, 2F); HRMS (ESI): C_{13}H_{12}F_{10}NO_{2}^{+} for [M + H]^{+} calculated 428.0703, found 428.0709.

3-(4-Chlorobenzyl)-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyloxazolidin-2-one (2f): ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.91 – 4.86 (m, 1H), 4.45 (d, J = 15.0 Hz, 1H), 4.34 (d, J = 15.0 Hz, 1H), 3.62 (t, J = 8.7 Hz, 1H), 3.18 (t, J = 8.7 Hz, 1H), 2.75 – 2.61 (m, 1H), 2.39 (dd, J = 35.0, 17.3, 7.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 134.3, 133.9, 129.7, 129.3, 67.0, 49.7, 47.8, 36.1 (t, J = 20.9 Hz), (carbon peaks of –C₄F₉ are omitted due to complicated C-F splitting); ¹⁹F NMR (377 MHz, CDCl₃) δ -81.0 (t, J = 8.8 Hz, 3F), -112.7 – -112.9 (m, 2F), -124.4 – -124.5 (m, 2F), -126.0 (s, 2F), -126.0 (t, J = 12.6 Hz, 2F); HRMS (ESI): C_{15}H_{12}ClF₉NO₂⁺ for [M + H]⁺ calculated 444.0407, found 444.0413.

3-(4-Bromobenzyl)-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyloxazolidin-2-one (2g): ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 4.91 – 4.84 (m, 1H), 4.44 (d, J = 14.9 Hz, 1H), 4.33 (d, J = 15.0 Hz, 1H), 3.62 (t, J = 8.7 Hz, 1H), 3.18 (t, J = 8.2 Hz, 1H), 2.69 (qd, J = 19.5, 5.4 Hz, 1H), 2.39 (dd, J = 33.3, 17.3, 7.3 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 134.3, 132.3, 130.0, 122.4, 67.0, 49.7, 47.9, 36.1 (t, J = 20.9 Hz), (carbon peaks of –C₄F₉ are omitted due to complicated C-F splitting); ¹⁹F NMR (377 MHz, CDCl₃) δ -81.0 (t, J = 9.2 Hz, 3F), -112.7 – -112.9 (m, 2F), -124.4 – -124.5 (m, 2F), -126.0 (s, 2F), -126.0 (t, J = 12.5 Hz, 2F); HRMS (ESI): C_{15}H_{12}BrF₉NO₂⁺ for [M + H]⁺ calculated 487.9902, 489.9882, found 487.9899, 489.9878.

3-(4-Methoxybenzyl)-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyloxazolidin-2-one (2h): ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.2 Hz, 2H), 4.88 – 4.81 (m, 1H), 4.41 (d, J = 14.7 Hz, 1H), 4.32 (d, J = 14.7 Hz, 1H),
3.80 (s, 3H), 3.60 (t, J = 8.7 Hz, 1H), 3.16 (t, J = 8.2 Hz, 1H), 2.67 (td, J = 19.7, 5.2 Hz, 1H), 2.37 (ddd, J = 33.9, 17.3, 7.3 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.7, 157.0, 129.8, 127.3, 114.4, 66.9, 55.4, 49.6, 47.9, 36.3, 36.1 (t, J = 21.0 Hz), 35.9, (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -81.0 (t, J = 8.3 Hz, 3F), -112.7 (dd, J = 12.6 Hz, 2F), -124.4 (dd, J = 12.6 Hz, 2F), -125.9 (dd, J = 13.4, 10.8 Hz, 2F); HRMS (ESI): C$_{16}$H$_{15}$F$_9$NO$_3^{-}$ for [M + H]$^+$ calculated 440.0903, found 440.0895.

3-(Benzo[d][1,3]dioxol-5-ylmethyl)-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)oxazolidin-2-one (2i): $^1$H NMR (400 MHz, CDCl$_3$) δ 6.78 – 6.71 (m, 3H), 5.96 (s, 2H), 4.89 – 4.82 (m, 1H), 4.37 (d, J = 14.7 Hz, 1H), 4.27 (d, J = 14.7 Hz, 1H), 3.62 (t, J = 8.7 Hz, 1H), 3.17 (t, J = 8.2 Hz, 1H), 2.74 – 2.60 (m, 1H), 2.39 (ddd, J = 23.9, 17.3, 7.1 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.9, 148.4, 147.8, 129.1, 108.7, 108.6, 101.4, 66.9, 49.6, 48.3, 36.1 (t, J = 21.1 Hz), (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.6 (t, J = 8.3 Hz, 2F), -112.7 – -112.8 (m, 2F), -124.5 (s, 2F), -126.0 (t, J = 12.6 Hz, 2F); HRMS (ESI): C$_{16}$H$_{15}$F$_9$NO$_3^{-}$ for [M + H]$^+$ calculated 454.0695, found 454.0694.

3-Benzyl-5-(2,2,3,3,4,4,5,5,5,5,6,6,7,7,7-tridecafluoroheptyl)oxazolidin-2-one (2j): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.28 (m, 5H), 4.92 – 4.85 (m, 1H), 4.51 (d, J = 14.8 Hz, 1H), 4.40 (d, J = 14.8 Hz, 1H), 3.65 (t, J = 8.7 Hz, 1H), 3.21 (dd, J = 9.0, 7.4 Hz, 1H), 2.76 – 2.61 (m, 1H), 2.40 (ddd, J = 34.5, 17.0, 7.1 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.0, 135.4, 129.1, 128.4, 128.3, 66.9, 49.7, 48.5, 36.0 (t, J = 21.2 Hz), (carbon peaks of –C$_3$F$_7$ are omitted due to complicated C-F splitting); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.6 (t, J = 9.6 Hz, 3F), -113.5 – -113.6 (m, 2F), -127.7 – -127.8 (t, J = 18.5 Hz, 2F); HRMS (ESI): C$_{16}$H$_{15}$F$_9$NO$_4^{-}$ for [M + H]$^+$ calculated 360.0829, found 360.0834.

3-Benzyl-5-(2,2,3,3,4,4,4-hepttafluorobutyl)oxazolidin-2-one (2j): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.28 (m, 5H), 4.94 – 4.81 (m, 1H), 4.50 (d, J = 14.8 Hz, 1H), 4.47 (d, J = 14.8 Hz, 1H), 3.63 (t, J = 8.7 Hz, 1H), 3.20 (dd, J = 9.0, 7.4 Hz, 1H), 2.75 – 2.61 (m, 1H), 2.39 (ddd, J = 34.5, 17.0, 7.1 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.0, 135.4, 129.1, 128.4, 128.3, 66.9, 49.7, 48.5, 36.0 (t, J = 21.2 Hz), (carbon peaks of –C$_3$F$_7$ are omitted due to complicated C-F splitting); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.6 (t, J = 9.6 Hz, 3F), -113.5 – -113.6 (m, 2F), -127.7 – -127.8 (t, J = 18.5 Hz, 2F); HRMS (ESI): C$_{16}$H$_{15}$F$_9$NO$_4^{-}$ for [M + H]$^+$ calculated 360.0829, found 360.0834.

3-Benzyl-5-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)oxazolidin-2-one (2k): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.28 (m, 5H), 4.94 – 4.81 (m, 1H), 4.50 (d, J = 14.8 Hz, 1H), 4.47 (d, J = 14.8 Hz, 1H), 3.63 (t, J = 8.7 Hz, 1H), 3.20 (dd, J = 9.0, 7.4 Hz, 1H), 2.75 – 2.61 (m, 1H), 2.39 (ddd, J = 34.5, 17.0, 7.1 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.0, 135.4, 129.1, 128.4, 128.3, 66.9, 49.7, 48.5, 36.0 (t, J = 21.2 Hz), (carbon peaks of –C$_3$F$_7$ are omitted due to complicated C-F splitting); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -80.6 (t, J = 9.6 Hz, 3F), -113.5 – -113.6 (m, 2F), -127.7 – -127.8 (t, J = 18.5 Hz, 2F); HRMS (ESI): C$_{16}$H$_{15}$F$_9$NO$_4^{-}$ for [M + H]$^+$ calculated 360.0829, found 360.0834.
Hz, 1H), 4.38 (d, J = 14.7 Hz, 1H), 3.63 (t, J = 8.5 Hz, 1H), 3.19 (t, J = 7.8 Hz, 1H), 2.69 (q, J = 16.7 Hz, 1H), 2.46 – 2.32 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.0, 135.3, 129.1, 128.4, 128.3, 67.0, 49.7, 48.5, 36.2 (t, J = 21.2 Hz), (carbon peaks of –C$_{6}$F$_{13}$ are omitted due to complicated C-F splitting); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -80.8 (t, J = 9.9 Hz, 3F), -112.4 – -112.6 (m, 2F), -121.8 (s, 2F), -122.8 (s, 2F), -123.5 (s, 2F), -126.1 (td, J = 14.8, 6.8 Hz, 2F); HRMS (ESI): C$_{17}$H$_{13}$F$_{13}$NO$_2$ for [M + H]$^+$ calculated 510.0733, found 510.0734.

3-benzyl-5-(2,2,2-trifluoroethyl)oxazolidin-2-one (2l): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.27 (m, 5H), 4.75 (dt, J = 14.3 Hz, 1H), 4.48 (d, J = 14.8 Hz, 1H), 4.38 (d, J = 14.9 Hz, 1H), 3.60 (t, J = 8.7 Hz, 1H), 3.24 - 3.11 (m, 1H), 2.78 – 2.58 (m, 1H), 2.49 – 2.31 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.1, 135.3, 129.1, 128.34, 128.29, 124.9 (q, J = 276.9 Hz), 67.4 (q, J = 3.3 Hz), 49.2, 48.4, 39.0 (q, J = 28.4 Hz); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -63.7 (t, J = 10.3 Hz, 3F); HRMS (ESI): C$_{12}$H$_{13}$F$_{3}$NO$_2$ for [M + H]$^+$ calculated 260.0893, found 260.0891.

4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,3-dioxolan-2-one (2m): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.0 Hz, 1H), 3.12 – 2.80 (m, 2H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 33.6 (t, J = 20.1 Hz), 68.6, 70.13, 154.4, (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (377 MHz, DMSO-$d_6$) δ -80.6 (dd, J = 11.6, 8.0 Hz, 3F), -111.2 (dd, J = 27.6, 22.4, 9.4 Hz, 1F), -113.3 (ddd, J = 272.1, 18.5, 8.1 Hz, 1F), -123.2 – -124.7 (m, 2F), -125.2 – -126.4 (m, 2F); calcd. for C$_8$F$_6$O$_3$ [M + H]$^+$ = 321.0168 Found: 321.0172.

1H NMR (400 MHz, CDCl$_3$) δ 5.08 (ddd, J = 12.0, 7.5 Hz, 0.28 H), 4.76 (t, J = 8.7 Hz, 0.28 H), 4.65 (q, J = 5.9 Hz, 0.72 H), 4.41 (dd, J = 12.2, 6.0 Hz, 0.72 H), 2.67 (ddd, J = 35.2, 18.4, 6.2 Hz, 1 H), 2.46 (ddd, J = 22.4, 17.3, 5.8 Hz, 1 H), 1.81 – 1.34 (m, 8 H), 0.92 – 0.91 (m, 3 H); $^{13}$C NMR (101
MHz, CDCl$_3$) δ 153.5, 82.0, 79.3, 74.6 (t, $J = 2.7$ Hz), 72.3 (d, $J = 4.4$ Hz), 35.4 (t, $J = 21.4$ Hz), 33.4, 31.33, 31.30, 31.0 (t, $J = 21.6$ Hz), 29.3, 25.1, 24.3, 22.5, 14.0, (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -81.0 (t, $J = 9.3$ Hz, 3F), -112.5 – -112.6 (m, 2F), -124.2 – 124.3 (m, 2F), -125.9 (t, $J = 12.1$ Hz); calcd. for C$_{13}$H$_{16}$F$_9$O$_3^+$ [M + H]$^+$ = 391.0950, Found: 391.0945

1-Benzyl-2-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)aziridine (3a): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32-7.23 (m, 5H), 3.63 (d, $J = 13.3$ Hz, 1H), 3.19 (d, $J = 13.4$ Hz, 1H), 2.31 (td, $J$ = 19.3, 5.8 Hz, 2H), 1.84 (dd, $J$ = 5.9, 3.2 Hz, 1H), 1.65 (d, $J = 3.0$ Hz, 1H), 1.53 (d, $J = 6.3$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.1, 128.1, 128.0, 126.9, 109.0, 62.9, 34.1(t, $J = 20.74$ Hz), 31.8, 30.8 (t, $J = 4.74$ Hz), (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); GC-MS (EI, 70 eV) m/z (%) = 364.96 (6), 274.06 (100), 132.15 (27), 91 (41).
Control Experiments

Table S1 Control experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (equiv.)</th>
<th>Visible light (nm)</th>
<th>Yield of 2a (%)[b]</th>
<th>Yield of 3a (%)[b]</th>
</tr>
</thead>
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<td>1</td>
<td>–</td>
<td>420-700</td>
<td>21</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>TBD (1.5)</td>
<td>420-700</td>
<td>92</td>
<td>trace</td>
</tr>
<tr>
<td>3[c]</td>
<td>TBD (1.5)</td>
<td>420-700</td>
<td>0</td>
<td>81</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.5 mmol), C₄F₉I (1.0 mmol), MeCN (2 mL), CO₂ (1 bar), rt. [b] Isolated yield. [c] Without CO₂, and Ar (1 bar).

**¹H NMR investigation**

TBD (0.0522 g, 0.375 mmol), allyl alcohol (0.0145 g, 0.25 mmol) and 1.2 mL deuterium acetonitrile were added to a 10 mL Schlenk tube equipped with a magnetic stir bar. Then the flask was subjected to three cycles of pressurization and depressurization with CO₂ using the “freeze–pump–thaw” method. In CO₂ atmosphere, perfluorobutyl iodide (86 µL, 0.5 mmol) was added and the contents were stirred under a 300 W Xe lamp (420 – 700nm). The reaction system was monitored with ¹H NMR spectroscopy at intervals. Before light output, most of allyl alcohol, TBD and CO₂ converted into allylic carbonate suspend in acetonitrile (signals of allylic carbonate emerged at δ = 6.03 - 5.92 (m, 1H), 5.24 (ddd, J = 17.3, 3.7, 1.8 Hz, 1H), 5.08 (ddd, J = 10.5, 3.4, 1.6 Hz, 1H), 4.34 (dt, J = 5.2, 1.5 Hz, 2H); signals of remainder allylic alcohol appeared at δ = 5.96 (ddt, J = 17.2, 10.2, 4.8 Hz, 1H), 5.22 (ddd, J = 17.2, 3.8, 1.8 Hz, 1H), 5.06 (ddd, J = 10.4, 3.4, 1.6 Hz, 1H), 4.04 (dt, J = 4.8, 1.7 Hz, 2H)) (Figure 1, 0 h). With light output, the solubility of allyl carbonate increased due to a little increase in reaction temperature, assigned to an enhancement on the intensity of ¹H NMR signal 4.34 ppm. Meanwhile, peaks corresponding to 4-nonafluoropentyl-ethylene carbonate 2m appeared at δ = 5.17, 4.64, 4.22 ppm, indicating the start of this reaction (Figure 1, 1 h). As the reaction progressed at 4 h, a set of new signals emerged at δ = 4.31, 3.82, 3.67 ppm, assigned to the iodo-perfluoroalkylated carbonate intermediate D, which was corroborated indirectly in mass spectra (Figure S1). At 6 h, the raw materials converted completely, following a rapid
transformation from intermediate D to 2m only in 10 min.

Fig. 1 $^1$H NMR spectra for the visible light-driven carboxylative cyclization reaction of allyl alcohol 1m, CO$_2$ and C$_4$F$_9$I in CD$_3$CN.

GC-MS (EI, 70 eV) m/z (%)

As the reaction progressed at 4 h, the crude reaction mixture was analyzed by GC-MS rapidly, as follows.
Radical-Trapping Experiments

TBD (0.1044 g, 0.75 mmol) and 4-OH-TEMPO (0.1722 g, 1 mmol) were charged to the tube in a 100 mL steel autoclave. Then the autoclave was subjected to three cycles of pressurization and depressurization with CO$_2$. In CO$_2$ atmosphere, N-benzylprop-2-en-1-amine 1a (0.0736 g, 0.5 mmol), MeCN (2 mL) and perfluoroalkyl iodide (172 µL, 1 mmol) were added and the contents were stirred for 12 h under a 300 W Xe lamp (420 nm – 700 nm). Thereafter, the autoclave was cooled to room temperature and carefully depressurized. The crude reaction mixture was then analyzed by GC-MS.

TBD (0.1044 g, 0.75 mmol) was charged to the tube in a 100 mL steel autoclave. Then the autoclave was subjected to three cycles of pressurization and depressurization with CO$_2$. In CO$_2$ atmosphere, allyl ether 4 (0.1963 g, 2 mmol), MeCN (2 mL) and perfluoroalkyl iodide (86 µL, 0.5 mmol) were added and the contents were stirred for 12 h under a 300 W Xe lamp (420 nm – 700 nm). Thereafter,
the autoclave was cooled to room temperature and carefully depressurized. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25/1) to provide the colourless oil 5 (yield 61%).

3-(Iodomethyl)-4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)tetrahydrofuran (5): (dr = 50:11): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.20 – 4.19 (m, 0.22H), 4.08 – 4.00 (m, 2.22H), 3.78 (dd, $J$ = 9.1, 4.6 Hz, 1H), 3.67 (t, $J$ = 8.2 Hz, 1H), 3.64 – 3.56 (m, 0.44H), 3.33 (dd, $J$ = 10.0, 5.1 Hz, 0.22H), 3.21 (dd, $J$ = 9.8, 5.3 Hz, 1H), 3.23 – 3.18 (t, $J$ = 10.1 Hz, 0.22H), 3.11 (t, $J$ = 10.1 Hz, 1H), 2.88 – 2.82 (m, 1H), 2.78 – 2.69 (m, 1H), 2.49 – 2.27 (m, 1.66H), 2.22 – 2.02 (m, 1.22H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 74.2 (d, $J$ = 3.5 Hz), 73.9, 73.6, 71.8 (d, $J$ = 3.9 Hz), 47.9, 45.2, 39.4, 35.8, 33.8 (t, $J$ = 21.6 Hz), 28.3 (t, $J$ = 21.8 Hz), 6.7, 2.8, (carbon peaks of –C$_4$F$_9$ are omitted due to complicated C-F splitting); $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -81.0 – -81.2 (m, 3F), -112.5 – -115.2 (m, 2F), -124.36 (s, 2F), -125.9 – -126.0 (m, 2F); HRMS (ESI): C$_{10}$H$_{11}$F$_{9}$IO for [M+H]$^+$ calculated 444.9705, found 444.9702.

References

$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
\[1^1H\text{ NMR (400 MHz, CDCl}_3\text{)}\]

\[1^3C\text{ NMR (101 MHz, CDCl}_3\text{)}\]
$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{C NMR (101 MHz, CDCl}_3\text{)}$
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl₃)

$^{13}$C NMR (101 MHz, CDCl₃)
$^1$H NMR (400 MHz, DMSO-$d_6$)

$^{13}$C NMR (101 MHz, DMSO-$d_6$)
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
\[ \text{C}_9 \text{F}_9 \text{NMR (101 MHz, CDCl}_3) \]

\[ \text{F}_9 \text{NMR (377 MHz, CDCl}_3) \]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)

$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (101 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{19}$F NMR (377 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, DMSO-$d_6$)

$^1$C NMR (101 MHz, DMSO-$d_6$)
$^{19}$F NMR (377 MHz, DMSO-$d_6$)

$^1$H NMR (400 MHz, CDCl$_3$)

$\text{dr} = 18:7$
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{19}$F NMR (377 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, DMSO-$d_6$)

$^{13}$C NMR (101 MHz, DMSO-$d_6$)

46
$\text{C}_4\text{F}_9$\[\text{O}][\text{I}]$

5 (d.r. = 50 : 11)

$^1\text{H}$ NMR (400 MHz, CDCl$_3$)

$\text{C}_4\text{F}_9$\[\text{O}][\text{I}]$

5 (d.r. = 50 : 11)

$^{13}\text{C}$ NMR (101 MHz, CDCl$_3$)
$^{19}\text{F NMR (377 MHz, CDCl}_3\text{)}$

$^{1}\text{H NMR (400 MHz, CD}_3\text{CN)}$
$^{13}$C NMR (101 MHz, CD$_3$CN)