Electronic Supplementary Information

Photo- and dioxygen-enabled radical C(sp$^3$)—N(sp$^2$) cross-coupling: synthesis of $N^2$-perfluoroalkacylguanidines

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1. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Some guanidines 2 were prepared according to literature reported procedure. The products were purified by column chromatography over silica gel. $^1$H, $^{19}$F and $^{13}$C NMR spectra were recorded at 25 °C on a Varian 600MHz or 500 MHz or 400 MHz or 300 MHz for $^1$H, at 564 MHz or 470 MHz or 376 MHz for $^{19}$F and at 150 MHz or 125 MHz or 100 MHz for $^{13}$C, respectively, in CDCl$_3$ or (CD$_3$)$_2$SO. Chemical shifts are reported in ppm relative to the residual signals of the deuterated solvents as the internal standard (CDCl$_3$: $\delta$ H = 7.26, $\delta$ C = 77.16 ppm, (CD$_3$)$_2$SO: $\delta$ H = 2.50, $\delta$ C = 39.52 ppm). $^1$H NMR spectra were recorded using TMS as the internal reference, and $^{19}$F NMR spectra were recorded using CF$_3$COOH as external reference. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants, $J$, are reported in Hertz. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. High-resolution mass-spectra were obtained on an Agilent 1100 LCMsD mass spectrometer. Melting points (m.p.) are uncorrected.

2. The generated nitrogen-centered radicals by single-electron oxidation of N–H substrates

![Figure S1: Representative Nitrogen-Centered Radical Intermediates.](image)

3. Representative Experimental Procedure

Representative procedure for the preparation of 3 (with 3a as an example): A 25-mL round-bottomed flask, equipped with a magnetic stirring bar, is charged with 1a (1.0 mmol, 0.13
mL), 2a (1.1 mmol, 0.19 mL) and Cs₂CO₃ (1.5 mmol, 489 mg) in MeCN (2 mL). The reaction mixture was irradiated with 36 W CFL. After the starting material 1a was consumed as indicated by TLC. The reaction mixture was poured into water and then extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phase was washed with water (3 x 10 mL), dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on 200-300 mesh silica gel that was dealt with Et₃N/PE (1:9) (petroleum ether : ethyl acetate = 1:1) to give N-(bis(dimethylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide 3a (215 mg, 69%) as a white solid (Rf = 0.25, petroleum ether : ethyl acetate = 1 : 3).

4. Mechanistic Studies

1) The possibility of radical homolytic cleavage of perfluorobutyl iodide (2a) under 36 W CFL irradiation to generate perfluorobutyl radical and iodine radical can be excluded according to the photostability experiment, reported in the literature.²

2) We have conducted a heavy oxygen water experiment to elucidate the source of oxygen in products 3.

A 5 mL round-bottomed flask equipped with a magnetic stirring bar, 1a (0.1 mmol, 12.5 µL), 2a (1.1 mmol, 18.9 µL) and Cs₂CO₃ (0.15 mmol, 48.9 mg) were dissolved in super dry CH₃CN (0.5 mL). H₂O¹⁸ (0.1 mmol, 1.8 µL) was added to the solution and the mixture was irradiated by 36 W CFL. After 12 h, the labeled product O¹⁸-3c was detected by HRMS analysis.

3) 2,3-Dimethyl-but-2-ene can be used as a trapping agent for singlet oxygen. Upon addition of 2,3-dimethyl-but-2-ene to the reaction system, product 4 was detected by $^1$H NMR spectroscopy, indicating the presence of $^1$O₂.

A solution of 1a, 2a and Cs₂CO₃ in CH₃CN (0.5 mM) was put into a 25 mL round-bottomed flask with a magnetic stirring bar. A 30-fold excess of 2,3-dimethyl-2-butene was added to the solution and the sample was irradiated by 36 W CFL. After 20 h, the yield of the product 3a decreased obviously as indicated by TLC. $^1$H NMR spectra was acquired with simultaneous saturation of the large signal at about 1.6 ppm due to unreacted 2,3-dimethyl-2-butene, 2.9 ppm due to achieved product 3a and 2.0 ppm derived from solvent CH₃CN. The characteristic two olefin proton signals for trapped hydroperoxide appear in the open window of 4.97 and 5.01 ppm, which is consistent with that reported in the literature.³
Figure S3. Parallel $^1$H NMR spectra of TMG and C$_4$I$_9$ reaction mixture: (A) in the presence of 30-fold excess 2,3-dimethyl-2-butene. (B) no additive. red ball in A: signals at 4.97 and 5.01 ppm correspond to the two olefin protons for trapped product 4.

5. DFT Calculation
Computational Details:
All geometries were optimized without symmetry constraints at the level of the (U)B3LYP-D3 functional. The solvent effect was considered by employing the SMD model and acetonitrile (CH$_3$CN) solvent. The LanL2DZ and corresponding Hay–Wadt effective core potential (ECP) were applied for the core electrons of I, while the standard 6-31G(d) basis set was used for the other main-group elements. The vibrational frequency was calculated to check the nature of each stationary structure at the same theoretical level with optimization. No imaginary frequency was found for all reactants, intermediates, and products. All the DFT calculations were performed with the Gaussian 09 package.

Figure S4. The energy level diagram of TCTC II.
alternative O$_2$-facilitated SET process

Scheme S1. Proposed alternative mechanism for the O$_2$-facilitated SET process.

Figure S5. The energy profiles of O$_2$-facilitated SET process.
6. Analytical Data for Compounds 3

\[ \text{N-(bis(dimethylamino)methylene)-2,2,3,3,4,4,4-heptfluorobutanamide (3a)} \]

\[ \text{N} \]
\[ \text{O} \]
\[ 3a \]

215 mg, 69% yield; White solid; m. p. 46-47 °C. \( ^1 \text{H NMR} \) (500 MHz, CDCl\(_3\)): \( \delta \) 2.99 (s, 12H); \n\( ^{13} \text{C NMR} \) (125 MHz, CDCl\(_3\)): \( \delta \) 40.3, 106.4-107.5 (m), 108.2, 108.5, 108.8, (t, \( J = 37.5 \) Hz), 109.3-110.6 (m), 114.6-116.9 (m), 114.2, 114.5, 114.9 (t, \( J = 43.8 \) Hz), 116.5, 116.8, 117.1 (t, \( J = 37.5 \) Hz), 118.8, 119.1, 119.5 (t, \( J = 43.8 \) Hz), 121.0, 121.3, 121.7 (t, \( J = 43.8 \) Hz), 161.3, 161.5, 161.7 (t, \( J = 31.3 \) Hz), 168.4; \n\( ^{19} \text{F NMR} \) (470 MHz, CDCl\(_3\)): \( \delta \) -128.3 (s, 2F), -120.0 (q, \( J = 4.5 \) Hz, 2F), -82.6 (t, \( J = 8.9 \) Hz, 3F); \nHRMS (ESI) (m/z): Calcd for C\(_9\)H\(_{12}\)F\(_7\)N\(_3\)O (M+H): 312.0947, found 312.0951.

\( (E)-\text{N-(amino(dimethylamino)methylene)-2,2,3,3,4,4,4-heptfluorobutanamide (3b)} \]

\[ \text{N} \]
\[ \text{O} \]
\[ 3b \]

173 mg, 61% yield; White solid; m. p. 83-84 °C. \( ^1 \text{H NMR} \) (400 MHz, DMSO-\( d_6 \)): \( \delta \) 2.97 (s, 3H), 3.05 (s, 3H), 7.85 (s, 1H), 8.58 (s, 1H); \n\( ^{13} \text{C NMR} \) (100 MHz, DMSO-\( d_6 \)): \( \delta \) 36.1, 37.1, 105.5, 105.8, 106.2, 106.6 (q, \( J = 36.7 \) Hz), 110.8-113.7 (m), 115.9 116.2, 116.5 (t, \( J = 30.0 \) Hz), 118.7, 119.1, 119.4 (t, \( J = 35.0 \) Hz), 121.5, 121.9, 122.2 (t, \( J = 35.0 \) Hz), 160.3, 163.1, 163.3, 163.5 (t, \( J = 20.0 \) Hz); \n\( ^{19} \text{F NMR} \) (376 MHz, DMSO-\( d_6 \)): \( \delta \) -126.0 (s, 2F), -117.4 (s, 2F), -80.2 (d, \( J = 7.9 \) Hz, 3F); \nHRMS (ESI) (m/z): Calcd for C\(_7\)H\(_8\)F\(_7\)N\(_3\)O (M+H): 284.0634, found 284.0637.

\( (E)-\text{N-(amino(piperidin-1-yl)methylene)-2,2,3,3,4,4,4-heptfluorobutanamide (3c)} \]

\[ \text{N} \]
\[ \text{O} \]
\[ 3c \]

210 mg, 65% yield; White solid; m. p. 109-110 °C. \( ^1 \text{H NMR} \) (300 MHz, CDCl\(_3\)): \( \delta \) 1.65 (m, 6H),
3.57 (s, 4H), 7.45 (s, 2H);

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 23.9, 25.2, 45.2, 106.7-107.4 (m), 108.4, 108.7, 108.9 (t, $J = 37.5$ Hz), 110.2-110.9 (m), 114.7, 115.0, 115.3 (t, $J = 45.0$ Hz), 116.6, 116.9, 117.3 (t, $J = 52.5$ Hz), 118.5, 118.8, 119.2 (t, $J = 52.5$ Hz), 120.4, 120.7 121.1 (t, $J = 52.5$ Hz), 159.1, 166.3, 166.4, 166.6 (t, $J = 22.5$ Hz);

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -126.4 (s, 2F), -118.7 (q, $J = 4.1$ Hz, 2F), -80.7 (t, $J = 9.0$ Hz, 3F);

HRMS (ESI) ($m/z$): Calcd for C$_{10}$H$_{12}$F$_7$N$_3$O (M+H)$^+$ : 324.0947, found 324.0950.

$(E)$-N-(amino(morpholino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3d)

215 mg, 66% yield; White solid; m. p. 81-82 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.62 (s, 8H), 8.13 (s, 1H), 8.72 (s, 1H);

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 44.1, 65.4, 105.5, 105.8, 106.1, 106.5 (q, $J = 33.3$ Hz), 108.1-109.1 (m), 110.7-111.8 (m), 113.0, 113.3, 113.6 (t, $J = 30.0$ Hz), 115.8, 116.2, 116.5 (t, $J = 35.0$ Hz), 118.7, 119.0, 119.4 (t, $J = 35.0$ Hz), 121.5, 121.9, 122.2 (t, $J = 35.0$ Hz), 159.3, 163.7, 163.9, 164.2 (t, $J = 25.0$ Hz);

$^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta$ -126.0 (s, 2F), -117.5 (d, $J = 7.9$ Hz, 2F), -80.3 (s, 3F);

HRMS (ESI) ($m/z$): Calcd for C$_9$H$_{10}$F$_7$N$_3$O$_2$ (M+H)$^+$ : 326.0739, found 326.0743.

$(E)$-N-(amino(1H-pyrazol-1-yl)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3e)

184 mg, 60% yield; White solid; m. p. 127-128 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.37 (s, 1H), 6.54 (s, 1H), 6.85 (s, 1H), 7.87 (s, 1H), 8.60 (d, $J = 1.5$ Hz, 1H);

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 104.1-106.3(m), 107.1-108.9 (m), 110.8, 111.2-113.4 (m), 114.7, 115.7, 116.0, 116.4 (t, $J = 35.0$ Hz), 118.5, 118.8, 119.2 (t, $J = 35.0$ Hz), 121.3, 121.6, 122.0 (t, $J = 35.0$ Hz), 130.0, 144.9, 164.7, 164.9 165.2 (t, $J = 25.0$ Hz), 167.4;

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -126.1 (s, 2F), -118.4 (q, $J =4.5$ Hz, 2F), -80.3 (t, $J = 9.0$ Hz, 3F);

HRMS (ESI) ($m/z$): Calcd for C$_9$H$_5$F$_7$N$_4$O (M+H)$^+$ : 307.0430, found 307.0433.
(E)-N-(amino(methylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3f)

\[
\begin{align*}
\text{C}_5\text{F}_7 & \quad \text{\(NH\)} \\
\text{\(\text{NH}_2\)} & \quad \text{\(O\)} \\
\text{3f}
\end{align*}
\]

159 mg, 59% yield; White solid; m. p. 89-90 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 2.73 (d, \(J = 11.2\) Hz, 3H), 7.58 (s, 1H), 8.26 (s, 1H), 8.53 (s, 1H);

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 27.4, 105.6, 105.9, 106.2, 106.5 (q, \(J = 30.0\) Hz), 108.1-109.5 (m), 110.8-112.2 (m), 113.0, 113.3, 113.7 (t, \(J = 35.0\) Hz) 115.8, 116.2, 116.5 (t, \(J = 35.0\) Hz), 118.7, 119.0, 119.4 (t, \(J = 35.0\) Hz), 121.5, 121.9, 122.2 (t, \(J = 35.0\) Hz), 161.9, 164.1, 164.4, 164.6 (t, \(J = 25.0\) Hz);

\(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): \(\delta\) -126.7 (s, 2F), -119.2 (d, \(J = 3.9\) Hz, 2F), -80.7 (t, \(J = 8.3\) Hz, 3F);

HRMS (ESI) (m/z): Calcd for C\(_6\)H\(_6\)F\(_7\)N\(_3\)O (M+H): 270.0477, found 270.0475.

(\(E\))-N-(amino(isopropylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3g)

\[
\begin{align*}
\text{C}_5\text{F}_7 & \quad \text{\(NH\)} \\
\text{\(\text{NH}_2\)} & \quad \text{\(O\)} \\
\text{3g}
\end{align*}
\]

187 mg, 63% yield; White solid; m. p. 126-127 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 1.09-1.15 (m, 6H), 3.72-4.00 (m, 6H), 7.23 (s, 1H), 7.67 (s, 1H), 8.36-8.51 (m, 1H);

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 21.9, 22.2, 42.5, 105.5, 105.8, 106.1, 106.4 (q, \(J = 30.0\) Hz) 107.8-109.3 (m), 110.3-114.7 (m), 115.8, 116.2, 116.5 (t, \(J = 35.0\) Hz), 118.7, 119.0, 119.4 (t, \(J = 35.0\) Hz), 121.6, 121.9, 122.2 (t, \(J = 30.0\) Hz), 160.1, 164.1-164.9 (m);

\(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): \(\delta\) -126.0 (s, 2F), -117.3- -117.6 (m, 2F), -80.3 (s, 3F);

HRMS (ESI) (m/z): Calcd for C\(_8\)H\(_{10}\)F\(_7\)N\(_3\)O (M+H): 298.0790, found 298.0786.

(\(E\))-N-(amino(phenylamino)methylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3h)

\[
\begin{align*}
\text{C}_5\text{F}_7 & \quad \text{\(NH\)} \\
\text{\(\text{NH}_2\)} & \quad \text{\(O\)} \\
\text{3h}
\end{align*}
\]

S9
189 mg, 57% yield; White solid; m. p. 71-72 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 7.19 (s, 1H), 7.35-7.39 (m, 4H), 7.61 (s, 2H), 8.71 (s, 1H), 9.82 (s, 1H);

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 105.5, 105.8, 106.1, 106.5 (t, \(J = 33.3\) Hz), 108.0-109.1 (m), 110.7-113.3 (m), 115.8, 116.1, 116.5 (t, \(J = 35.0\) Hz), 118.6, 119.0, 119.3 (t, \(J = 35.0\) Hz), 123.0, 125.2, 129.0, 136.6, 159.7, 165.2, 165.4, 165.7 (t, \(J = 25.0\) Hz);

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -126.5 (s, 2F), -119.2 (q, \(J = 8.3\) Hz, 2F), -80.7 (t, \(J = 8.6\) Hz, 3F);

HRMS (ESI) (m/z): Calcd for C\(_{11}\)H\(_8\)F\(_7\)N\(_3\)O (M+H)\(^+\) : 332.0634, found 332.0630.

\(N\)-(diaminomethylene)-2,2,3,3,4,4,4-heptafluorobutanamide (3i)

\(133\) mg, 52% yield; White solid; m. p. 85-86 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 7.27 (s, 2H), 7.44 (s, 2H);

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 105.3, 105.6, 105.8, 106.0 (q, \(J = 23.3\) Hz), 107.3-109.0 (m), 109.7-113.1 (m), 115.7, 116.0, 116.3 (t, \(J = 30.0\) Hz), 118.5, 118.9, 119.2 (t, \(J = 35.0\) Hz), 121.4, 121.7, 122.1 (t, \(J = 35.0\) Hz), 163.4, 163.6, 163.9 (t, \(J = 25.0\) Hz), 166.7;

\(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): \(\delta\) -126.1 (s, 2F), -117.9 (d, \(J = 7.9\) Hz, 2F), -80.1 (s, 3F);

HRMS (ESI) (m/z): Calcd for C\(_5\)H\(_4\)F\(_7\)N\(_3\)O (M+H)\(^+\) : 256.0321, found 256.0325.

2,2,3,3,4,4,4-Heptafluoro-\(N\)-(imidazolidin-2-ylidene)butanamide (3j)

\(169\) mg, 60% yield; White solid; m. p. 157-158 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 3.58 (s, 4H), 8.44 (s, 2H);

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 41.6, 105.8, 106.1, 106.4 (t, \(J = 30.0\) Hz), 108.1-109.2 (m), 110.6-111.8 (m), 113.0, 113.3, 133.7 (t, \(J = 35.0\) Hz), 115.8, 116.2, 116.5 (t, \(J = 35.0\) Hz), 118.7, 119.0, 119.4 (t, \(J = 35.0\) Hz), 121.6, 121.9, 122.2 (t, \(J = 30.0\) Hz), 164.5, 164.7, 164.9, 165.1 (t, \(J = 20.0\) Hz);
**19F NMR** (376 MHz, DMSO-d$_6$): $\delta$ -126.1 (s, 2F), -117.5 (q, $J$ = 8.2 Hz, 2F), -80.3 (t, $J$ = 8.5 Hz, 3F);

**HRMS** (ESI) (m/z): Calcd for C$_7$H$_6$F$_7$N$_3$O (M+H)$^+$ : 282.0477, found 282.0479.

**Methyl (E)-N′-(2,2,3,3,4,4-heptafluorobutanoyl)carbamimidothioate (3k)**

177 mg, 62% yield; White solid; m. p. 66-67 °C. **1H NMR** (300 MHz, CDCl$_3$): $\delta$ 2.54 (s, 3H), 6.58 (s, 1H), 9.71 (s, 1H);

**13C NMR** (150 MHz, CDCl$_3$): $\delta$ 9.2, 101.9-104.0 (m), 105.4, 110.1-111.8, 112.0, 112.3, 112.7 (t, $J$ = 37.5 Hz), 113.7, 113.9, 114.2 (t, $J$ = 37.5 Hz), 115.8, 162.1, 162.3, 162.5 (t, $J$ = 30.0 Hz), 173.6;

**19F NMR** (376 MHz, DMSO-d$_6$): $\delta$ -126.1 (s, 2F), -117.9 (q, $J$ = 4.3 Hz, 2F), -80.0 (t, $J$ = 8.3 Hz, 3F);

**HRMS** (ESI) (m/z): Calcd for C$_6$H$_5$F$_7$N$_3$O (M+H)$^+$ : 287.0089, found 287.0091.

**N-(bis(dimethylamino)methylene)-2,2,3,3,3-pentafluoropropanamide (3l)**

188 mg, 72% yield; White solid; m. p. 50-51 °C. **1H NMR** (400 MHz, CDCl$_3$): $\delta$ 2.99 (s, 12H);

**13C NMR** (100 MHz, CDCl$_3$): $\delta$ 40.2, 104.5, 104.9, 105.2, 105.6 (q, $J$ = 33.3 Hz ), 107.1, 107.4, 107.8, 108.2 (q, $J$ = 36.7 Hz ), 109.7, 110.0, 110.4 (t, $J$ = 35.0 Hz), 114.2, 114.5, 114.9 (t, $J$ = 35.0 Hz), 117.2, 117.4, 117.7 (t, $J$ = 25.0 Hz), 119.9, 120.2, 120.6 (t, $J$ = 35.0 Hz), 122.7, 123.1, 123.4 (t, $J$ = 35.0 Hz), 161.2, 161.4, 161.7 (t, $J$ = 25.0 Hz), 168.4;

**19F NMR** (CDCl$_3$, 376 MHz): $\delta$ -120.6 (s, 2F), -82.3 (s, 3F);

**HRMS** (ESI) (m/z): Calcd for C$_8$H$_{12}$F$_5$N$_2$O (M+H)$^+$ : 262.0979, found 262.0981.

**N-(bis(dimethylamino)methylene)-2,2,3,3,4,4,5,5,6,6,6-undecafluorohexanamide (3m)**
280 mg, 68% yield; White solid; m. p. 51-52 °C. $^1$H NMR (500 MHz, CDCl$_3$): δ 2.99 (s, 12H); $^{13}$C NMR (75.0 MHz, CDCl$_3$): δ 40.3, 105.1-107.9 (m), 106.4-107.5 (m), 108.3-110.5 (m), 111.0-114.1 (m), 114.9, 115.8, 116.3 (t, J = 45.0 Hz), 118.8, 119.2, 119.6 (t, J = 30.0 Hz), 120.9, 121.3, 121.7 (t, J = 30.0 Hz), 161.2, 161.5, 161.8 (t, J = 22.5 Hz), 168.3;

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -126.2 (q, J = 5.5 Hz, 2F), -122.4 (s, 2F), -122.0 (s, 2F), -117.1 (t, J = 12.8 Hz, 2F), -80.8 (m, 3F);

HRMS (ESI) (m/z): Calcd for C$_{11}$H$_{12}$F$_{11}$N$_3$O (M+H)$^+$: 412.083, found 412.080.

$N$-(bis(dimethylamino)methylene)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide (3n)

378 mg, 74% yield; White solid; m. p. 38-39 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ 2.99 (s, 12H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 39.8, 104.7, 106.0, 106.4, 106.7 (q, J = 33.3 Hz), 106.6-108.8 (m), 109.5-111.1 (m), 111.6-114.2 (m), 114.8, 115.2, 155.5 (t, J = 35.0 Hz), 117.7, 118.0, 118.4 (t, J = 35.0 Hz), 120.6, 120.9, 121.2 (t, J = 30.0 Hz), 158.8, 159.1, 159.3 (t, J = 25.0 Hz), 166.9;

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -126.1 (s, 2F), -122.7 (s, 2F), -122.0 (s, 2F), -117.1 (t, J = 12.8 Hz, 2F), -80.8 (m, 3F);

HRMS (ESI) (m/z): Calcd for C$_{13}$H$_{12}$F$_{13}$N$_3$O (M+H)$^+$: 512.0819, found 512.0817.

$N$-(bis(dimethylamino)methylene)-2-chloro-2,2-difluoroacetamide (3o)

137 mg, 60% yield; White solid; m. p. 178-179 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ 2.99 (s, 12H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 39.9, 117.8, 120.8, 123.8, 161.0, 161.2, 161.5 (t, J = 25.0 Hz), 167.1;
\(^{19}\text{F NMR}\) (376 MHz, DMSO-\(d_6\)): \(\delta\) -60.3 (s, 2F);
\(\text{HRMS (ESI)}\ (m/z)\): Calcd for C\(_7\)H\(_{12}\)ClF\(_2\)N\(_3\)O (M+H\(^+\)) : 228.0715, found 228.0717

7. References


8. Copies of $^1$H and $^{13}$C NMR Spectra for Compounds 3.