Supporting Information for:

Metal-Free Cascade Cyclization of Alkenes toward Polyfluorinated Oxindoles

Shi Tang,*a,c Zhi-Hao Li,a Ming-Wei Wang,a Zhi-Ping Li,a and Rui-Long Sheng*b

a College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000 (China)
bShanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032(China)
cCollege of Chemistry and Chemical Engineering, Central South University, Changsha 410083(China)

General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Flash column chromatography was performed using silica gel (200-300 mesh) and a petroleum ether/ethyl acetate combination was used as the eluent. Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F 254 (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO 4 solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra ( 1 H NMR and 13 C NMR) were recorded on a Varian Mercury 400 or 500 ( 1 H NMR, 400 MHz; 13 C NMR, 101 MHz; 1 H NMR, 500 MHz, 13 C NMR, 125 MHz,) spectrometer with solvent resonance ( 1 H NMR, CHCl 3 at 7.26 ppm, and SiMe 4 at 0 ppm; 13 C NMR, CDCl 3 at 77.0
pm and SiMe$_4$ at 0 ppm) as the internal standard. $^1$HNMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad), coupling constants (Hz), and integration. $^{19}$F NMR spectra were obtained by the same NMR spectrometer.

**Chemicals.** Unless otherwise noted, reagents were commercially available and were used without further purification. Anhydrous THF was distilled from sodium/benzophenone prior to use. Preparation of $N$-arylacrylamides 1 were prepared according to literature procedures.$^1$

**3. General Procedures**

**General procedure for the synthesis of perfluorinated oxindoles.** To a mixture of $N$-arylacrylamide 1 (0.3 mmol), AIBN (2.0 equiv.), perfluoroalkyl iodine (2 equiv.) in CH$_3$CN (2.0 mL) was added tBuOO-tBu (2.0 equiv.) dropwise, and then the resulting solution was stirred at 105 °C for 12 h. The solvent was evaporated under reduced pressure and the resulted mixture was filtered through a Florisil pad, diluted with Et$_2$O, and washed with water and then brine. The organic layer was dried over anhydrous MgSO$_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the corresponding perfluorinated oxindole in a yield listed in Scheme 1 and 2.

**1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a).$^{1a}$** $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.36-7.22 (m, 2H), 7.08 (t, $J$ = 7.5 Hz, 1H), 6.88 (d, $J$ = 8.0 Hz, 1H), 3.23 (s, 3H), 2.97-2.43 (m, 2H), 1.41 (s, 3H).

**1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a).$^{1a}$**
nonafluoropentyl)indolin-2-one (3b). Yellowish oil. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.33-7.23 (m, 2H), 7.06 (t, \( J = 7.2 \) Hz, 1H), 6.89 (d, 2\( J = 8.0 \) Hz, 2H), 3.93-3.62 (m, 2H); \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 178.1, 141.7, 131.5, 128.4, 123.7, 122.4, 121.4, 125.0-114.2 (m), 44.1, 36.9 (t, \( J = 21 \) Hz), 34.7, 26.0, 12.2; \( ^{19} \)F NMR (376 MHz, CDCl\(_3\)) \( \delta \): -81.0 (t, \( J = 9.4 \) Hz, 3F), -108.8 (AB, m, \( J_{F,F} = 268 \) Hz, 1F), -114.7 (AB, m, \( J_{F,F} = 273 \) Hz, 1F), -124.6 (br, 2F), -126.0~ -125.6 (m, 2F); HRMS m/z (ESI) calcd for C\(_{16}\)H\(_{15}\)F\(_9\)NO [M+H]\(^+\): 408.1005, found: 408.1007.

1-Ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3c). Yellowish oil. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.34-7.13 (m, 7H), 7.04 (t, \( J = 8.4 \) Hz, 1H), 6.75 (d, \( J = 8.0 \) Hz, 2H), 4.94 (d, \( J = 3.6 \) Hz, 2H), 2.93 (dd, \( J = 35.6, 14.4 \) Hz, 1H), 2.65 (dd, \( J = 31.2, 15.2, 8.0 \) Hz, 1H), 1.48 (s, 3H); \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 178.6, 141.9, 135.7, 131.2, 127.3, 123.6, 122.6, 109.5, 44.3, 44.0, 36.6 (t, \( J = 20.4 \) Hz), 26.5; \( ^{19} \)F NMR (376 MHz, CDCl\(_3\)) \( \delta \): -81.1 (t, \( J = 8.1 \) Hz, 3F), -107.6 (d, \( J_{F,F} = 264 \) Hz, 1F), -114.3 (d, \( J_{F,F} = 270 \) Hz, 1F), -124.5 (br, 2F), -125.4~ -126.1 (m, 2F); HRMS m/z (ESI) calcd for C\(_{21}\)H\(_{17}\)F\(_9\)NO [M+H]\(^+\): 470.1161, found: 470.1163.

1,3,5-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e). Yellowish solid. m.p. 62-63 °C. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.12-7.05 (m, 2H), 6.76 (d, \( J = 8.4 \) Hz, 1H), 3.21 (s, 3H), 2.85 (dd, \( J = 35.2, 15.6 \) Hz, 1H), 2.56 (ddd, \( J = 31.2, 15.2, 8.0 \) Hz, 1H), 2.34 (s, 3H), 1.40 (s, 3H); \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 178.5, 140.4, 132.2, 131.3, 128.8, 124.4, 125.0-114.1 (m), 108.1, 44.2, 36.9 (t, \( J = 23 \) Hz), 26.5, 25.9, 21.1; \( ^{19} \)F NMR (376 MHz, CDCl\(_3\)) \( \delta \): -81.0 (t, \( J = 8.0 \) Hz, 3F), -108.9 (d, \( J_{F,F} = 272 \) Hz, 1F), -114.7 (d, \( J_{F,F} = 273 \) Hz, 1F), -124.6 (br, 2F), -125.0~ -126.2 (m, 2F); HRMS m/z (ESI) calcd for C\(_{16}\)H\(_{15}\)F\(_9\)NO [M+H]\(^+\): 408.1005, found: 408.1002.

5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f). Yellowish oil. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.34-7.13 (m, 7H), 7.04 (t, \( J = 8.4 \) Hz, 1H), 6.75 (d, \( J = 8.0 \) Hz, 2H), 4.94 (d, \( J = 3.6 \) Hz, 2H), 2.93 (dd, \( J = 35.6, 14.4 \) Hz, 1H), 2.65 (dd, \( J = 31.2, 15.2, 8.0 \) Hz, 1H), 1.48 (s, 3H); \( ^{13} \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 178.5, 140.4, 132.2, 131.3, 128.8, 124.4, 125.0-114.1 (m), 108.1, 44.2, 36.9 (t, \( J = 23 \) Hz), 26.5, 25.9, 21.1; \( ^{19} \)F NMR (376 MHz, CDCl\(_3\)) \( \delta \): -81.0 (t, \( J = 8.0 \) Hz, 3F), -108.9 (d, \( J_{F,F} = 272 \) Hz, 1F), -114.7 (d, \( J_{F,F} = 273 \) Hz, 1F), -124.6 (br, 2F), -125.0~ -126.2 (m, 2F); HRMS m/z (ESI) calcd for C\(_{16}\)H\(_{15}\)F\(_9\)NO [M+H]\(^+\): 408.1005, found: 408.1002.
**nonafluoropentyl)indolin-2-one (3f).** Yellowish oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.92-6.74 (m, 3H), 3.79 (s, 3H), 3.21 (s, 3H), 2.86 (dd, $J = 35.0, 15.6$ Hz, 1H), 2.56 (ddd, $J = 30.8, 15.6, 8.4$ Hz, 1H), 1.41 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.2, 156.4, 136.3, 132.7, 125.0-114.1 (m), 112.5, 111.3, 108.7, 55.8, 44.6, 36.6 (t, $J = 31.1$ Hz), 26.5, 25.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -81.0 (t, $J = 8.0$ Hz, 3F), -108.8 (d, $J_{F-F} = 268$ Hz, 1F), -114.9 (d, $J_{F-F} = 273$ Hz, 1F), -124.6 (br, 2F), -125.2~ -126.3 (m, 2F); HRMS $m/z$ (ESI) calcd for C$_{16}$H$_{15}$F$_9$NO $[M+H]^+$: 424.0954, found: 424.0926.

**5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5- nonafluoropentyl)indolin-2-one (3g).** Yellowish solid.

m.p. 78-79 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06-6.95 (m, 2H), 6.93-6.75 (m, 1H), 3.22 (s, 3H), 2.87 (dd, $J = 34.8$ Hz, 15.2 Hz, 1H), 2.56 (ddd, $J = 30.8, 15.6, 8.0$ Hz, 1H), 1.42 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.2, 159.3 (d, $J = 241.9$ Hz), 138.8, 132.9, 125.0-114.2 (m), 114.8 (d, $J = 27.6$ Hz), 111.8 (d, $J = 25.5$ Hz), 109.0 (d, $J = 8.2$Hz), 44.6, 36.9 (t, $J = 20.2$ Hz), 26.6, 25.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -81.0 -81.0 (t, $J = 8.0$ Hz, 3F), -108.7 (d, $J_{F-F} = 273$ Hz, 1F), -114.6 (d, $J_{F-F} = 266.9$ Hz, 1F), -120.4 (s, 1F), -124.6 (br, 2F), -125.2~ -126.2 (m, 2F); HRMS $m/z$ (ESI) calcd for C$_{16}$H$_{12}$F$_{10}$NO $[M+H]^+$ 412.0754, found: 412.0758.

**chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5- nonafluoropentyl)indolin-2-one (3h).** Yellowish solid.

m.p. 73-74 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31-7.21 (m, 2H), 6.79 (d, $J = 8.4$ Hz, 1H), 3.20 (s, 3H), 2.87 (dd, $J = 35.2, 15.6$ Hz, 1H), 2.65 (ddd, $J = 30.8, 15.6, 8.4$ Hz, 1H), 1.41 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.0, 141.4, 132.9, 128.1, 125.0-114.0 (m), 124.1, 109.5, 44.4, 36.9 (t, $J = 20.2$Hz), 26.6, 25.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -81.0 (t, $J = 8.0$ Hz, 3F), -108.7 (d, $J_{F-F} = 273$ Hz, 1F), -114.6 (d, $J_{F-F} = 266.9$ Hz, 1F), -120.4 (s, 1F), -124.6 (br, 2F), -125.2~ -126.2 (m, 2F); HRMS $m/z$ (ESI) calcd for C$_{15}$H$_{12}$ClF$_9$NO $[M+H]^+$ 428.0459, found: 428.0462.

**1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5- nonafluoropentyl)-
5-(trifluoromethyl)indolin-2-one (3i). Yellowish solid. m.p. 92-93 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, $J = 8.4$ Hz), 7.50 (s, 1H), 6.96(d, $J = 8.4$ Hz, 1H), 3.27 (s, 3H), 2.92 (dd, $J = 35.2$ Hz, 15.6 Hz, 1H), 2.63 (ddd, $J = 30.8$, 15.6, 8.4 Hz, 1H), 1.45 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.4, 145.8, 131.7, 126.3 (q, $J = 3.8$Hz), 124.0 (q, $J = 32.9$ Hz), 124.4 (q, $J = 272.8$ Hz), 124.0-114.0 (m). 109.5, 44.1, 36.9 (t, $J = 20.1$ Hz), 26.6, 25.7; $^{19}$F NMR (282 MHz, CDCl$_3$) δ: -61.3 (t, $J = 8.0$ Hz, 3F), -81.0 (t, $J = 8.0$ Hz, 3F)), -108.5 (d, $J_{F-F} = 274$ Hz, 1F), -114.7 (d, $J_{F-F} = 272$ Hz, 1F), -124.6 (br, 2F), -125.3~ -127.0 (m, 2F); HRMS m/z (ESI) calcd for C$_{16}$H$_{12}$F$_{12}$NO [M+H]$^+$: 462.0722, found: 462.0726.

Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindoline-5-carboxylate (3i). Yellowish oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (dd, $J = 8.4$, 1.6 Hz, 1H), 7.93 (s, 1H), 6.91(d, $J = 8.4$Hz, 1H), 3.27 (s, 3H), 4.36 (q, $J = 7.2$Hz, 2H), 2.91 (dd, $J = 35.2$, 15.6 Hz, 1H), 2.64 (ddd, $J = 30.8$, 15.6, 8.4 Hz, 1H), 1.44 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.8, 166.2, 146.8, 131.1, 125.0, 124.8, 125.0-114.0 (m), 108.0, 61.0, 43.9, 36.2 (t, $J = 20.2$ Hz), 26.5, 25.8, 14.4; $^{19}$F NMR (282 MHz, CDCl$_3$) δ: -81.0 (t, $J = 8.0$ Hz, 3F), -108.7 (d, $J_{F-F} = 265$ Hz, 1F), -114.7 (d, $J_{F-F} = 268$ Hz, 1F), -124.5 (br, 2F), -125.2~ -126.9 (m, 2F); HRMS m/z (ESI) calcd for C$_{18}$H$_{17}$F$_9$NO$_3$ [M+H]$^+$: 466.1060, found: 466.1063.

Ethyl 1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k). Yellowish solid. m.p. 115-116 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.10 (d, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 7.5$Hz, 1H), 3.52 (s, 3H), 2.89 (dd, $J = 35.2$, 15.6 Hz, 1H), 2.65-2.50(m, 4H), 1.40 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 179.2, 140.4, 132.0, 131.7, 125.0-114.0 (m), 122.3, 121.3, 119.9, 43.3, 36.0 (t, $J = 20.3$ Hz), 29.7, 26.3, 18.9; $^{19}$F NMR (470 MHz, CDCl$_3$) δ: -81.1 (t, $J = 8.0$ Hz, 3F), -109.0 (A-B, $J_{F-F} = 269$ Hz, 1F), -114.7 (A-B, $J_{F-F} = 272$ Hz, 1F), -124.6 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS m/z (ESI) calcd for C$_{16}$H$_{15}$F$_9$NO [M+H]$^+$:
Mixture of 1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3l) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3l’). 3l:3l’ = 0.9:1. 

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23-6.68 (m, 3H), 3.21(s, 3H), 3.10-2.48 (m, 2H), 2.36(s, 3H), 1.46(s, 1.6H), 1.40(s, 1.4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 179.6, 179.3, 143.8, 143.6, 139.4, 135.5, 129.1, 129.0, 125.9, 124.1, 125.0-114.0 (m), 123.9, 122.2, 110.2, 107.0, 45.2, 44.7, 37.7 (t, $J$ = 20.4Hz), 36.7 (t, $J$ = 20.2Hz), 27.2, 26.6, 24.5, 24.1, 22.5, 18.9; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$: -81.0 (t, $J$ = 12.4 Hz, 3F), -107.9—117.9 (m, 2F), -124.7 (br, 2F), -125.1~ -126.7 (m, 2F); HRMS m/z (ESI) C$_{16}$H$_{15}$F$_{9}$NO [M+H]$^+$: 408.1005, found: 408.1004

Ethyl 4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m). Yellowish solid.

m.p. 98-99 °C. $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.97 (d, $J$ = 8.4 Hz, 1H), 6.89 (d, $J$ = 8.0 Hz, 1H), 3.51 (s, 3H), 3.13 (ddd, $J$ = 31.2, 15.2, 7.6 Hz, 1H), 2.85 (dd, $J$ = 35.2, 15.2 Hz, 1H), 2.56 (s, 3H), 1.51 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.8, 142.2, 133.4, 129.0, 127.9, 114.0-125.0 (m), 123.4, 118.8, 44.5, 36.1, 36.0 (t, $J$ = 20.1 Hz), 29.9, 22.9, 16.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -81.0 (t, $J$ = 8.0 Hz, 3F), -112.7 (A-B, $J_{F-F}$ = 270 Hz, 1F), -115.6 (A-B, $J_{F-F}$ = 272 Hz, 1F), -124.7 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS m/z (ESI) calcd for C$_{16}$H$_{14}$ClF$_9$NO [M+H]$^+$: 442.0615, found: 442.0618.

1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n). Yellowish solid.

m.p. 83-84 °C. $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23 (dd, $J$ = 4.8, 1.2 Hz, 1H), 7.23-7.09 (m, 2H), 3.25(s, 3H), 2.94-2.77 (m, 2H), 1.46 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.9, 152.2, 143.0, 137.9, 114.0-
125.0 (m), 123.2, 114.7, 46.2, 36.1 (t, \( J = 20.3\) Hz), 26.2, 24.1; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \( \delta \): -81.0 (t, \( J = 8.0\) Hz, 3F), -109.8 (A-B, \( J_{F,F} = 274\) Hz, 1F), -113.5 (A-B, \( J_{F,F} = 261\) Hz, 1F), -124.5 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS \( m/z \) (ESI) calcd for C\(_{14}\)H\(_{12}\)F\(_9\)N\(_2\)O \([M+H]^+\): 395.0801, found: 395.0798.

**(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindolin-3-yl)methyl acetate (3o).** Yellowish oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.38-7.24 (m, 2H), 7.07 (d, \( J = 7.6\) Hz, 1H), 6.86 (d, \( J = 8.0\) Hz, 1H), 4.38 (d, \( J = 10.8\) Hz, 1H), 4.07 (d, \( J = 10.8\) Hz, 1H), 2.99-2.69 (m, 2H), 1.97 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \): 175.2, 170.0, 143.5, 129.3, 126.9, 124.8-114.0 (m), 122.7, 108.6, 67.4, 47.9, 33.1 (t, \( J = 20.0\) Hz), 36.5, 20.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \): -81.1 (t, \( J = 3.4\) Hz, 3F), -108.1 (A-B, \( J_{F,F} = 272\) Hz, 1F), -114.1 (A-B, \( J_{F,F} = 276\) Hz, 1F), -124.4 (br, 2F), -125.2~ -126.8 (m, 2F); HRMS \( m/z \) (ESI) calcd for C\(_{17}\)H\(_{15}\)F\(_9\)NO\(_3\) \([M+H]^+\): 452.0903, found: 452.0907.

**(1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3q).** \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.36-7.26 (m, 2H), 7.11 (t, \( J = 7.5\) Hz, 1H), 6.90 (d, \( J = 7.5\) Hz, 1H), 3.26 (s, 3H), 2.90-2.78 (m, 1H), 2.72-2.63 (m, 1H), 1.42 (s, 3H).

**(1,3,5-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3r).** \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.15-7.08 (m, 2H), 6.79 (d, \( J = 8.0\) Hz, 1H), 3.23 (s, 3H), 2.87-2.77 (m, 1H), 2.70-2.58 (m, 1H), 2.37 (s, 3H), 1.41 (s, 3H).

**(3-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s).** Yellowish solid. m.p. 87-88 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.11 (d, \( J = 7.5\) Hz, 2H), 7.07 (d, \( J = 7.5\) Hz, 1H), 6.98 (d, \( J = 7.5\) Hz, 1H), 3.53 (s, 3H), 2.89 (dd, \( J = 35.5\), 15.5 Hz, 1H), 2.65-2.49 (m, 4H), 1.41 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 179.3,
140.6, 132.8, 131.8, 122.5, 125.0-114.0 (m), 121.4, 120.1, 43.5, 36.9 (t, \(J = 20.5\) Hz), 26.4, 24.8, 19.1; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta\): -80.3 (t, \(J = 8.0\) Hz, 3F), -109.6 (A-B, \(J_{F-F} = 270\) Hz, 1F), -115.6 (A-B, \(J_{F-F} = 271\) Hz, 1F), -127.2~ -128.6 (m, 2F); HRMS \textit{m/z} (ESI) calcd for C\(_{15}\)H\(_{15}\)F\(_7\)NO \([M+H]^+\): 358.1037, found: 358.1039.

5-Methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3t). Yellowish solid. m.p. 92-93 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 6.92-6.75 (m, 3H), 3.78 (s, 3H), 3.21 (s, 3H), 2.86 (dd, \(J = 35.2, 14.5\) Hz, 1H), 2.56 (ddd, \(J = 29.0, 14.5, 7.5\) Hz, 1H), 1.40 (s, 3H); 13\(^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\): 178.3, 136.0, 136.3, 132.7, 125.0-108.0 (m), 121.4, 112.5, 108.7, 55.8, 44.6, 36.9 (t, \(J = 20.2\) Hz), 26.5, 25.9; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -80.8 (t, \(J = 8.0\) Hz, 3F), -108.6 (A-B, \(J_{F-F} = 268\) Hz, 1F), -114.9 (A-B, \(J_{F-F} = 262\) Hz, 1F), -121.7 (br, 2F), -122.9 (br, 2F), -123.7 (br, 2F), -125.2~ -126.7 (m, 2F); HRMS \textit{m/z} (ESI) calcd for C\(_{18}\)H\(_{15}\)F\(_3\)NO \([M+H]^+\): 524.0890, found: 524.0893.

1,3,7-Trimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3u). Yellowish solid. m.p. 83-84 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.15-6.90 (m, 3H), 3.51 (s, 3H), 2.86 (dd, \(J = 35.2, 15.2\) Hz, 1H), 2.6-2.45 (m, 4H), 1.39 (s, 3H); 13\(^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\): 179.3, 140.5, 132.1, 131.8, 125.0-107.0 (m), 122.4, 121.3, 120.1, 43.5, 37.2 (t, \(J = 20.4\) Hz), 26.3, 25.3, 18.9; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\): -80.8 (t, \(J = 8.0\) Hz, 3F), -108.6 (A-B, \(J_{F-F} = 268\) Hz, 1F), -114.4 (A-B, \(J_{F-F} = 262\) Hz, 1F), -121.7 (br, 2F), -122.8 (br, 2F), -123.7 (br, 2F), -125.3~ -126.8 (m, 2F); HRMS \textit{m/z} (ESI) calcd for C\(_{18}\)H\(_{15}\)F\(_3\)NO \([M+H]^+\): 508.0941, found: 508.0937.

1,3-Dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-c]pyridin-2(3H)-one (3v). Yellowish oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.26 (dd, \(J = 5.5, 8.4\) Hz, 1H), 7.86-7.68 (m, 3H), 3.88 (s, 3H), 2.87 (dd, \(J = 35.2, 14.5\) Hz, 1H), 2.57 (ddd, \(J = 29.0, 14.5, 7.5\) Hz, 1H), 1.41 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 178.3, 140.5, 132.1, 131.8, 125.0-107.0 (m), 122.4, 121.3, 120.1, 43.5, 37.2 (t, \(J = 20.4\) Hz), 26.3, 25.3, 18.9; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\): -80.8 (t, \(J = 8.0\) Hz, 3F), -108.6 (A-B, \(J_{F-F} = 268\) Hz, 1F), -114.4 (A-B, \(J_{F-F} = 262\) Hz, 1F), -121.7 (br, 2F), -122.8 (br, 2F), -123.7 (br, 2F), -125.3~ -126.8 (m, 2F); HRMS \textit{m/z} (ESI) calcd for C\(_{18}\)H\(_{15}\)F\(_3\)NO \([M+H]^+\): 508.0941, found: 508.0937.
7.55 (d, \( J = 7.0 \) Hz, 1H), 7.02 (dd, \( J = 7.5, 5.0 \) Hz, 1H), 3.36 (s, 3H), 2.90 (dd, \( J = 35.5, 15.5 \) H, 1H), 2.63 (ddd, \( J = 31.0, 15.5, 8.0 \) Hz, 1H), 1.49 (s, 3H); \(^{13}\!C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 178.2, 156.2, 147.5, 131.4, 125.4, 125.0-109.0 (m), 118.2.8, 43.9, 36.7 (t, \( J = 20.4 \) Hz), 25.6, 25.1; \(^{19}\!F\) NMR (470 MHz, CDCl\(_3\)) \( \delta \): -80.8 (t, \( J = 8.0 \) Hz, 3F), -108.3 (A-B, \( J_{F-F} = 272 \) Hz, 1F), -114.0 (A-B, \( J_{F-F} = 270 \) Hz, 1F), -121.7 (br, 2F), -122.9 (br, 2F), -123.7 (br, 2F), -125.4- -126.9 (m, 2F); HRMS \( m/z \) (ESI) calcd for C\(_{20}\)H\(_{15}\)F\(_{13}\)N\(_2\O\)[M+H]\(^+\): 495.0737, found: 495.0734.

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1,3,7-trimethylindolin-2-one (3w). Yellowish solid. m.p. 101-102 °C. \(^1\!H\) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.15-6.93 (m, 3H), 3.53 (s, 3H), 2.90 (dd, \( J = 35.5, 15.5 \) Hz, 1H), 2.68-2.50 (m, 4H), 1.41 (s, 3H); \(^{13}\!C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 179.3, 140.6, 132.2, 131.8, 125.0-108.0 (m), 122.4, 121.4, 120.3, 120.1, 120.0-108.0 (m), 43.5, 37.2 (t, \( J = 20.2 \)Hz), 29.8, 26.4, 19.0; \(^{19}\!F\) NMR (470 MHz, CDCl\(_3\)) \( \delta \): -80.9 (t, \( J = 8.0 \) Hz, 3F), -108.9 (A-B, \( J_{F-F} = 269 \) Hz, 1F), -114.0 (A-B, \( J_{F-F} = 270 \) Hz, 1F), -121.8 (br, 2F), -122.1 (br, 4F), -122.9 (br, 2F), -123.8 (br, 2F), -126.1- -126.8 (m, 2F); HRMS \( m/z \) (ESI) calcd for C\(_{20}\)H\(_{15}\)F\(_{17}\)NO [M+H]\(^+\): 608.0877, found: 608.0879.

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,11,11,11-Henicosafluoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x). Yellowish solid. m.p. 121-123 °C. \(^1\!H\) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.63 (dd, \( J = 8.0, 6.0 \) Hz, 1H), 7.54 (s, 1H), 6.99 (d, \( J = 8.5 \) Hz), 2.96 (ddd, \( J = 35.5, 15.5, 8.0 \) Hz, 1H), 2.68 (ddd, \( J = 30.5, 15.5, 8.0 \) Hz, 1H), 1.40 (s, 3H); \(^{13}\!C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 178.4, 145.7, 131.7, 126.3 (q, \( J = 4.0 \) Hz), 125.1 (q, \( J = 32.5 \) Hz), 125.0-108.0 (m), 121.4, 120.7, 44.1, 37.1 (t, \( J = 20.4 \) Hz), 26.6, 25.8; \(^{19}\!F\) NMR (470 MHz, CDCl\(_3\)) \( \delta \): -62.0 (s, 3F), -80.7 (t, \( J = 8.0 \) Hz, 3F), -108.4 (A-B, \( J_{F-F} = 270 \) Hz, 1F), -114.0 (A-B, \( J_{F-F} = 272 \) Hz, 1F), -121.6 (br, 2F), 121.6-122.2 (m, 8F),
-122.8 (br, 4F), -123.9 (br, 2F), -126.1~ -126.8 (m, 2F); HRMS m/z (ESI) calcd for C$_{22}$H$_{12}$F$_{24}$NO [M+H]$^+$: 762.0631, found: 762.0628.


1 Copies of $^1$H NMR and $^{13}$C NMR spectra
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a)
3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a)
3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3a)
1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3b)
1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3b)
1-ethyl-3-methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3b)
3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3c)
3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile(3c)
3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile(3c)
1,3,5-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e)
trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e)
1,3,5-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3e)
5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f).
methoxy-1,3-dimethyl-3-(2,2,3,3,4,5,5,5-nonafluoropentyl)indolin-2-one (3f).
5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3f).
5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g)
5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g)
5-fluoro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3g)
chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h)
dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h)
chloro-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3h)
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-(trifluoromethyl)indolin-2-one (3i)
dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-(trifluoromethyl)indolin-2-one (3i)
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-5-(trifluoromethyl)indolin-2-one (3i)
Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindoline-5-carboxylate (3j)
Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindoline-5-carboxylate (3j)
Ethyl 1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindoline-5-carboxylate (3j)
Ethyl 1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k).
1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k).
Ethyl 1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3k).
mixture of 1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3l) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-
nonafluoropentyl)indolin-2-one (3l')
mixture of 1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3l) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-
nonafluoropentyl)indolin-2-one (3l′)
1,3,4-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3l) and 1,3,6-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3l')
4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m)
4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m)
4-chloro-1,3,7-trimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)indolin-2-one (3m)
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n)
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n)
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,5-nonfluoropentyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3n)
(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindolin-3-yl)methyl acetate (3o)
(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindolin-3-yl)methyl acetate (3o)
(1-Methyl-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-2-oxoindolin-3-yl)methyl acetate (3o)
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3q)
1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3q)
1,3,5-trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (3r)
1,3,5-trimethyl-3-(2,2,2-trifluoropropyl)indolin-2-one (3r)
3-(2,2,3,3,4,4,4-heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s)
3,3,4,4,4-heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s)
3-(2,2,3,3,4,4,4-heptafluorobutyl)-1,3,7-trimethylindolin-2-one (3s)
5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3t)
methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3t)
5-methoxy-1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)indolin-2-one (3t)
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-c]pyridin-2(3H)-one (3u).
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-c]pyridin-2(3H)-one (3u).
1,3-dimethyl-3-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-1H-pyrrolo[2,3-c]pyridin-2(3H)-one (3u).

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,3,7-trimethylindolin-2-one (3v)
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,3,7-trimethylindolin-2-one (3v)
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,3,7-trimethylindolin-2-one (3v)
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,3,7-trimethylindolin-2-one

(3w)
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,3,7-trimethylindolin-2-one (3w)
3-((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)-1,3,7-trimethylindolin-2-one (3w)
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-henicosafluoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x)
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-henicosfluoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x)
3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-henicosfluoroundecyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3x)