Visible-light-mediated difluoromethylphosphonation of alkenes for the synthesis of CF2P-containing heterocycles

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1. General information.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker advance III 400 spectrometer (400 MHz for $^1$H and 101 MHz for $^{13}$C) in CDCl$_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for $^1$H, or to chloroform δ = 77.0 for $^{13}$C as internal standard.$^{31}$P and $^{39}$F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants are reported in Hertz (Hz). High resolution mass spectroscopic (HRMS) and mass spectra were measured using Bruker micro TOF-Q mass spectrometer and Thermo Scientific DS II mass spectrometer. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates, spots were detected with UV light (254 nm) and revealed with phosphomolybdic acid solutions. The starting materials were purchased from Aldrich, Across Organics, J&K Chemicals or TCI and used without further purification. Substrates 1, 2 and 4 were prepared according to the reported procedure.$^{[1-2]}$ Solvents were dried and purified according to the procedure from “Purification of Laboratory Chemicals book”.

Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. Optimization of the reaction conditions.

Table S1. Optimization of the reaction conditions.

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* Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), fac-[Ir(ppy)$_3$] (0.5 mol %), Na$_2$CO$_3$ (0.4 mmol), CH$_3$CN (2 mL), 24 h. * Isolated yields based on 1a. * In a dark environment.
3. General procedure for photocatalyzed nucleophilic cyclization of alkenes

In a 10 ml Schlenk tube charged with a magnetic stir bar, 1a (0.2 mmol), 2a (0.4 mmol), \textit{fac}-[Ir(ppy)$_3$] (0.5 mol %), Na$_2$CO$_3$ (0.4 mmol) were added. The tube was evacuated and backfilled with Ar for 3 times. 2 mL CH$_3$CN was then added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for 24h. After the reaction completed, the mixture was concentrated under vacuum, and the residue was purified by flash chromatography on silica gel to afford the product 3a.

\textbf{Gram-scale (20 mmol) reaction:}

In a 500 mL flask charged with a magnetic stir bar, 1a (20 mmol), 2b (40 mmol), \textit{fac}-[Ir(ppy)$_3$] (0.04 mmol), Na$_2$CO$_3$ (40 mmol) were added. The flask was evacuated and backfilled with Ar for 3 times. 300 mL CH$_3$CN was then added under Ar. The tube flask placed at a distance (app.5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for 36h. After the reaction completed, the solvent CH$_3$CN was recovered by distillation under reduced pressure. The remaining solid residue was diluted with CH$_2$Cl$_2$ (200 mL) and washed with H$_2$O (150 mL). The aqueous phase was extracted twice with CH$_2$Cl$_2$ (100 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the product 3b.
4. Characterization data of products

Diethyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)ethyl)phosphonate (3a) Flash silica gel chromatography (PE: EA = 1:1) gave 60 mg of 3a as a colorless oil in 82% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.37 (m, 4H), 7.34 – 7.30 (m, 1H), 4.30 – 4.17 (m, 4H), 2.93 – 2.57 (m, 5H), 2.51 – 2.39 (m, 1H), 1.39 – 1.31 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.5, 142.4, 128.4, 127.8, 124.4, 119.4 (td, $J$ = 262.7, 216.0 Hz), 85.4 (d, $J$ = 9.3 Hz), 64.6 (t, $J$ = 7.4 Hz), 43.9 (td, $J$ = 18.9, 14.7 Hz), 33.8, 28.0, 16.1 (dd, $J$ = 5.2, 1.8 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -110.67 (ddd, $J$ = 663.5, 300.1, 104.2 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 5.73 (t, $J$ = 104.2 Hz). HRMS Calculated for C$_{16}$H$_{21}$F$_2$NaO$_5$P [M+Na]$^+$: 385.0987, found: 385.0986.

Diisopropyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)ethyl)phosphonate (3b) Flash silica gel chromatography (PE: EA = 1:1) gave 67 mg of 3b as a colorless oil in 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.36 (m, 4H), 7.31 (t, $J$ = 7.0 Hz, 1H), 4.88 – 4.75 (m, 2H), 2.92 – 2.53 (m, 5H), 2.53 – 2.30 (m, 1H), 1.37 – 1.31 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.6, 142.6, 128.4, 127.9, 124.5, 119.2 (td, $J$ = 262.5, 217.6 Hz), 85.6 (d, $J$ = 9.6 Hz), 73.9 (t, $J$ = 7.1 Hz), 43.9 (td, $J$ = 18.9, 14.6 Hz), 33.7 (s), 28.1 (s), 23.9 (dd, $J$ = 5.7, 3.5 Hz), 23.5 (dd, $J$ = 4.8, 2.0 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -111.74 (ddd, $J$ = 746.6, 298.0, 104.0 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 3.91 (t, $J$ = 104.1 Hz). HRMS Calculated for C$_{18}$H$_{26}$F$_2$O$_5$P [M+H]$^+$: 391.1480, found: 391.1478.

Ethyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)ethyl)(phenyl)phosphinate (3c) Flash silica gel chromatography (PE: EA = 2:3) gave 52 mg of 3c as a colorless oil in 66% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (td, $J$ = 13.0, 7.8 Hz, 2H), 7.64 (dd, $J$ = 15.6, 7.9 Hz, 1H), 7.51 (ddt, $J$ = 11.3, 7.6, 3.9 Hz, 2H), 7.40 – 7.27 (m, 5H), 4.32 – 4.11 (m, 2H), 2.97 – 2.68 (m, 3H), 2.68 – 2.52 (m, 2H), 2.47 – 2.33 (m, 1H), 1.37 (dt, $J$ = 12.6, 7.0 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.6 (d, $J$ = 2.4 Hz), 142.6 (d, $J$ = 49.5 Hz), 133.8 (dd, $J$ = 4.9, 2.9 Hz), 133.1 (t, $J$ = 9.3 Hz), 128.7 (d, $J$ = 13.3 Hz), 128.5 (d, $J$ = 6.5 Hz), 127.9 (d, $J$ = 2.3 Hz), 124.5 (d, $J$ = 11.5 Hz), 124.3 (dd, $J$ = 133.1, 10.6 Hz), 120.9 (dd, $J$ = 268.0, 264.2, 153.0, 11.7 Hz), 85.7 (dd, $J$ = 8.4, 4.1 Hz), 63.0 (dd, $J$ = 8.4, 7.3 Hz), 43.14 – 42.39 (m), 33.9 (d, $J$ = 42.9 Hz), 28.1 (d, $J$ = 4.9 Hz), 16.4 (dd, $J$ = 5.7, 3.0 Hz). $^{19}$F NMR (376 MHz,
CDCl\textsubscript{3} \(\delta -109.82 \text{ } -112.49\) (m). \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) \(\delta 26.30\) (ddd, \(J = 96.7, 88.5, 9.1\) Hz). HRMS Calculated for C\textsubscript{20}H\textsubscript{22}F\textsubscript{2}O\textsubscript{4}P [M+H]\textsuperscript{+}: 395.1218, found: 395.1217.

Diisopropyl (1,1-difluoro-2-(5-oxo-2-(p-tolyl)tetrahydrofuran-2-y1)ethyl)phosphonate (3e) Flash silica gel chromatography (PE: EA = 1:1) gave 70 mg of 3e as a colorless oil in 86% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.30\) (d, \(J = 8.2\) Hz, 2H), 7.18 (d, \(J = 8.2\) Hz, 2H), 4.89 – 4.74 (m, 2H), 2.89 – 2.68 (m, 3H), 2.67 – 2.60 (m, 2H), 2.49 – 2.39 (m, 1H), 1.37 – 1.32 (m, 12H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 175.7, 159.1, 134.4, 125.9, 119.2\) (td, \(J = 262.5, 217.8\) Hz), 85.7 (d, \(J = 9.6\) Hz), 73.9 (t, \(J = 7.5\) Hz), 43.9 (dd, \(J = 33.4, 18.9\) Hz), 33.6, 28.2, 23.9 (dd, \(J = 5.2, 3.5\) Hz), 23.5 (dd, \(J = 4.8, 2.1\) Hz), 20.8. \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta -111.67\) (ddd, \(J = 772.2, 298.0, 104.3\) Hz), \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) \(\delta 3.96\) (t, \(J = 104.2\) Hz). HRMS Calculated for C\textsubscript{19}H\textsubscript{28}F\textsubscript{2}O\textsubscript{5}P [M+H]\textsuperscript{+}: 405.1637, found: 405.1637.

Diisopropyl (1,1-difluoro-2-(2-(4-methoxyphenyl)-5-oxotetrahydrofuran-2-y1)ethyl)phosphonate (3f) Flash silica gel chromatography (PE: EA = 1:1) gave 60 mg of 3f as a colorless oil in 71% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.34\) (d, \(J = 8.8\) Hz, 2H), 6.90 (d, \(J = 8.8\) Hz, 2H), 4.90 – 4.74 (m, 2H), 3.80 (s, 3H), 2.89 – 2.68 (m, 3H), 2.67 – 2.60 (m, 2H), 2.49 – 2.39 (m, 1H), 1.37 – 1.32 (m, 12H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 175.7, 159.1, 134.4, 125.9, 119.2\) (td, \(J = 262.5, 217.8\) Hz), 113.7, 85.6 (d, \(J = 9.8\) Hz), 73.9 (t, \(J = 6.8\) Hz), 55.1, 44.0 (dd, \(J = 33.3, 18.8\) Hz), 33.6, 28.3, 23.9 (t, \(J = 3.7\) Hz), 23.5 (d, \(J = 4.9\) Hz). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta -111.82\) (ddd, \(J = 761.2, 298.0, 104.3\) Hz, 2F). \textsuperscript{31}P NMR
Diisopropyl (1,1-difluoro-2-(2-(4-fluorophenyl)-5-oxotetrahydrofuran-2-yl)ethyl)phosphonate (3g)
Flash silica gel chromatography (PE: EA = 1:1) gave 74 mg of 3g as a colorless oil in 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.39 (m, 2H), 7.10 – 7.04 (m, 2H), 4.87– 4.76 (m, 2H), 2.90 – 2.56 (m, 5H), 2.49 – 2.39 (m, 1H), 1.38 – 1.32 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 175.2, 162.1 (d, J = 247.3 Hz), 138.2 (d, J = 3.2 Hz), 126.5 (d, J = 8.2 Hz), 119.8 (dt, J = 262.6, 217.3 Hz), 115.3 (d, J = 21.6 Hz), 85.2 (d, J = 9.7 Hz), 73.9 (dd, J = 7.1, 4.7 Hz), 44.0 (td, J = 18.9, 14.6 Hz), 33.9, 28.0, 23.8 (t, J = 3.3 Hz), 23.5 (d, J = 4.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -111.83 (ddd, J = 673.2, 298.0, 103.7 Hz), -114.18. ³¹P NMR (162 MHz, CDCl₃) δ 3.77 (t, J = 103.7 Hz). HRMS Calculated for C₁₉H₂₈F₂O₆P [M+H⁺]: 421.1586, found: 421.1585.

Diisopropyl (2-(2-(4-chlorophenyl)-5-oxotetrahydrofuran-2-yl)-1,1-difluoroethyl)phosphonate (3h)
Flash silica gel chromatography (PE: EA = 1:1) gave 68 mg of 3h as a colorless oil in 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.34 (m, 4H), 4.85 – 4.76 (m, 2H), 2.90 – 2.58 (m, 5H), 2.44 (dt, J = 20.6, 9.4 Hz, 1H), 1.37 – 1.32 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 175.1, 141.0, 133.7, 128.5, 126.1, 119.0 (td, J = 262.7, 217.8 Hz), 85.0 (d, J = 9.6 Hz), 73.9 (dd, J = 6.5, 5.4 Hz), 43.8 (dd, J = 33.6, 18.8 Hz), 33.9, 27.9, 23.8 (t, J = 3.3 Hz), 23.4 (d, J = 4.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -111.83 (ddd, J = 673.2, 298.0, 103.7 Hz), -114.18. ³¹P NMR (162 MHz, CDCl₃) δ 3.77 (t, J = 103.7 Hz). HRMS Calculated for C₁₈H₂₈NF₃O₅ClP [M+NH₄⁺]: 442.1356, found: 442.1355.

Diisopropyl (1,1-difluoro-2-(5-oxo-2-(m-tolyl)tetrahydrofuran-2-yl)ethyl)phosphonate (3i)
Flash silica gel chromatography (PE: EA = 2:1) gave 63 mg of 3i as a colorless oil in 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.18 (m, 3H), 7.12 (d, J = 7.3 Hz, 1H), 4.82 (ddq, J = 19.1, 12.6, 6.3 Hz, 2H), 2.90 – 2.57 (m, 5H), 2.48– 2.41 (m, 1H), 2.36 (s, 3H), 1.38 – 1.32 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 175.7, 142.9, 138.3, 128.7, 128.4, 125.2, 121.6, 1119.4 (td, J = 263.1, 218.6 Hz), 85.8 (d, J = 9.5 Hz), 74.0 (dd, J = 8.9, 7.4 Hz), 44.0 (td, J = 19.0, 14.5 Hz), 33.6, 28.3, 24.0 (dd, J = 7.7, 3.5 Hz), 23.6 (t, J = 4.5 Hz), 21.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.62 (ddd, J = 771.2, 297.9, 104.2 Hz). ³¹P
NMR (162 MHz, CDCl₃) δ 3.94 (t, J = 104.2 Hz). HRMS Calculated for C₁⁹H₂₈F₂O₅P [M+H]⁺: 405.1637, found: 405.1636.

Diisopropyl (1,1-difluoro-2-(5-oxo-2-(o-tolyl)tetrahydrofuran-2-yl)ethyl)phosphonate (3j) Flash silica gel chromatography (PE: EA = 1:1) gave 67 mg of 3j as a colorless oil in 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.53 (m, 1H), 7.23 – 7.19 (m, 3H), 4.89 – 4.77 (m, 2H), 3.00 (ddd, J = 12.6, 9.6, 6.5 Hz, 1H), 2.89 – 2.77 (m, 2H), 2.77 – 2.67 (m, 1H), 2.67 – 2.56 (m, 1H), 2.50 (dd, J = 15.3, 5.5 Hz, 1H), 2.45 (s, 3H), 1.38 – 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 175.5, 141.2, 133.2, 132.4, 128.0, 126.0, 124.8, 119.7 (dt, J = 261.6, 215.7 Hz), 86.3 (d, J = 9.5 Hz), 73.9 (dd, J = 9.5, 7.2 Hz), 41.8 (td, J = 18.9, 14.3 Hz), 32.8, 28.1, 23.9 (dd, J = 8.1, 3.5 Hz), 23.6 (t, J = 5.2 Hz), 21.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.96 (ddd, J = 400.9, 297.0, 104.4 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 3.85 (t, J = 104.2 Hz). HRMS Calculated for C₁⁹H₂₈F₂O₅P [M+H]⁺: 405.1637, found: 405.1635.

Diisopropyl (2-(2-(2,5-dimethylphenyl)-5-oxotetrahydrofuran-2-yl)-1,1-difluoroethyl)phosphonate (3k) Flash silica gel chromatography (PE: EA = 1:1) gave 63 mg of 3k as a colorless oil in 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.36 (m, 1H), 7.08 (d, J = 7.7 Hz, 1H), 7.03 (d, J = 8.8 Hz, 1H), 4.90 – 4.77 (m, 2H), 3.05 – 2.93 (m, 1H), 2.87 – 2.68 (m, 3H), 2.64 – 2.43 (m, 2H), 2.39 (s, 3H), 2.32 (s, 3H), 1.38 – 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 175.6, 141.2, 135.5, 132.4, 129.8, 128.6, 125.3, 119.7 (td, J = 263.7, 216.8 Hz), 86.3 (d, J = 9.4 Hz), 73.9 (dd, J = 10.8, 7.2 Hz), 41.8 (td, J = 18.9, 14.1 Hz), 32.6 (d, J = 2.5 Hz), 28.1, 23.9 (dd, J = 9.4, 3.4 Hz), 23.5 (dd, J = 7.5, 5.0 Hz), 20.9, 20.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -113.00 (ddd, J = 400.8, 296.8, 104.6 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 3.88 (t, J = 104.4 Hz). HRMS Calculated for C₂₀H₃₀F₂O₅P [M+H]⁺: 419.1793, found: 419.1795.

Diisopropyl (1,1-difluoro-2-(5-oxo-2-phenyltetrahydrofuran-2-yl)propyl)phosphonate (3l) Flash silica gel chromatography (PE: EA = 2:1) gave 29 mg of 3l as a colorless oil in 36% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 4.92 – 4.78 (m, 2H), 3.02 – 2.83 (m, 2H), 2.62 – 2.48 (m, 2H), 2.38 – 2.29 (m, 1H), 1.36 (dt, J = 7.9, 6.2 Hz, 12H), 1.15 (d, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.0, 143.1, 128.5, 127.8, 125.1, 121.9 (td, J = 267.8, 215.4 Hz), 88.7 (d, J = 6.5 Hz), 73.9 (d, J = 22.7 Hz), 47.2 (dd, J = 34.4, 16.7 Hz), 32.8, 28.4, 24.1 (dd, J = 17.3, 2.8 Hz),
23.65 (t, J = 2.2 Hz), 10.84 (t, J = 5.3 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -109.35 (ddd, J = 411.7, 303.1, 106.5 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 4.49 (dd, J = 108.5, 104.5 Hz). HRMS Calculated for C$_{19}$H$_{28}$F$_{2}$O$_{5}$P [M+H]$^+$: 405.1637, found: 405.1634.

Diisopropyl (1,1-difluoro-2-(3-oxo-1-phenyl-1,3-dihydroisobenzofuran-1-yl)ethyl)phosphonate (3m)

Flash silica gel chromatography (PE: EA = 1:1) gave 84 mg of 3m as a colorless oil in 95% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, J = 7.6 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.50 (d, J = 13.3, 6.7, 3.9 Hz, 1H), 7.30 (qd, J = 5.2, 2.8 Hz, 1H), 5.83 – 4.75 (m, 2H), 4.83 – 4.75 (m, 2H), 3.40 – 3.11 (m, 2H), 1.36 – 1.29 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.0, 151.1, 140.0, 133.9, 129.2, 128.6, 128.3, 125.6, 124.9, 122.9, 118.7 (td, J = 263.6, 218.2 Hz), 85.9 (d, J = 9.3 Hz), 73.9 (dd, J = 7.2, 3.1 Hz), 41.7 (dd, J = 34.2, 18.7 Hz), 23.6 (ddd, J = 14.5, 7.9, 4.2 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -112.08 (ddd, J = 400.7, 298.2, 103.3 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 3.71 (t, J = 10.2 Hz). HRMS Calculated for C$_{22}$H$_{26}$F$_{2}$O$_{5}$P [M+H]$^+$: 439.1480, found: 439.1479.

Diisopropyl (2-(1-(4-chlorophenyl)-3-oxo-1,3-dihydroisobenzofuran-1-yl)-1,1-difluoroethyl)phosphonate (3n)

Flash silica gel chromatography (PE: EA = 2:1) gave 81 mg of 3n as a colorless oil in 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.53 (dd, J = 17.2, 7.9 Hz, 3H), 7.33 (d, J = 8.6 Hz, 2H), 4.79 (qd, J = 12.5, 6.2 Hz, 2H), 3.35 – 3.06 (m, 2H), 1.33 (dt, J = 8.4, 6.4 Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.8, 150.8, 138.6, 134.4, 134.2, 129.5, 128.8 126.1, 125.8, 124.9, 122.8, 118.7 (dt, J = 118.6, 84.4 Hz), 85.45 (d, J = 9.4 Hz), 74.09 (d, J = 6.9 Hz), 42.69 – 23.86 (m), 23.84 (t, J = 3.9 Hz), 23.54 (dd, J = 8.2, 4.8 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.84 (ddd, J = 400.6, 298.4, 102.9 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 3.60 (t, J = 102.8 Hz). HRMS Calculated for C$_{22}$H$_{26}$NF$_{2}$O$_{5}$ClP [M+NH$_4$]$^+$: 490.1356, found: 490.1355.
Diisopropyl (1,1-difluoro-2-(1-methyl-3-oxo-1,3-dihydropyran-2-yl)ethyl)phosphonate (3o) Flash silica gel chromatography (PE: EA = 2:1) gave 69 mg of 3o as a colorless oil in 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (dd, J = 6.8, 4.1 Hz, 1H), 7.69 (dd, J = 10.7, 4.3 Hz, 1H), 7.55 (dd, J = 16.6, 8.2, 5.1 Hz, 2H), 4.86 – 4.76 (m, 2H), 2.91 – 2.68 (m, 2H), 1.77 (s, 3H), 1.39 – 1.32 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 152.6, 134.0, 129.1, 125.5, 125.2, 121.6, 119.1 (td, J = 262.8, 217.8 Hz), 84.0 (d, J = 9.9 Hz), 73.9 (d, J = 6.7 Hz), 41.5 (dd, J = 34.2, 19.3 Hz), 26.9, 23.9 (d, J = 3.2 Hz), 23.5 (t, J = 4.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -112.49 (qd, J = 297.2, 103.9 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 3.79 (t, J = 103.8 Hz). HRMS Calculated for C₁₇H₂₄F₂O₅P [M+H⁺]: 377.1324, found: 377.1322.

Diisopropyl (1,1-difluoro-2-(3-oxo-1,3-dihydropyran-2-yl)ethyl)phosphonate (3p) Flash silica gel chromatography (PE: EA = 1:1) gave 33 mg of 3p as a colorless oil in 45% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (t, J = 8.1 Hz, 1H), 7.73 (t, J = 7.5 Hz, 1H), 7.58 (dd, J = 12.4, 7.6 Hz, 2H), 5.89 (dd, J = 7.4, 4.2 Hz, 1H), 4.96 – 4.86 (m, 2H), 2.80 – 2.51 (m, 2H), 1.44 – 1.39 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 169.7, 148.7, 134.3, 129.5, 125.6, 122.2, 118.5 (td, J = 264.6, 218.2 Hz), 74.5 (dd, J = 11.4, 4.9 Hz), 74.2 (dd, J = 13.3, 7.1 Hz), 39.4 (td, J = 20.7, 15.1 Hz), 24.0 (dd, J = 5.7, 3.6 Hz), 23.6 (t, J = 4.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -111.52 (qd, J = 298.8, 103.6 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 3.98 (dd, J = 104.7, 102.3 Hz). HRMS Calculated for C₁₆H₂₅F₂O₅P [M+NH₄⁺]: 380.1433, found: 380.1434.

Diisopropyl (difluoro(5-oxo-2-phenyltetrahydrofuran-3-yl)methyl)phosphonate (3q) Flash silica gel chromatography (PE: EA = 1:1) gave 61 mg of 3q as a colorless oil in 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.32 (m, 5H), 5.88 (d, J = 4.5 Hz, 1H), 4.91 – 4.82 (m, 2H), 3.29 – 3.15 (m, 1H), 2.92 (dd, J = 28.6, 18.5, 7.9 Hz, 2H), 1.39 – 1.37 (m, 9H), 1.34 (d, J = 6.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.3, 138.7, 128.7, 126.7, 125.2, 118.8 (dd, J = 265.6, 262.3, 215.3 Hz), 78.6 (d, J = 4.8 Hz), 74.5 (dd, J = 20.2, 7.2 Hz), 47.2 (td, J = 20.8, 15.3 Hz), 28.1 (t, J = 4.3 Hz), 23.9 (t, J = 3.9 Hz), 23.5 (d, J = 3.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -117.77 (ddd, J = 404.2, 302.2, 103.7 Hz, 2F). ³¹P NMR (162 MHz, CDCl₃) δ 3.37 (dd, J = 105.1, 102.1 Hz). HRMS Calculated for C₁₇H₂₇F₂O₅P [M+NH₄⁺]: 394.1589, found: 394.1592.
Diisopropyl (difuoro(6-oxo-2-phenyltetrahydro-2H-pyran-3-yl)methyl)phosphonate (3r) Flash silica gel chromatography (PE: EA = 2:1) gave 47 mg of 3r as a colorless oil in 60% yield. 1H NMR (400 MHz, CDCl3) δ 7.39 (t, J = 8.0 Hz, 2H), 7.33 (t, J = 6.0 Hz, 3H), 5.99 (d, J = 3.8 Hz, 1H), 4.92 – 4.84 (m, 2H), 2.96 – 2.82 (m, 1H), 2.79 – 2.70 (m, 1H), 2.55 (dt, J = 17.9, 5.7 Hz, 1H), 2.28 (td, J = 11.5, 5.5 Hz, 1H), 2.08 (dt, J = 15.8, 6.5 Hz, 1H), 1.39 (t, J = 7.1 Hz, 12H). 13C NMR (101 MHz, CDCl3) δ 170.4, 139.4, 128.6, 128.1, 125.5, 120.3 (dt, J = 265.6, 215.1 Hz), 77.8 (q, J = 4.5 Hz), 74.4 (t, J = 6.7 Hz), 42.1 (td, J = 19.0, 15.3 Hz), 27.2, 23.9 (dd, J = 6.9, 3.6 Hz), 23.6 (dd, J = 8.6, 4.9 Hz), 16.8. 19F NMR (376 MHz, CDCl3) δ -112.66 (ddd, J = 2146.5, 304.5, 104.7 Hz). 31P NMR (162 MHz, CDCl3) δ 3.67 (t, J = 104.7 Hz). HRMS Calculated for C18H29NF2O5P [M+NH4]+: 408.1746, found: 408.1745.

Diisopropyl (difuoro(7-oxo-2-phenyloxepan-3-yl)methyl)phosphonate (3s) Flash silica gel chromatography (PE: EA = 1:1) gave 26 mg of 3s as a colorless oil in 32% yield. 1H NMR (400 MHz, CDCl3) δ 7.42 – 7.28 (m, 5H), 5.66 (d, J = 8.5 Hz, 1H), 4.85 – 4.72 (m, 2H), 3.22 – 3.11 (m, 1H), 2.92 (dt, J = 13.7, 8.7 Hz, 1H), 2.54 (ddd, J = 13.6, 7.8, 3.1 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.15 – 2.01 (m, 2H), 1.88 – 1.81 (m, 1H), 1.36 (t, J = 6.2 Hz, 3H), 1.31 (dd, J = 9.3, 4.0 Hz, 9H). 13C NMR (101 MHz, CDCl3) δ 173.1, 139.6, 128.4 (d, J = 5.4 Hz), 127.2 (d, J = 1.2 Hz), 121.6 (td, J = 268.7, 215.1 Hz), 77.6 – 77.5 (m), 74.07 (dd, J = 18.9, 7.3 Hz), 46.4 (dd, J = 33.6, 16.4 Hz), 31.9, 23.9 (dd, J = 9.2, 3.5 Hz), 23.6 (dd, J = 8.9, 5.0 Hz), 23.1 (d, J = 5.9 Hz), 18.1 (d, J = 2.9 Hz). 19F NMR (376 MHz, CDCl3) δ -109.59 (ddd, J = 412.1, 306.0, 104.8 Hz). 31P NMR (162 MHz, CDCl3) δ 3.71 (dd, J = 105.8, 103.7 Hz). HRMS Calculated for C19H28F2O5P [M+H]+: 405.1637, found: 405.1638.

Diisopropyl (1,1-difuoro-2-(2-phenyltetrahydrofuran-2-yl)ethyl)phosphonate (5a) Flash silica gel chromatography (PE: EA = 3:1) gave 45 mg of 5a as a colorless oil in 60% yield. 1H NMR (400 MHz, CDCl3) δ 7.42 (d, J = 7.9 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 4.85 – 4.70 (m, 2H), 4.02 (q, J = 7.6 Hz, 1H), 3.86 (td, J = 8.2, 5.5 Hz, 1H), 2.78 – 2.56 (m, 2H), 2.37 – 2.25 (m, 2H), 2.02 – 1.93 (m, 1H), 1.80 – 1.69 (m, 1H), 1.32 (dt, J = 6.1, 5.2 Hz, 12H). 13C NMR (101 MHz, CDCl3) δ 145.7, 127.8, 126.5, 125.1, 119.9 (td, J = 262.3, 217.6 Hz), 83.9 (d, J = 9.7 Hz), 73.4 (t, J = 7.0 Hz), 67.1, 43.7 (td, J = 18.7, 13.8 Hz), 37.9, 25.0, 23.9 (dd, J = 6.7, 3.4 Hz), 23.5 (t, J = 5.0 Hz). 19F NMR (376 MHz, CDCl3) δ -111.49 (ddd, J = 716.9, 297.1, 106.9 Hz). 31P NMR (162 MHz, CDCl3) δ 4.88 (t, J = 107.0 Hz). HRMS Calculated for C19H28F2O4P [M+H]+: 377.1688, found: 377.1689.
Diisopropyl (1,1-difluoro-2-(2-phenyl-1-tosylpyrrolidin-2-yl)ethyl)phosphonate (5b) Flash silica gel chromatography (PE: EA = 2:1) gave 50 mg of 5b as a colorless oil in 47% yield. 1H NMR (400 MHz, CDCl3) δ 7.37 – 7.35 (m, 2H), 7.22 – 7.19 (m, 5H), 7.08 (d, J = 8.2 Hz, 2H), 4.94 – 4.85 (m, 2H), 3.80 – 3.65 (m, 2H), 3.51 – 3.46 (m, 1H), 3.19 – 3.04 (m, 1H), 2.62 (dt, J = 13.9, 7.1 Hz, 1H), 2.49 – 2.42 (m, 1H), 2.35 (s, 3H), 2.15 – 2.04 (m, 1H), 2.00 – 1.90 (m, 1H), 1.39 (dd, J = 10.8, 6.2 Hz, 12H). 13C NMR (101 MHz, CDCl3) δ 143.0, 142.3, 137.7, 128.9, 127.8, 127.0, 127.0, 126.8, 120.1 (td, J = 262.6, 219.4 Hz), 73.8 (dd, J = 6.8, 5.7 Hz), 69.9 (d, J = 10.8 Hz), 49.2, 40.9, 40.4 (dd, J = 33.2, 18.5 Hz), 24.1 (d, J = 3.4 Hz), 23.7 (dd, J = 4.9, 2.7 Hz), 23.2, 21.3. 19F NMR (376 MHz, CDCl3) δ -109.17 (qd, J = 295.7, 108.4 Hz). 31P NMR (162 MHz, CDCl3) δ 4.93 (t, J = 108.3 Hz). HRMS Calculated for C25H35NF2O5PS [M+NH4]+: 530.1936, found: 530.1933.

Diisopropyl (1,1-difluoro-2-(1-phenyl-2-tosylisoindolin-1-yl)ethyl)phosphonate (5c) Flash silica gel chromatography (PE: EA = 2:1) gave 87 mg of 5c as a colorless oil in 75% yield. 1H NMR (400 MHz, CDCl3) δ 7.25 – 7.24 (m, 2H), 7.20 – 7.13 (m, 2H), 7.08 (t, J = 7.7 Hz, 2H), 6.93 (d, J = 9.0 Hz, 5H), 6.78 (d, J = 7.8 Hz, 1H), 5.02 (d, J = 12.8 Hz, 1H), 4.86 (ddq, J = 28.2, 12.6, 6.2 Hz, 2H), 4.69 (d, J = 12.8 Hz, 1H), 4.25 – 4.11 (m, 1H), 2.28 (s, 3H), 1.43 (dd, J = 14.5, 6.2 Hz, 6H), 1.36 (dd, J = 6.1, 4.4 Hz, 6H). 13C NMR (101 MHz, CDCl3) δ 144.5, 142.5 (d, J = 1.8 Hz), 142.2, 137.2, 134.6, 128.7, 127.9, 127.8, 127.8, 127.4, 126.7, 123.8, 121.9, 120.2 (ddd, J = 266.1, 262.1, 218.7 Hz), 74.0 (dd, J = 11.5, 7.3 Hz), 72.6 (d, J = 10.4 Hz), 53.6 (d, J = 2.8 Hz), 39.3 (dd, J = 32.4, 16.6 Hz), 24.1 (dd, J = 11.4, 3.5 Hz), 23.8 (dd, J = 23.2, 4.9 Hz), 21.3. 19F NMR (376 MHz, CDCl3) δ -114.02 (qd, J = 398.1, 295.1, 106.1 Hz). 31P NMR (162 MHz, CDCl3) δ 4.27 (dd, J = 109.3, 102.9 Hz). HRMS Calculated for C29H38N2F2O5PS [M+NH4]+: 595.2202, found: 595.2197.

Diisopropyl (difluoro(2-phenyl-1-tosylpyrrolidin-3-yl)methyl)phosphonate (5d) Flash silica gel chromatography (PE: EA = 2:1) gave 51 mg of 5d as a colorless oil in 49% yield. 1H NMR (400 MHz, CDCl3) δ 7.64 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 8.1 Hz, 3H), 5.20 (d, J = 3.4 Hz, 1H), 4.73 (dp, J = 12.7, 6.3 Hz, 2H), 3.69 (dd, J = 15.6, 6.3 Hz, 1H), 3.49 (q, J = 8.1 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.39 (s, 3H), 2.19 – 2.14 (m, 2H), 1.31 (dd, J = 6.1, 3.4 Hz, 6H), 1.25 (d, J = 6.2 Hz, 6H). 13C NMR (101 MHz, CDCl3) δ 143.0, 142.8, 134.8, 129.2, 128.3, 127.3, 127.2, 126.3, 119.6 (dd, J = 266.7, 212.7 Hz), 73.9 (dd, J = 14.4, 7.2 Hz), 61.9 (d, J = 3.9 Hz), 52.3 (dd, J = 34.6, 19.5 Hz), 48.6, 24.3, 23.9 (dd, J = 8.8, 3.5 Hz), 23.5 (t, J = 4.4 Hz), 21.4. 19F NMR (376 MHz, CDCl3) δ -115.66 (dd, J = 405.7, 300.5, 106.3 Hz). 31P NMR (162 MHz, CDCl3) δ 4.05 (t, J = 105.8 Hz). HRMS Calculated for C25H36N2F2O3PS [M+NH4]+: 533.2045, found: 533.2040.
5. Mechanistic investigation

(1). Radical trapping experiments

a) Radical trapping experiment with TEMPO

Under the standard reaction conditions, two equivalents of radical scavenger TEMPO were added into the reaction. Then the tube was placed at a distance (app. 5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for 24h. After the reaction was finished, the mixture was concentrated under vacuum, and the residue was purified by flash chromatography on silica gel to afford the product 3b, 2b and 6. Since the polarities of the products 2b and 6 were very close, it was difficult to separate 2b and 6 apart. However, the respective yields could be calculated by the 1H NMR.

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\text{Diisopropyl (difluoro(2,2,6,6-tetramethylpiperidin-1-yl)(oxy)methyl)phosphonate (6) Flash silica gel chromatography (PE: EA = 5:1) gave 6 as a colorless oil in 36% yield. Pick the TEMPO-CF}_2\text{P(O)(O'Pr)}_2\text{ peak. } 1^\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 4.92 (\text{ddq, } J = 19.1, 12.6, 6.3 \text{ Hz, 2H), 1.59 (dd, } J = 12.9, 8.0 \text{ Hz, 6H), 1.41 (dd, } J = 14.0, 6.7 \text{ Hz, 12H), 1.20 (s, 12H). } 1^\text{3C NMR (101 MHz, CDCl}_3\text{) } \delta 118.7 (\text{dd, } J = 576.9, 293.3 \text{ Hz), 73.6 (d, } J = 6.7 \text{ Hz), 61.1, 40.3, 33.6 (t, } J = 5.1 \text{ Hz), 24.1 (d, } J = 3.2 \text{ Hz), 23.6 (d, } J = 5.4 \text{ Hz), 20.7, 16.8. } 1^\text{9F NMR (376 MHz, CDCl}_3\text{) } \delta -72.78 (\text{d, } J = 132.0 \text{ Hz). } 3^\text{1P NMR (162 MHz, CDCl}_3\text{) } \delta 0.13 (t, J = 132.0 \text{ Hz). HRMS Calculated for C}_{16}\text{H}_{33}\text{NF}_2\text{O}_4\text{P [M+H]}^+: 372.2110, found: 372.2113.}
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b) Radical trapping experiment with 1,1-Diphenylethylene

Under the standard reaction conditions, one equivalent of radical scavenger 1,1-diphenylethylene was added into the reaction. After that, the tube was placed at a distance (app. 5 cm) from 5 W blue LEDs lamb, and the resulting solution was stirred at ambient temperature under visible-light irradiation for
24h. After the reaction completed, the mixture was concentrated under vacuum, and the residue was purified by flash chromatography on silica gel to afford the product 3b and 7.

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\text{CF}_2\text{P(OiPr)}_2\text{Ph}
\]

Diisopropyl (1,1-difluoro-3,3-diphenylallyl)phosphonate (7) Flash silica gel chromatography (PE: EA = 5:1) gave 7 as a colorless oil in 56% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 – 7.27 (m, 8H), 7.24 (dt, \(J = 4.5, 3.0\) Hz, 2H), 6.16 (td, \(J = 16.1, 2.1\) Hz, 1H), 4.84 (dq, \(J = 12.5, 6.2\) Hz, 2H), 1.35 (dd, \(J = 10.7, 6.2\) Hz, 12H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.7 (dt, \(J = 8.4, 5.8\) Hz), 141.6, 138.2 (d, \(J = 1.3\) Hz), 129.5 (d, \(J = 1.2\) Hz), 128.7, 128.2, 127.9, 127.8, 127.4, 117.1 (td, \(J = 19.3, 14.1\) Hz), 117.0 (td, \(J = 260.8, 222.4\) Hz), 73.6 (d, \(J = 7.1\) Hz), 24.0 (d, \(J = 3.5\) Hz), 23.7 (d, \(J = 4.9\) Hz). \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -103.22 (d, \(J = 112.9\) Hz). \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 5.08 (t, \(J = 112.9\) Hz). RMS Calculated for C\(_{21}\)H\(_{26}\)F\(_2\)O\(_3\)P [M+H]\(^+\): 395.1582, found: 395.1581.

(2) Emission quenching experiments

Emission intensities were surveyed on a HORIBA AquaLog fluorescence spectrometer and equipped with a 1-cm quartz cell. Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM fac-Ir(ppy)\(_3\) in acetonitrile at room temperature. The solutions were irradiated at 390nm and fluorescence was measured from 400 nm to 700 nm. Control experiments showed that excited state of fac-Ir(ppy)\(_3\) was quenched by BrCF\(_2\)PO(OiPr)\(_2\).

![Figure S1. The Emission Quenching of fac-Ir(ppy)\(_3\) by BrCF\(_2\)PO(OiPr)\(_2\).](attachment:image.png)
(3). Electrochemistry experiments

Electrochemical investigation was studied on a Chi 660e electrochemical workstation. Cyclic voltammograms were obtained using a standard three electrode cell under argon at room temperature with a glassy carbon working electrode and a platinum wire auxiliary electrode. Ag/AgCl (0.01 mmol/L) reference electrode was used and the supporting electrolyte solution was 0.05 M (nBu)₄NPF₆. Measurement conditions: solvent, CH₃CN; concentration, 2×10⁻⁴ mol/L; supporting electrolyte, (nBu)₄NPF₆; work electrode, Pt/C; counter electrode, Pt; reference electrode, Ag/AgCl; scan speed, 0.1 V s⁻¹; temperature, room temperature.

**Figure S2.** The Emission Quenching of fac-Ir(ppy)₃ by substrate 1a.

**Figure S3.** Cyclic voltammetry of 2b.
Figure S4. Cyclic voltammetry of 2d.

The potential of diisopropyl bromodifluoromethylphosphate (2b) and (bromodifluoromethyl)diphenylphosphine oxide (2d) were investigated by cyclic voltammograms. Compound 2b shows an irreversible reduction event at -1.10 V (vs. SCE) in acetonitrile; and Compound 2d shows an irreversible reduction event at -1.15 V (vs. SCE) in acetonitrile.

6. References


7. Copies of NMR spectra

$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3a
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3a

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3a
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3a
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3b

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3b
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3b
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3b

$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum for 3c
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3c

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3c
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3c
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum for 3d

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3d
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3d
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3d

$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3e
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3e
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum for 3e

![Diagram of 3e with $^{19}\text{F NMR}$ spectrum]

$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$ spectrum for 3e

![Diagram of 3e with $^{31}\text{P NMR}$ spectrum]
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum for 3f
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3f

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3f
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3f
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3g

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3g
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3g
$^{31}\text{P NMR (162 MHz, CDCl}_3\text{) spectrum for 3g}$

$^{1}\text{H NMR (400 MHz, CDCl}_3\text{) spectrum for 3h}$
$1^3$C NMR (101 MHz, CDCl$_3$) spectrum for 3h
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3h

$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3h
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3i
$^{13}$C NMR (101 MHz, CDCl₃) spectrum for 3i

$^{19}$F NMR (376 MHz, CDCl₃) spectrum for 3i
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3i
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3j

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3j
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{)}$ spectrum for 3j

![Chemical Structure](image)
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3j

$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3k
$\textbf{13C NMR (101 MHz, CDCl$_3$) spectrum for 3k}$
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3k

$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3k
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3l
$^{13}$C NMR (101 MHz, CDCl₃) spectrum for 3l

$^{19}$F NMR (376 MHz, CDCl₃) spectrum for 3l
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3l
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3m

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3m
$^{19}\text{F NMR (376 MHz, CDCl}_3\) spectrum for 3l}$

![NMR spectrum](image)

3m
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3l

$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3n
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3n
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3n

![19F NMR spectrum for 3n](image)

$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3n

![31P NMR spectrum for 3n](image)
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3o
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3o

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3o
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3o
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3p

![1H NMR spectrum for 3p](image)

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3p

![13C NMR spectrum for 3p](image)
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3p
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3p

$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3q
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3q
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3q

3q

$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3q

3q
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3r
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3r

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3r
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 3r
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 3s

![1H NMR Spectrum](image)

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 3s
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 3s
$^{31}\text{P NMR (162 MHz, CDCl$_3$) spectrum for 3s}$

$^{1}\text{H NMR (400 MHz, CDCl$_3$) spectrum for 5a}$
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 5a
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 5a

![19F NMR spectrum for 5a](image)

$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 5a

![31P NMR spectrum for 5a](image)
$^{1}$H NMR (400 MHz, CDCl$_3$) spectrum for 5b
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 5b

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 5b
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 5b
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5c

$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 5c
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 5c
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 5c

$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 5d
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 5d
\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) spectrum for 5d

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)) spectrum for 5d
$^1$H NMR (400 MHz, CDCl$_3$) spectrum for 2a and 6
$^{13}$C NMR (101 MHz, CDCl$_3$) spectrum for 2a and 6

$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 2a and 6
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectrum for 7

$^{13}C$ NMR (101 MHz, CDCl$_3$) spectrum for 7
$^{19}$F NMR (376 MHz, CDCl$_3$) spectrum for 7

![Chemical structure of 7]

![NMR spectrum of 7]
$^{31}$P NMR (162 MHz, CDCl$_3$) spectrum for 7