Photoinduced Fragmentation-Rearrangement Sequence of Cycloketoxime Esters  
(Supporting Information)

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1. General Information.

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. All new compounds were fully characterized. NMR-spectra were recorded on ARX-400 MHz or a ARX-500 Associated. $^1$H NMR spectra data were reported as $\delta$ values in ppm relative to chloroform ($\delta$ 7.26) if collected in CDCls. $^{13}$C NMR spectra data were reported as $\delta$ values in ppm relative to chloroform ($\delta$ 77.00). $^1$H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doublet of quartets); app (apparent); br (broad). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). All reactions were carried out in flame-dried 25-mL Schlenk tubes with Teflon screw caps under argon. Photoredox catalysis $\textit{fac-}[\text{Ir(ppy)}_3]$ was purchased from Adamas-beta, and Cu(OTf)$_2$ was purchased from TCI. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of Cycloketoxime Esters

2-Arylcyclopentan-1-one $O$-benzoyl oximes were obtained from the corresponding 2-arylcyclopentan-1-ones, which were synthesized from the corresponding cyclopentane and aryl bromides according to the reported procedure$^{[1]}$. 

![Diagram of the reaction involving ketone, bromide, and hydroxylamine to form oxime, followed by esterification with an aromatic carboxylic acid, DCC, and DMAP to form the ester.](image-url)
The following experimental procedure is typical: flame-dried 50 mL schlenk tube filled with argon, Pd(OAc)$_2$ (56.2 mg, 0.25 mmol, 0.05 equiv), P(o-tol)$_3$ (152 mg, 0.5 mmol, 0.1 equiv), NaOAc (410.0 mg, 5.0 mmol, 1.0 equiv), cyclopentanones (5.0 mmol, 1.0 equiv), aryl bromides (6.5 mmol, 1.3 equiv), pyrrolidine (128.3 μL, 1.5 mmol, 0.3 equiv), 1,1,3,3-tetramethylbutylamine (250.0 μL, 1.5 mmol, 0.3 equiv) and 1,4-dioxane (25.0 mL), the tube was then sealed and heated at 110 °C under stirring for 12-24 hours, before cooled to room temperature. The mixture was filtered through a small plug of silica gel and eluted with ethyl acetate. The filtrate was then concentrated under vacuo and further purified by flash column chromatography to give the arylation product.

The ketone (1.0 equiv) was dissolved in abs EtOH (0.25 M) and treated with NaOH (2.0 equiv) in H$_2$O (0.5 M) followed by hydroxylamine hydrochloride (1.5 equiv). The mixture was allowed to stir at room temperature until the reaction was complete (TLC monitoring). The residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over Na$_2$SO$_4$, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

To a solution of ketoxime in DCM (0.1 M) was added the carboxylic acid (1.5 equiv) followed by EDCI (2.5 equiv) and DMAP (20.0 mol%). The mixture was stirred at room temperature under Ar until the reaction was complete (TLC monitoring). The mixture was diluted with water and extracted with DCM. The aqueous layer was extracted with DCM and the combined organic extracts were washed with brine, dried over Na$_2$SO$_4$, the solvent was removed under vacuum and the residue was subjected to column chromatography on SiO$_2$ with EtOAc–hexane as an eluent to give 2-arylcyclopentan-1-one O-benzoyl oximes (1).

2-Phenylcyclopentan-1-one O-(4-(trifluoromethyl)benzoyl) oxime (1aa)

According to the general procedure, 1aa was prepared from the commercially available cyclopentanone (5.0 mmol) and phenyl
bromide as a white solid (1.0 g, 58%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 8.2$ Hz, 2H), 7.73 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 6.6$ Hz, 4H), 7.26 – 7.21 (m, 1H), 4.07 (t, $J = 7.2$ Hz, 1H), 3.01 – 2.74 (m, 2H), 2.38 – 2.29 (m, 1H), 2.13 – 1.94 (m, 2H), 1.93 – 1.79 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.2, 162.6, 140.1, 134.6 (q, $J = 32.7$ Hz), 132.5, 129.9, 128.6, 127.8, 126.9, 125.5 (q, $J = 3.5$ Hz), 123.5 (q, $J = 272.8$ Hz), 49.2, 34.7, 30.0, 22.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 1748, 1511, 1324, 1242, 1066, 696; HRMS m/z (ESI) calcd for C$_{19}$H$_{16}$F$_3$N$_2$NaO$_2$ (M + Na)$^+$ 370.1025, found 370.1028.

4-(((2-Phenylcyclopentylidene)amino)oxy)carbonyl)benzonitrile (1ba)

According to the general procedure, 1ba was prepared from the commercially available cyclopentanone (2.0 mmol) and phenyl bromide as a white solid (385 mg, 63%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 8.6$ Hz, 2H), 7.77 (d, $J = 8.6$ Hz, 2H), 7.36 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 4.06 (t, $J = 7.1$ Hz, 1H), 2.98 – 2.90 (m, 1H), 2.85 – 2.76 (m, 1H), 2.38 – 2.30 (m, 1H), 2.11 – 1.82 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.4, 162.2, 140.0, 133.2, 130.0, 128.6, 127.8, 126.9, 117.9, 116.6, 49.2, 34.7, 30.1, 22.5; ATR-FTIR (cm$^{-1}$): 1745, 1280, 1243, 1070, 904; HRMS m/z (ESI) calcd for C$_{19}$H$_{16}$N$_2$NaO$_2$ (M + Na)$^+$ 327.1104, found 327.1101.

2-Phenylcyclopentan-1-one O-benzoyl oxime (1ca)

According to the general procedure, 1ca was prepared from the commercially available cyclopentanone (5.0 mmol) and phenyl bromide as a white solid (750 mg, 53%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 7.1$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 7.34 – 7.33 (m, 4H), 7.26 – 7.22 (m, 1H), 4.05 (t, $J = 7.2$ Hz, 1H), 2.98 – 2.78 (m, 2H), 2.36 – 2.29 (m, 1H), 2.05 – 1.98 (m, 2H), 1.88 – 1.79 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.5, 163.7, 140.3, 133.1, 129.5, 129.1, 128.5, 128.4, 127.8, 126.7, 49.0, 34.6, 29.8, 22.4; ATR-FTIR (cm$^{-1}$): 1746, 1690, 1290, 1211, 1058, 915; HRMS m/z (ESI) calcd for C$_{18}$H$_{17}$NNaO$_2$ (M + Na)$^+$ 302.1151, found 302.1151.
2-Phenylcyclopentan-1-one O-benzoic oxime (1da)

According to the general procedure, 1da was prepared from the commercially available cyclopentanone (2.0 mmol) and phenyl bromide as a yellow solid (391 mg, 60%): \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.31 (d, J = 8.8 \text{ Hz}, 2\text{H}), 8.22 (d, J = 8.8 \text{ Hz}, 2\text{H}), 7.38 – 7.29 (m, 4\text{H}), 7.26 – 7.20 (m, 1\text{H}), 4.07 (t, J = 7.2 \text{ Hz}, 1\text{H}), 3.00 – 2.92 (m, 1\text{H}), 2.87 – 2.78 (m, 1\text{H}), 2.39 – 2.30 (m, 1\text{H}), 2.12 – 1.75 (m, 3\text{H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 178.5, 161.9, 150.6, 140.0, 134.7, 130.6, 128.6, 127.8, 126.9, 123.7, 49.3, 34.7, 30.1, 22.5; ATR-FTIR (cm\(^{-1}\)): 1745, 1690, 1281, 1210, 1061, 852; HRMS m/z (ESI) calcd for C\(_{18}\)H\(_{16}\)N\(_2\)O\(_4\) (M + H\(^{+}\)) 347.1002, found 347.1006.

2-Phenylcyclopentan-1-one O-perfluorobenzoic oxime (1ea)

According to the general procedure, 1ea was prepared from the commercially available cyclopentanone (2.0 mmol) and phenyl bromide as a brown solid (395 mg, 53%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.37 – 7.17 (m, 5\text{H}), 4.12 – 3.98 (m, 1\text{H}), 2.92 – 2.83 (m, 1\text{H}), 2.77 – 2.60 (m, 1\text{H}) , 2.40 – 2.29 (m, 1\text{H}) 2.09 – 1.78 (m, 3\text{H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 178.9, 178.2, 156.7, 146.4, 142.0, 140.9, 139.6, 128.6, 128.1, 127.8, 127.0, 126.9, 126.5, 49.4, 48.6, 36.0, 34.7, 32.6, 30.4, 23.5, 22.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta -137.11 – -137.30 (m, 2\text{F}), -148.05 – -148.26 (m, 1\text{F}), -159.93 – -160.45 (m, 2\text{F}); ATR-FTIR (cm\(^{-1}\)): 1760, 1651, 1524, 1500, 1420, 1325, 1062; HRMS m/z (ESI) calcd for C\(_{18}\)H\(_{16}\)F\(_5\)NaO\(_2\) (M + Na\(^{+}\)) 392.0680, found 392.0681.

2-(4-(tert-Butyl)phenyl)cyclopentan-1-one O-(4-(trifluoromethyl)benzoyl) oxime (1ab)

According to the general procedure, 1ab was prepared from the commercially available cyclopentanone (5.0 mmol) and 1-bromo-4-(tert-butyl)benzene as a white solid (1.1 g, 55%): \(^1\)H
NMR (500 MHz, CDCl₃) δ 8.18 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.04 (t, J = 7.3 Hz, 1H), 2.97 – 2.91 (m, 1H), 2.85 – 2.78 (m, 1H), 2.40 – 2.22 (m, 1H), 2.15 – 1.97 (m, 2H), 1.93 – 1.78 (m, 1H), 1.31 (s, 9H); 13C NMR (126 MHz, CDCl₃) δ 178.4, 162.6, 149.6, 136.9, 134.5 (q, J = 32.7 Hz), 132.5, 129.9, 127.4, 125.5 (q, J = 3.3 Hz), 123.5 (q, J = 272.7 Hz), 48.8, 34.5, 34.3, 31.3, 29.9, 22.5; 19F NMR (471 MHz, CDCl₃) δ -63.1; ATR-FTIR (cm⁻¹): 1750, 1601, 1545, 1460, 1261, 1066, 756; HRMS m/z (ESI) calcd for C₂₃H₂₄F₃N₃NaO₂ (M + Na)⁺ 426.1651, found 426.1650.

2-(O-tolyl)cyclopentan-1-one O-(4-(trifluoromethyl)benzoyl) oxime (1ac)

According to the general procedure, 1ac was prepared from the commercially available cyclopentanone (5.0 mmol) and 1-bromo-2-methylbenzene as a white solid (650 mg, 36%): ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.21 – 7.08 (m, 4H), 4.22 (t, J = 7.3 Hz, 1H), 3.02 – 2.83 (m, 2H), 2.40 (s, 3H), 2.36 – 2.26 (m, 1H), 2.07 – 2.01 (m, 1H), 1.94 – 1.83 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 178.7, 162.6, 139.4, 135.9, 134.6 (q, J = 32.8 Hz), 132.5, 130.6, 129.9, 127.1, 126.8, 126.2, 125.5 (q, J = 3.6 Hz), 123.5 (q, J = 270.4 Hz), 46.5, 34.0, 30.5, 22.5, 19.9; ¹⁹F NMR (471 MHz, CDCl₃) δ -63.1; ATR-FTIR (cm⁻¹): 1749, 1601, 1515, 1460, 1383, 1066, 741; HRMS m/z (ESI) calcd for C₂₀H₁₈F₃N₃O₂ (M + Na)⁺ 384.1182, found 384.1185.

2-([1,1'-Biphenyl]-4-yl)cyclopentan-1-one O-(4-(trifluoromethyl)benzoyl) oxime (1ad)

According to the general procedure, 1ad was prepared from the commercially available cyclopentanone (5.0 mmol) and 4-bromo-1,1'-biphenyl as a white solid (953 mg, 45%): ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.64 – 7.54 (m, 4H), 7.48 – 7.38 (m, 4H), 7.34 (t, J = 7.4 Hz, 1H), 4.11 (t, J = 7.6 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.88 – 2.81 (m, 1H), 2.41 – 2.34 (m, 1H), 2.14 – 2.03 (m, 2H),
1.92 – 1.87 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.2, 162.6, 140.8, 139.8, 139.1, 134.6 (q, $J=32.8$ Hz), 132.5, 129.9, 128.7, 128.3, 127.4, 127.2, 127.0, 125.5 (q, $J=3.6$ Hz), 123.5 (q, $J=272.8$ Hz), 49.0, 34.7, 30.0, 22.5; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 1748, 1650, 1550, 1454, 1260, 712; HRMS m/z (ESI) calcd for C$_{25}$H$_{20}$F$_3$N$_2$O$_2$ (M + Na)$^+$ 446.1338, found 446.1340.

2-(Benzo[d][1,3]dioxol-5-yl)cyclopentan-1-one $O$-(4-(trifluoromethyl)benzoyl) oxime (1ae)

According to the general procedure, 1ae was prepared from the commercially available cyclopentanone (5.0 mmol) and 5-bromobenzo[d][1,3]dioxole as a yellow solid (768 mg, 39%): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J=8.2$ Hz, 2H), 7.72 (d, $J=8.3$ Hz, 2H), 6.90 – 6.63 (m, 3H), 5.92 (q, $J=1.3$ Hz, 2H), 3.97 (t, $J=7.1$ Hz, 1H), 2.95 – 2.89 (m, 1H), 2.81 – 2.74 (m, 1H), 2.32 – 2.27 (m, 1H), 2.22 – 2.19 (m, 1H), 2.06 – 1.93 (m, 2H), 1.87 – 1.80 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.2, 162.5, 147.8, 146.4, 134.5 (q, $J=32.6$ Hz), 133.7, 132.5, 129.9, 125.5 (q, $J=3.7$ Hz), 123.5 (q, $J=272.8$ Hz), 121.0, 108.3, 108.2, 100.9, 49.0, 34.8, 29.9, 22.4; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 1752, 1611, 1511, 1324, 1248, 1075, 746; HRMS m/z (ESI) calcd for C$_{20}$H$_{16}$F$_3$NaO$_4$ (M + Na)$^+$ 414.0924, found 414.0930.

2-(4-Fluorophenyl)cyclopentan-1-one $O$-(4-(trifluoromethyl)benzoyl) oxime (1af)

According to the general procedure, 1af was prepared from the commercially available cyclopentanone (5.0 mmol) and 1-bromo-4-fluorobenzene as a white solid (723 mg, 40%): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J=8.1$ Hz, 2H), 7.73 (d, $J=8.3$ Hz, 2H), 7.29 (dd, $J=8.6$, 5.3 Hz, 2H), 7.03 (t, $J=8.7$ Hz, 2H), 4.03 (t, $J=7.3$ Hz, 1H), 2.98 – 2.92 (m, 1H), 2.83 – 2.76 (m, 1H), 2.37 – 2.31 (m, 1H), 2.05 – 1.97 (m, 2H), 1.91 – 1.83 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.0, 162.7 (d, $J=20.7$ Hz), 160.8, 135.7 (d, $J=3.3$ Hz), 134.6 (q, $J=32.8$ Hz), 132.4, 129.9, 129.4 (d, $J=8.0$ Hz), 125.5 (q, $J=3.7$ Hz), 123.5 (q, $J=272.8$ Hz), 115.4 (d, $J=21.4$ Hz), 48.6, 34.8,
29.9, 22.4; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.2, -116.1; ATR-FTIR (cm$^{-1}$): 1749, 1640, 1451, 1263, 708; HRMS m/z (ESI) calcd for C$_{10}$H$_{15}$F$_4$NaO$_2$ (M + Na)$^+$ 388.0931, found 388.0933.

Methyl 4-(2-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclopentyl)benzoate (1ag) According to the general procedure, 1ag was prepared from the commercially available cyclopentanone (5.0 mmol) and methyl 4-bromobenzoate as a yellow solid (674 mg, 33%): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J$ = 8.1 Hz, 2H), 7.73 (d, $J$ = 8.3 Hz, 2H), 7.25 (d, $J$ = 8.7 Hz, 2H), 6.88 (d, $J$ = 8.7 Hz, 2H), 4.01 (t, $J$ = 7.2 Hz, 1H), 3.79 (s, 3H), 3.00 – 2.87 (m, 1H), 2.84 – 2.73 (m, 1H), 2.36 – 2.23 (m, 1H), 2.07 – 1.96 (m, 2H), 1.90 – 1.80 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.4, 162.6, 158.4, 134.6 (q, $J$ = 32.7 Hz), 132.5, 131.9, 129.9, 128.8, 125.5 (q, $J$ = 3.7 Hz), 123.5 (q, $J$ = 272.8 Hz), 114.0, 55.2, 48.5, 34.6, 29.9, 22.4; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 1749, 1721, 1550, 1450, 1015, 832; HRMS m/z (ESI) calcd for C$_{21}$H$_{18}$F$_3$NNaO$_4$ (M + H)$^+$ 428.1080, found 428.1085.

2-(Naphthalen-2-yl)cyclopentan-1-one O-(4-(trifluoromethyl)benzoyl) oxime (1ah) According to the general procedure, 1ah was prepared from the commercially available cyclopentanone (5.0 mmol) and 2-bromonaphthalene as a white solid (1.0 g, 51%): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J$ = 8.1 Hz, 2H), 7.88 – 7.79 (m, 3H), 7.77 – 7.72 (m, 3H), 7.50 – 7.42 (m, 3H), 4.24 (t, $J$ = 7.7 Hz, 1H), 3.02 – 2.96 (m, 1H), 2.91 – 2.84 (m, 1H), 2.44 – 2.37 (m, 1H), 2.22 – 2.15 (m, 1H), 2.11 – 2.03 (m, 1H), 1.97 – 1.86 (m, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.1, 162.6, 137.4, 134.6 (q, $J$ = 32.9 Hz), 133.4, 132.5, 132.4, 130.0, 128.4, 127.8, 127.6, 126.4, 126.1, 126.2, 125.7, 125.5 (q, $J$ = 3.7 Hz), 123.5 (q, $J$ = 272.8 Hz), 49.4, 34.6, 30.1, 22.6; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 1749, 1515, 1462, 1270, 1089, 756; HRMS m/z (ESI) calcd for C$_{23}$H$_{18}$F$_3$NNaO$_4$ (M + Na)$^+$ 420.1182, found 420.1185.
2-(Benzo[b]thiophen-5-yl)cyclopentan-1-one \(O\)-(4-(trifluoromethyl)benzoyl) oxime (1ai)

According to the general procedure, 1ai was prepared from the commercially available cyclopentanone (5.0 mmol) and 5-bromobenzo[b]thiophene as a white solid (870 mg, 43%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 (d, \(J = 8.1\) Hz, 2H), 7.85 (d, \(J = 8.4\) Hz, 1H), 7.80 – 7.69 (m, 3H), 7.43 (d, \(J = 5.4\) Hz, 1H), 7.35 – 7.28 (m, 2H), 4.19 (t, \(J = 7.9\) Hz, 1H), 3.02 – 2.94 (m, 1H), 2.91 – 2.78 (m, 1H), 2.43 – 2.35 (m, 1H), 2.20 – 2.02 (m, 2H), 1.95 – 1.83 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 178.3, 162.6, 139.9, 138.4, 136.2, 134.6 (q, \(J = 32.7\) Hz), 132.5, 129.9, 126.8, 125.5 (q, \(J = 3.7\) Hz), 124.4, 123.8, 123.5 (q, \(J = 272.8\) Hz), 122.7, 49.2, 34.9, 30.0, 22.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.1; ATR-FTIR (cm\(^{-1}\)): 1747, 1511, 1411, 1277, 1074, 860; HRMS m/z (ESI) calcd for C\(_{21}\)H\(_{16}\)F\(_3\)N\(_2\)O\(_2\)S (M + Na\(^+\)) 426.0746, found 426.0750.

2-Phenylcyclobutan-1-one \(O\)-(4-(trifluoromethyl)benzoyl) oxime (1aj) \((E/Z\) mixture\)

According to the general procedure, 1aj was prepared from the corresponding ketone which was synthesized according to the reported literature\(^2\) as a brown solid (3.0 mmol, 553 mg, 55%): \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.17 (d, \(J = 8.2\) Hz, 1.35H), 7.73 (d, \(J = 8.4\) Hz, 1.38H), 7.51 – 7.46 (m, 1.3H), 7.43 – 7.24 (m, 5H), 4.72 – 4.53 (m, 1H), 3.30 – 3.07 (m, 2H), 2.68 – 2.58 (m, 1H), 2.34 – 2.16 (m, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 171.6, 169.9, 162.7, 138.9, 138.4, 134.7 (q, \(J = 32.8\) Hz), 132.3, 130.0, 129.8, 129.0, 128.7, 127.4, 127.3, 127.2, 127.1, 125.5 (q, \(J = 3.7\) Hz), 125.2 (q, \(J = 3.6\) Hz), 123.5 (q, \(J = 272.7\) Hz), 51.4, 49.6, 29.5, 29.3, 24.4, 23.2; \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -63.15 , -63.19; ATR-FTIR (cm\(^{-1}\)): 1750, 1654, 1501, 1454, 1277, 1074, 860; HRMS m/z (ESI) calcd for C\(_{18}\)H\(_{10}\)F\(_3\)N\(_2\)O\(_2\) (M + Na\(^+\)) 356.0869, found 356.0873.

2-Phenylcyclohexan-1-one \(O\)-(4-(trifluoromethyl)benzoyl) oxime (1ak)
According to the general procedure, 1a was prepared from the commercially available ketone (2.0 mmol, CAS:1444-65-1) as a white solid (594 mg, 82%): 

\[ ^1H\text{ NMR (}500\text{ MHz, CDCl}_3\text{)} \delta 8.19 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.41 - 7.34 (m, 4H), 7.32 - 7.24 (m, 1H), 4.02 (t, J = 4.9 Hz, 1H), 2.98 - 2.93 (m, 1H), 2.57 - 2.44 (m, 1H), 2.37 - 2.32 (m, 1H), 2.12 - 2.05 (m, 1H), 1.88 - 1.68 (m, 4H); \]

\[ ^13C\text{ NMR (}126\text{ MHz, CDCl}_3\text{)} \delta 172.1, 163.0, 138.7, 134.6 (q, J = 32.7 Hz), 132.7, 130.0, 128.6, 127.7, 126.8, 125.5 (q, J = 3.7 Hz), 123.5 (q, J = 273.1 Hz), 45.5, 31.0, 26.4, 25.4, 22.1; \]

\[ ^19F\text{ NMR (}471\text{ MHz, CDCl}_3\text{)} \delta -63.1; \]

\[ \text{ATR-FTIR (cm}^{-1}\text{):} 1748, 1635, 1515, 1464, 1260, 1110, 710; \]

\[ \text{HRMS m/z (ESI) calcd for C}_{20}H_{19}F_{3}NO_{2} (M + H)^+ 362.1362, \text{ found 362.1366}. \]

Methyl 4-(5,5-dimethyl-2-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclohexyl) benzoate (1al) (E/Z mixture)

According to the general procedure, 1al was prepared from the corresponding ketone which was synthesized according to the reported literature\[^{[3]}\] as a white solid (3.0 mmol, 906 mg, 68%): 

\[ ^1H\text{ NMR (}400\text{ MHz, CDCl}_3\text{)} \delta 8.12 (d, J = 8.1 Hz, 1.5H), 8.03 - 7.98 (m, 2H), 7.72 - 7.68 (m, 2H), 7.55 (d, J = 8.3 Hz, 0.52H), 7.41 (d, J = 8.3 Hz, 1.51H), 7.31 (d, J = 8.2 Hz, 0.56H), 4.42 (t, J = 7.0 Hz, 0.34H), 3.90 (s, 3H), 3.88 - 3.86 (m, 0.64H), 3.16 (dt, J = 15.2, 4.4 Hz, 1H), 2.45 - 2.36 (m, 1H), 2.04 - 1.98 (m, 1H), 1.90 - 1.59 (m, 3H), 1.18 (s, 2H), 1.04 (s, 1H), 1.02 (s, 2H), 0.85 (s, 1H); \]

\[ ^13C\text{ NMR (}101\text{ MHz, CDCl}_3\text{)} \delta 171.9, 170.0, 167.0, 162.7, 146.1, 144.7, 132.6, 130.2, 129.9, 129.8, 129.7, 128.8, 126.7, 125.5 (q, J = 3.6 Hz), 125.4, 125.3, 52.0, 47.0, 45.5, 44.1, 40.9, 38.0, 36.9, 31.1, 30.9, 30.2, 30.1, 29.2, 27.5, 25.1, 23.7; \]

\[ ^19F\text{ NMR (}376\text{ MHz, CDCl}_3\text{)} \delta -63.17, -63.24; \]

\[ \text{ATR-FTIR (cm}^{-1}\text{):} 1747, 1720, 1600, 1545, 1462, 1380, 1260, 1069, 720; \]

\[ \text{HRMS m/z (ESI) calcd for C}_{24}H_{24}F_{3}NNaO_{4} (M + Na)^+ 470.1550, \text{ found 470.1556}. \]
According to the general procedure, 1am was prepared from the corresponding ketone which was synthesized according to the reported literature\cite{3} as a brown solid (3.0 mmol, 739 mg, 61%): ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.06 (dd, J = 10.8, 6.7 Hz, 1H), 3.79 (s, 3H), 3.12 – 3.08 (m, 1H), 2.39 – 2.33 (m, 1H), 2.10 (td, J = 12.5, 2.4 Hz, 1H), 1.99 – 1.90 (m, 4H), 1.62 – 1.55 (m, 1H), 1.46 – 1.39 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 173.9, 162.8, 158.5, 134.6 (q, J = 32.7 Hz), 132.7, 132.5, 129.9, 128.3, 125.5 (q, J = 3.7 Hz), 123.5 (q, J = 272.7 Hz), 113.9, 55.2, 47.6, 30.9, 30.7, 27.4, 26.3, 25.4; ¹⁹F NMR (471 MHz, CDCl₃) δ -63.2; ATR-FTIR (cm⁻¹): 1747, 1600, 1515, 1462, 1293, 1201, 1060, 855; HRMS m/z (ESI) calcd for C₂₂H₂₂F₃NNaO₃ (M + Na)⁺ 428.1444, found 428.1444.

According to the general procedure, 1an was prepared from the corresponding ketone which was synthesized according to the reported literature\cite{3} as a brown solid (3.0 mmol, 670 mg, 49%): ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.1 Hz, 2H), 7.68 – 7.54 (m, 3H), 7.47 – 7.32 (m, 2H), 7.24 – 7.21 (m, 2H), 6.87 – 6.80 (m, 2H), 4.28 – 4.24 (m, 1H), 3.78 (s, 3H), 2.97 – 2.74 (m, 2H), 2.12 – 1.62 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 173.3, 162.6, 158.3, 138.9, 134.8, 134.3, 133.0, 132.3, 130.7, 130.1, 129.9, 129.6, 129.3, 129.0, 128.5, 128.1, 127.0, 125.7, 125.3 (q, J = 3.9 Hz), 114.2, 113.9, 55.3, 44.7, 31.9, 30.5, 24.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.1, -63.2; ATR-FTIR (cm⁻¹): 1752, 1611, 1511, 1324, 1248, 1075, 747; HRMS m/z (ESI) calcd for C₂₆H₂₂F₃NNaO₃ (M + Na)⁺ 476.1444, found 476.1447.
2-(4-Methoxyphenyl)cyclooctan-1-one \( O-(4\text{-}(\text{trifluoromethyl})\text{benzoyl}) \) oxime (1ao)

According to the general procedure, 1ao was prepared from the corresponding ketone which was synthesized according to the reported literature\cite{3} as a brown solid (3.0 mmol, 695 mg, 55\%): \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.16 (d, \(J = 8.2\) Hz, 2H), 7.73 (d, \(J = 8.3\) Hz, 2H), 7.34 (d, \(J = 8.7\) Hz, 2H), 6.86 (d, \(J = 8.7\) Hz, 2H), 3.94 (dd, \(J = 12.7, 3.1\) Hz, 1H), 3.78 (s, 3H), 2.79 (dt, \(J = 12.7, 4.1\) Hz, 1H), 2.38 – 2.24 (m, 1H), 2.09 – 2.00 (m, 2H), 1.91 – 1.72 (m, 6H), 1.51 – 1.40 (m, 2H); \(^{13}\text{C}\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 174.9, 162.8, 158.7, 134.6 (q, \(J = 32.9\) Hz), 132.7, 132.2, 129.9, 128.5, 125.6 (q, \(J = 3.7\) Hz), 123.5 (q, \(J = 272.7\) Hz), 113.9, 55.2, 47.7, 26.8, 26.4, 26.3, 24.8, 24.8; \(^{19}\text{F}\) NMR (471 MHz, CDCl\(_3\)) \(\delta\) -63.2; ATR-FTIR (cm\(^{-1}\)) 1748, 1545, 1460, 1290, 1209, 1066, 741; HRMS m/z (ESI) calcd for C\(_{23}\)H\(_{24}\)F\(_3\)NNaO\(_3\) (M + Na\(^+\)) 442.1600, found 442.1602.

4-(4-(\text{tert-Butyl})phenyl)-2-methylhexan-3-one \( O-(4\text{-}(\text{trifluoromethyl})\text{benzoyl}) \) oxime (1ap) (E/Z mixture)

According to the general procedure, 1ap was prepared from the corresponding ketone which was synthesized according to the reported literature\cite{3} as a colorless (3.0 mmol, 562 mg, 43\%): \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (d, \(J = 8.1\) Hz, 0.6H), 8.08 (d, \(J = 8.3\) Hz, 1.41H), 7.76 – 7.70 (m, 2H), 7.38 – 7.28 (m, 2.59H), 7.20 (d, \(J = 8.3\) Hz, 1.41H), 4.46 – 4.29 (m, 0.69H), 3.61 (t, \(J = 7.6\) Hz, 0.24H), 3.06 – 2.99 (m, 0.23H), 2.67 – 2.60 (m, 0.68H), 2.19 – 1.84 (m, 2H), 1.31 – 1.28 (m, 11H), 1.20 (d, \(J = 7.0\) Hz, 1H), 1.05 (t, \(J = 7.4\) Hz, 2H), 0.99 – 0.94 (m, 3H), 0.90 (d, \(J = 7.1\) Hz, 1H); \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 175.9, 175.1, 162.8, 150.0, 150.0, 136.7, 135.6, 134.5 (q, \(J = 32.7\) Hz), 132.8, 130.0, 128.1, 127.5, 125.5, 125.4, 123.5 (q, \(J = 272.8\) Hz), 50.7, 46.9, 34.4, 32.1, 31.3, 31.3, 30.5, 26.7, 24.0, 22.0, 21.7, 19.4, 19.3, 12.7, 12.4; \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.15, -63.16; ATR-FTIR (cm\(^{-1}\)) 1749, 1601, 1515, 1467, 1071, 741; HRMS m/z (ESI) calcd for C\(_{25}\)H\(_{30}\)F\(_3\)NNaO\(_2\) (M + Na\(^+\)) 456.2121,
found 456.2126.

3. Experimental Procedures and Characterization of Photoinduced Fragmentation-Rearrangement

4-Cyano-1-phenylbutyl 4-(trifluoromethyl)benzoate (2aa)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1aa (0.2 mmol, 69.4 mg), fac-Ir(ppy)_3 (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 10:1) to afford 56.1 mg (81%) of 2aa as a colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.19 (d, \(J = 8.1\) Hz, 2H), 7.72 (d, \(J = 8.3\) Hz, 2H), 7.43 – 7.32 (m, 5H), 6.04 (dd, \(J = 7.6, 5.9\) Hz, 1H), 2.40 (t, \(J = 7.1\) Hz, 2H), 2.30 – 2.22 (m, 1H), 2.15 – 2.08 (m, 1H), 1.86 – 1.67 (m, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 164.5, 139.2, 134.6 (q, \(J = 32.7\) Hz), 133.2, 130.0, 128.8, 128.5, 126.2, 125.4 (q, \(J = 3.7\) Hz), 123.5 (q, \(J = 272.8\) Hz), 119.1, 76.1, 35.2, 21.6, 16.9; \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) -63.1; ATR-FTIR (cm\(^{-1}\)): 2246, 1727, 1412, 1590, 1515, 1462, 1171, 1064, 775; HRMS m/z (ESI) calcd for C\(_{19}\)H\(_{17}\)F\(_3\)N\(_2\)O\(_2\) (M + H)\(^+\) 348.1206, found 348.1203.

4-Cyano-1-phenylbutyl 4-cyanobenzoate (2ba)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ba (0.2 mmol, 60.8 mg), fac-Ir(ppy)_3 (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to
remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 5:1) to afford 46.6 mg (77%) of 2ba as a colorless oil: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.16 (d, $J = 8.3$ Hz, 2H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.42 – 7.32 (m, 5H), 6.02 (dd, $J = 7.5$, 6.1 Hz, 1H), 2.39 (t, $J = 7.1$ Hz, 2H), 2.29 – 2.21 (m, 1H), 2.14 – 2.08 (m, 1H), 1.83 – 1.66 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.0, 139.0, 133.7, 132.2, 130.0, 128.8, 128.5, 126.2, 119.0, 117.8, 116.5, 76.4, 35.0, 21.5, 16.9; ATR-FTIR (cm$^{-1}$): 2245, 2224, 1722, 1659, 1632, 1412, 1310, 1019, 762; HRMS m/z (ESI) calcd for C$_{19}$H$_{16}$N$_2$NaO$_2$ (M + Na)$^+$ 327.1104, found 327.1099.

1-(4-((tert-Butyl)phenyl)-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ab)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ab (0.2 mmol, 80.6 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 10:1) to afford 62.5 mg (78%) of 2ab as a colorless oil: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.41 – 7.34 (m, 4H), 6.03 (dd, $J = 7.5$, 6.1 Hz, 1H), 2.40 (t, $J = 7.1$ Hz, 2H), 2.29 – 2.22 (m, 1H), 2.14 – 2.07 (m, 1H), 1.84 – 1.68 (m, 2H), 1.31 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.5, 151.5, 136.1, 134.5 (q, $J = 32.6$ Hz), 133.3, 130.0, 126.1, 125.7, 125.4 (q, $J = 3.6$ Hz), 123.5 (q, $J = 272.8$ Hz), 119.1, 76.0, 35.1, 31.2, 21.7, 16.9; $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.1; ATR-FTIR (cm$^{-1}$): 2246, 1723, 1513, 1432, 1324, 1245, 1066, 775; HRMS m/z (ESI) calcd for C$_{23}$H$_{24}$F$_3$NNaO$_2$ (M + Na)$^+$ 426.1651, found 426.1655.

4-Cyano-1-(o-tolyl)butyl 4-(trifluoromethyl)benzoate (2ac)
Flame-dried 25 mL Schlenk tube filled with 1ab (0.2 mmol, 60.1 mg), fac-Ir(ppy)₃ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 10:1) to afford 60.1 mg (83%) of 2ab as a yellow oil: ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.43 – 7.42 (m, 1H), 7.24 – 7.18 (m, 3H), 6.26 (dd, J = 8.2, 5.2 Hz, 1H), 2.49 (s, 3H), 2.42 (t, J = 7.1 Hz, 2H), 2.27 – 2.19 (m, 1H), 2.11 – 2.04 (m, 1H), 1.91 – 1.83 (m, 1H), 1.80 – 1.71 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 164.5, 137.8, 134.9, 134.6 (q, J = 32.6 Hz), 133.2, 130.7, 130.0, 128.2, 126.5, 125.5 (q, J = 3.6 Hz), 123.5 (q, J = 272.7 Hz), 72.9, 34.6, 21.7, 19.2, 17.0; ¹⁹F NMR (471 MHz, CDCl₃) δ -63.1; ATR-FTIR (cm⁻¹): 2247, 1725, 1603, 1556, 1328, 1068, 766; HRMS m/z (ESI) calcd for C₁₂H₁₉F₃N₂O₂ (M + H)+ 362.1362, found 362.1361.

1-[(1,1'-Biphenyl]-4-yl]-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ad)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ad (0.2 mmol, 84.6 mg), fac-Ir(ppy)₃ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 56.9 mg (67%) of 2ab as a colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.63 – 7.58 (m, 4H), 7.50 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 6.09 (dd, J = 7.5, 6.0 Hz, 1H), 2.43 (t, J = 7.1 Hz, 2H), 2.34 – 2.27 (m, 1H), 2.19 – 2.12 (m, 1H), 1.89 – 1.73 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 164.5, 141.5, 140.4, 138.2, 134.6 (q, J = 32.6 Hz),
133.2, 130.0, 128.8, 127.1, 126.7, 125.5 (q, $J = 3.6$ Hz), 123.5 (q, $J = 272.8$ Hz), 119.1, 76.0, 35.1, 21.6, 17.0; $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.1; ATR-FTIR (cm$^{-1}$): 2247, 1725, 1596, 1536, 1469, 1085, 796; HRMS m/z (ESI) calcd for C$_{25}$H$_{20}$F$_3$NNaO$_2$ (M + Na)$^+$ 446.1338, found 446.1334.

1-(Benzo[d][1,3]dioxol-5-yl)-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ae)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ae (0.2 mmol, 78.2 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 5:1) to afford 67.4 mg (86%) of 2ag as a colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.2 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 6.91 – 6.88 (m, 2H), 6.79 (d, $J = 7.9$ Hz, 1H), 5.96 – 5.95 (m, 2H), 5.92 (dd, $J = 7.5$, 6.3 Hz, 1H), 2.40 (t, $J = 7.1$ Hz, 2H), 2.26 – 2.18 (m, 1H), 2.09 – 2.02 (m, 1H), 1.82 – 1.66 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.4, 148.0, 147.7, 134.6 (q, $J = 32.6$ Hz), 133.2, 133.0, 130.0, 125.4 (q, $J = 3.8$ Hz), 123.5 (q, $J = 272.8$ Hz), 120.3, 119.1, 108.3, 106.6, 101.2, 76.1, 35.1, 21.6, 16.9; $^{19}$F NMR (471 MHz, CDCl$_3$) δ -63.1; ATR-FTIR (cm$^{-1}$): 2246, 1722, 1565, 1413, 1336, 1069, 765; HRMS m/z (ESI) calcd for C$_{20}$H$_{16}$F$_3$NNaO$_4$ (M + Na)$^+$ 414.0924, found 414.0925.

4-Cyano-1-(4-fluorophenyl)butyl 4-(trifluoromethyl)benzoate (2af)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1af (0.2 mmol, 73.0 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The
residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 40.2 mg (55%) of 2af as a colorless oil: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.2$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.41 – 7.39 (m, 2H), 7.07 (t, $J = 8.6$ Hz, 2H), 6.00 (dd, $J = 7.8$, 5.9 Hz, 1H), 2.41 (t, $J = 7.0$ Hz, 2H), 2.29 – 2.21 (m, 1H), 2.12 – 2.04 (m, 1H), 1.84 – 1.67 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 164.5, 162.6 (d, $J = 247.5$ Hz), 135.1 (d, $J = 3.1$ Hz), 134.7 (q, $J = 32.7$ Hz), 133.0, 130.0, 128.2 (d, $J = 8.2$ Hz), 125.5 (q, $J = 3.7$ Hz), 123.5 (q, $J = 272.8$ Hz), 119.1, 115.8 (d, $J = 21.7$ Hz), 75.5, 35.1, 21.6, 17.0; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.2, -113.0; ATR-FTIR (cm$^{-1}$): 2247, 1723, 1068, 1550, 1466, 1069, 758; HRMS m/z (ESI) calcd for C$_{19}$H$_{15}$F$_4$O$_2$N (M + Na)$^+$ 388.0931, found 388.0926.

4-Cyano-1-(4-(methoxycarbonyl)phenyl)butyl 4-(trifluoromethyl)benzoate (2ag)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ag (0.2 mmol, 81.0 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 56.5 mg (70%) of 2ag as a yellow oil: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 5.98 (t, $J = 6.9$ Hz, 1H), 3.80 (s, 3H), 2.39 (t, $J = 7.1$ Hz, 2H), 2.29 – 2.21 (m, 1H), 2.12 – 2.05 (m, 1H), 1.82 – 1.64 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 164.5, 159.7, 134.5 (q, $J = 32.6$ Hz), 133.3, 131.2, 130.0, 127.8, 125.4 (q, $J = 3.6$ Hz), 123.5 (q, $J = 272.8$ Hz), 119.1, 114.1, 75.9, 55.2, 35.0, 21.7, 16.9; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 2246, 1720, 1515, 1412, 1066, 747; HRMS m/z (ESI) calcd for C$_{21}$H$_{18}$F$_3$NNaO$_2$ (M + Na)$^+$ 428.1080, found 428.1083.

4-Cyano-1-(naphthalen-2-yl)butyl 4-(trifluoromethyl)benzoate (2ah)
Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ag (0.2 mmol, 79.4 mg), fac-Ir(ppy)₃ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 58.6 mg (74%) of 2ah as a colorless oil: *¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.1 Hz, 2H), 7.90 – 7.83 (m, 4H), 7.73 (d, J = 8.3 Hz, 2H), 7.56 – 7.50 (m, 3H), 6.21 (t, J = 7.0 Hz, 1H), 2.41 (t, J = 7.1 Hz, 2H), 2.37 – 2.31 (m, 1H), 2.25 – 2.16 (m, 1H), 1.91 – 1.69 (m, 2H); *¹³C NMR (126 MHz, CDCl₃) δ 164.5, 136.5, 134.6, 129.8, 128.0, 127.7, 126.5, 126.4, 125.7, 125.5, 119.0, 76.3, 35.0, 21.7, 17.0. *¹⁹F NMR (376 MHz, CDCl₃) δ -63.1; ATR-FTIR (cm⁻¹): 2247, 1724, 1609, 1566, 1411, 1077, 699; HRMS m/z (ESI) calcd for C₂₃H₁₈F₃N₂O₂ (M + Na)⁺ 420.1182, found 420.1183.

1-(Benzo[b]thiophen-5-yl)-4-cyanobutyl 4-(trifluoromethyl)benzoate (2ai)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ai (0.2 mmol, 90.2 mg), fac-Ir(ppy)₃ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 68.9 mg (76%) of 2ai as a colorless oil: *¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 9.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 5.4 Hz, 1H), 7.42 (dd, J = 8.3, 1.4 Hz, 1H), 7.34 (d, J = 5.5 Hz, 1H), 6.16 (t, J = 7.0 Hz, 1H), 2.40 (t, J = 7.1 Hz, 2H), 2.37 – 2.30 (m, 1H), 2.21 – 2.14 (m, 1H), 1.87 – 1.69 (m, 2H); *¹³C NMR (126 MHz, CDCl₃) δ 164.5, 139.7, 139.6, 135.4,
134.5 (q, \( J = 32.7 \) Hz), 133.2, 130.0, 127.5, 125.4 (q, \( J = 3.6 \) Hz), 123.7, 123.5 (q, \( J = 272.9 \) Hz), 122.9, 122.3, 121.6, 119.1, 76.4, 35.3, 21.6, 16.9; \(^{19}\text{F NMR (471 MHz, CDCls)} \delta -63.1; \ ATR-FTIR (cm \(^{-1}\))\): 2245, 1721, 1510, 1375, 1276, 1065, 703; HRMS m/z (ESI) calcd for C\(_{21}\)H\(_{16}\)F\(_{3}\)N\(_{2}\)NaO\(_{2}\) (M + H\(^{+}\)) 426.0746, found 426.0748.

3-Cyano-1-phenylpropyl 4-(trifluoromethyl)benzoate (2aj)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1aj (0.2 mmol, 66.6 mg), fac-Ir(ppy)_3 (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 10:1) to afford 35.8 mg (54%) of 2aj as a colorless oil: \(^{1}\text{H NMR (500 MHz, CDCls)} \delta 8.21 (d, \( J = 8.2 \) Hz, 2H), 7.73 (d, \( J = 8.2 \) Hz, 2H), 7.42 – 7.35 (m, 5H), 6.11 (t, \( J = 5.9 \) Hz, 1H), 2.49 – 2.30 (m, 4H); \(^{13}\text{C NMR (126 MHz, CDCls)} \delta 164.3, 138.2, 134.8 (q, \( J = 32.7 \) Hz), 132.9, 130.2, 129.0, 128.8, 126.1, 125.5 (q, \( J = 3.6 \) Hz), 123.5 (q, \( J = 272.8 \) Hz), 118.8, 32.0, 13.7; \(^{19}\text{F NMR (471 MHz, CDCls)} \delta -63.2; \ ATR-FTIR (cm \(^{-1}\))\): 2246, 1726, 1611, 1510, 1507, 1436, 1066, 788; HRMS m/z (ESI) calcd for C\(_{18}\)H\(_{14}\)F\(_{3}\)N\(_{2}\)NaO\(_{2}\) (M + Na\(^{+}\)) 356.0869, found 356.0864.

5-Cyano-1-phenylpentyl 4-(trifluoromethyl)benzoate (2ak)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ak (0.2 mmol, 72.2 mg), fac-Ir(ppy)_3 (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 10:1) to afford 34.9 mg (48%) of 2ak as a
colorless oil: \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.18 (d, \( J = 8.5 \) Hz, 2H), 7.71 (d, \( J = 8.4 \) Hz, 2H), 7.42 – 7.31 (m, 5H), 6.00 (t, \( J = 6.8 \) Hz, 1H), 2.34 (t, \( J = 7.0 \) Hz, 2H), 2.17 – 2.10 (m, 1H), 2.01 – 1.94 (m, 1H), 1.75 – 1.69 (m, 2H), 1.64 – 1.45 (m, 2H); \( ^{13}C \) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 164.6, 139.7, 134.5 (q, \( J = 32.8 \) Hz), 133.4, 130.0, 128.7, 128.3, 126.3, 125.4 (q, \( J = 3.6 \) Hz), 123.6 (d, \( J = 272.7 \) Hz), 119.3, 76.8, 35.5, 25.1, 24.6, 17.0; \( ^{19}F \) NMR (471 MHz, CDCl\(_3\)) \( \delta \) -63.1; ATR-FTIR (cm\(^{-1}\)): 2247, 1726, 1516, 1466, 1079, 762; HRMS m/z (ESI) calcd for C\(_{20}\)H\(_{18}\)F\(_3\)N\(_2\)NaO\(_2\) (M + Na\(^+\)) 384.1182, found 384.1177.

6-Cyano-1-(4-methoxyphenyl)hexyl 4-(trifluoromethyl)benzoate (2al)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1al (0.2 mmol, 89.5 mg), fac-Ir(ppy)_3 (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 48.5 mg (54%) of 2al as a colorless oil: \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.16 (d, \( J = 8.1 \) Hz, 2H), 8.02 (d, \( J = 8.3 \) Hz, 2H), 7.73 (d, \( J = 8.3 \) Hz, 2H), 7.46 (d, \( J = 8.3 \) Hz, 2H), 6.14 (dd, \( J = 9.3 \), 3.1 Hz, 1H), 3.90 (s, 3H), 2.43 – 2.25 (m, 2H), 2.19 (dd, \( J = 15.1 \), 9.3 Hz, 1H), 1.82 – 1.65 (m, 3H), 1.03 (d, \( J = 7.2 \) Hz, 6H); \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.5, 164.3, 146.1, 134.8 (q, \( J = 32.8 \) Hz), 132.9, 130.1, 130.1, 130.0, 126.1, 125.6 (q, \( J = 3.6 \) Hz), 123.5 (d, \( J = 272.8 \) Hz), 120.0, 74.1, 52.2, 47.4, 37.8, 33.1, 26.8, 26.8, 12.4; \( ^{19}F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -63.2; ATR-FTIR (cm\(^{-1}\)): 2246, 1727, 1720, 1600, 1545, 1412, 1383, 1264, 1070, 852; HRMS m/z (ESI) calcd for C\(_{25}\)H\(_{24}\)F\(_3\)N\(_2\)NaO\(_4\) (M + Na\(^+\)) 470.1550, found 470.1556.

6-Cyano-1-(4-methoxyphenyl)hexyl 4-(trifluoromethyl)benzoate (2am)
Flame-dried 25 mL Schlenk tube filled with argon was charged with 1am (0.2 mmol, 81.0 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 51.6 mg (63%) of 2am as a colorless oil: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 5.95 (t, $J = 7.0$ Hz, 1H), 3.80 (s, 3H), 2.31 (t, $J = 7.0$ Hz, 2H), 2.14 – 2.07 (m, 1H), 1.96 – 1.89 (m, 1H), 1.67 – 1.61 (m, 2H), 1.54 – 1.28 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 164.6, 159.5, 134.3 (q, $J = 32.6$ Hz), 133.6, 132.0, 129.9, 127.9, 125.3 (q, $J = 3.6$ Hz), 123.6 (q, $J = 272.7$ Hz), 119.6, 113.9, 76.9, 55.2, 35.8, 28.3, 25.2, 24.8, 17.0; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 2247, 1727, 1514, 1327, 1085, 1065, 786; HRMS m/z (ESI) calcd for C$_{22}$H$_{22}$F$_3$NNaO$_3$ (M + Na)$^+$ 428.1444, found 428.1445.

4-(2-Cyanophenyl)-1-(4-methoxyphenyl)butyl 4-(trifluoromethyl)benzoate (2an)

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1an (0.2 mmol, 90.6 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 69.1 mg (76%) of 2an as a colorless oil: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 8.2$ Hz, 2H), 7.69 (d, $J = 8.3$ Hz, 2H), 7.59 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.49 (td, $J = 7.7$, 1.3 Hz, 1H), 7.36 (d, $J = 8.7$ Hz, 2H), 7.30 – 7.27 (m, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 6.01 – 5.98 (m, 1H), 3.79 (s,
3H), 2.90 (t, \( J = 7.8 \) Hz, 2H), 2.22 – 2.15 (m, 1H), 2.04 – 1.96 (m, 1H), 1.87 – 1.65 (m, 2H); \(^{13}\text{C}\ NMR (126 MHz, CDCl\text{3}) \delta 164.6, 159.4, 145.7, 134.3 (q, \( J = 32.7 \) Hz), 133.6, 132.8, 132.8, 131.9, 130.0, 129.3, 127.9, 126.6, 125.3 (q, \( J = 3.6 \) Hz), 123.6 (q, \( J = 272.7 \) Hz), 118.0, 113.9, 112.3, 76.7, 55.2, 35.6, 34.1, 26.9; \(^{19}\text{F}\ NMR (471 MHz, CDCl\text{3}) \delta -63.1; \ ATR-FTIR (cm\(^{-1}\)) : 2246, 2224, 1727, 1565, 1512, 1413, 1066, 778; \ HRMS m/z (ESI) calcd for C\text{26}H\text{22}F\text{3}N\text{NaO}\text{3} (M \text{ + Na})\text{+} 476.1444, found 476.1444.

7-Cyano-1-(4-methoxyphenyl)heptyl 4-(trifluoromethyl)benzoate (2ao)

Flame-dried 25 mL Schlenk tube filled with argon was charged with \textbf{1ao} (0.2 mmol, 83.3 mg), fac-Ir(ppy)\text{3} (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 7:1) to afford 57.9 mg (69\%) of \textbf{2ao} as a colorless oil; \(^{1}\text{H}\ NMR (400 MHz, CDCl\text{3}) \delta 8.16 (d, \( J = 8.1 \) Hz, 2H), 7.70 (d, \( J = 8.3 \) Hz, 2H), 7.35 (d, \( J = 8.7 \) Hz, 2H), 6.90 (d, \( J = 8.7 \) Hz, 2H), 5.94 (t, \( J = 7.0 \) Hz, 1H), 3.80 (s, 3H), 2.31 (t, \( J = 7.1 \) Hz, 2H), 2.12 – 2.05 (m, 1H), 1.95 – 1.87 (m, 1H), 1.66 – 1.59 (m, 2H), 1.48 – 1.26 (m, 6H); \(^{13}\text{C}\ NMR (101 MHz, CDCl\text{3}) \delta 164.7, 159.5, 134.4 (q, \( J = 32.7 \) Hz), 133.8, 132.2, 130.0, 128.0, 125.4 (q, \( J = 3.4 \) Hz), 123.6 (q, \( J = 272.6 \) Hz), 119.7, 114.0, 77.0, 55.3, 36.0, 28.5, 25.3, 25.2, 17.1; \(^{19}\text{F}\ NMR (376 MHz, CDCl\text{3}) \delta -63.1; \ ATR-FTIR (cm\(^{-1}\)) : 2246, 1725, 1514, 1332, 1277, 1066, 795; \ HRMS m/z (ESI) calcd for C\text{23}H\text{24}F\text{3}N\text{NaO}\text{3} (M \text{ + Na})\text{+} 442.1600, found 442.1595.

1-(4-(tert-Butyl)phenyl)propyl 4-(trifluoromethyl)benzoate (2ap)

Flame-dried 25 mL Schlenk tube filled with argon was charged with \textbf{1ap} (0.2 mmol, 86.7 mg), fac-Ir(ppy)\text{3} (0.002 mmol, 1.3 mg), absolute
dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was concentrated under vacuum to remove DMF. The residue was then purified by flash chromatography on silica gel (PE : EA = 50:1) to afford 37.3 mg (51%) of 2ap as a colorless oil: 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J$ = 8.1 Hz, 2H), 7.70 (d, $J$ = 8.2 Hz, 2H), 7.39 – 7.33 (m, 4H), 5.96 – 5.88 (m, 1H), 2.13 – 2.04 (m, 1H), 2.02 – 1.91 (m, 1H), 1.31 (s, 9H), 0.97 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.7, 151.0, 137.0, 134.3 (d, $J$ = 32.7 Hz), 133.8, 130.0, 126.3, 125.4, 125.4 (q, $J$ = 3.8 Hz), 123.6 (q, $J$ = 272.5 Hz), 78.6, 34.5, 31.3, 30.0, 10.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.1; ATR-FTIR (cm$^{-1}$): 1725, 1545, 1512, 1460, 1380, 1259, 1052, 756; HRMS m/z (ESI) calcd for C$_{21}$H$_{23}$F$_3$NaO$_2$ (M + Na)$^+$ 387.1542, found 387.1545.

4. Mechanistic Experiments

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ab (0.1 mmol, 40.3 mg), 1ba (0.1 mmol, 30.4 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. The yield was determined by GC-MS.
Flame-dried 25 mL Schlenk tube filled with argon was charged with 1aa (0.2 mmol, 69.4 mg), 1c (0.2 mmol, 24.4 mg), 1e (0.2 mmol, 42.4 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. The yield was determined by GC-MS.

Flame-dried 25 mL Schlenk tube filled with argon was charged with 1ea (0.2 mmol, 73.8 mg), 1c (0.2 mmol, 24.4 mg), fac-Ir(ppy)$_3$ (0.002 mmol, 1.3 mg), absolute dry DMF (2.0 mL, 0.1 M) was then added with syringe under Ar. The formed mixture was then irradiated by a 5W blue LEDs strip for 24 h at room temperature. The yield was determined by GC-MS.

5. Electrochemical studies

General Experimental Detail

Cyclic voltammograms were recorded in a single cell, constructed from a glass vial, fitted with three electrodes. A glassy carbon disk electrode was used as a working electrode and a platinum wire was used as a counter electrode. The potential was recorded with the reference electrode saturated calomel electrode (SCE) immersed in
0.1 M solution of Et₄NClO₄ in 10 ml DMF. And the concentration of cycloketoxime esters is 0.05 M. The solutions were deoxygenated with a stream of nitrogen for 15 min before each experiment. Samples were examined at 8 different scan rates 0.05 V s⁻¹ – 2.00 V s⁻¹. As a result, we have used the $E_{\text{pmax}}$ (potential corresponding to the maximum reductive current in the voltammogram from the fastest scan-rate, 2 V s⁻¹).

**Cyclic voltammograms**

![Cyclic voltammograms](image)

- $E_{\text{p}} = -2.56$ V
- $E_{\text{p}} = -1.00$ V
- $E_{\text{p}} = -0.98$ V
6. References

7. Copies of NMR Spectra