Photoredox-Promoted Alkyl Radical Addition/Semipinacol Rearrangement Sequence of Alkenylcyclobutanols: Rapid Access to Cyclic Ketones

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# Table of Contents

1. General Information ........................................................................................................... S3

2. General Procedure ........................................................................................................... S4

3. Optimization of the Reaction Conditions
   3.1 The effect of bases on the reaction .................................................................................. S5
   3.2 The effect of the loading of photo-catalyst ....................................................................... S5
   3.3 Screen the other parameters for the reaction ................................................................. S5
   3.4 Unsuccessful substrates ............................................................................................... S6

4. Spectral Data of the Products
   4.1 Spectral data of the desired products 3a-r ..................................................................... S7
   4.2 Spectral data of the desired products 5a-k ..................................................................... S12

5. Mechanism Investigation and the Proposed Mechanism ......................................................... S16

6. X-Ray Crystal Structure of 3r ............................................................................................ S18

7. Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra ......................................................... S19
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods. Flash column chromatography was performed using 200-300 mesh silica gel. $^1$H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers (CDCl$_3$: 77.0 ppm). HRMS was recorded on Agilent technologies 6224 TOF LC/MS instrument or Bruker ultraflXtreme MALDI-TOF/TOF mass spectrometer. All 1-(1-Arylvinyl)cyclobutanol derivatives 1 were prepared in accordance with the reported method. Substrates 2 and 4 were synthesized according to the known literatures, respectively.

References
2. General Procedure

2.1 General procedure for the synthesis of 3a-s

![Reaction Scheme]

**Procedure:** To a dried Schlenk tube was treated with 1 (0.2 mmol, 1.0 equiv), 2 (0.4 mmol, 2.0 equiv), and fac-Ir(ppy)₃ (0.006 mmol, 3 mol%). Subsequently, DMA (2 ml) was added. This mixture solution was degassed for 3 times via ‘freeze-pump-thaw’ procedure. After that, this resulting solution was stirred at a distance of ~2 cm under irradiation by 6 W white LEDs at room temperature for 12 h. The mixture was extracted with ethyl acetate for three times. The organic layer was dried over anhydrous Na₂SO₄, concentrated in vacuum and purified by chromatography on silica gel using petroleum ether/diethyl ether (80:1 to 60:1) as the eluent, furnishing the desired product 3a.

2.2 General procedure for the synthesis of 5a-k

![Reaction Scheme]

**Procedure:** To a dried Schlenk tube was treated with 1 (0.2 mmol, 1.0 equiv), 4 (0.3 mmol, 1.5 equiv), and fac-Ir(ppy)₃ (0.004 mmol, 2 mol%). Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via ‘freeze-pump-thaw’ procedure. After that, this resulting solution was stirred at a distance of ~2 cm under irradiation by 6 W blue LEDs at room temperature for 15 h. The mixture was extracted with ethyl acetate for three times. The organic layer was dried over anhydrous Na₂SO₄, concentrated in vacuum and purified by chromatography on silica gel using petroleum ether/diethyl ether (5:1 to 4:1) as the eluent, affording the desired product 5a.
3. Optimization of the Reaction Conditions

3.1 The effect of bases on the reaction

![Chemical structure](image)

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<td>iPr&lt;sub&gt;2&lt;/sub&gt;NEt complex</td>
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<sup>a</sup> 1a (0.2 mmol), 2a (0.22 mmol), and fac-Ir(ppy)<sub>3</sub> (1 mol%) in 2 ml of DMF at rt under the irradiation of 6 W blue LEDs for 12 h. <sup>b</sup> Isolated yields. DMF: N,N-dimethylformamide; Et<sub>3</sub>N: triethylamine; iPr<sub>2</sub>NEt: N,N-Diisopropylethylamine.

3.2 The effect of the loading of photocatalyst

![Chemical structure](image)

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<sup>a</sup> 1a (0.2 mmol), 2a (0.22 mmol), and fac-Ir(ppy)<sub>3</sub> (x mol%) in 2 ml of DMF at rt under the irradiation of 6 W blue LEDs for 12 h. <sup>b</sup> Isolated yields. DMF: N,N-dimethylformamide.

3.3 Screen other parameters for the reaction

![Chemical structure](image)

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<td>Solvent</td>
<td>Yield (%)</td>
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<td>----------</td>
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<td>-----------</td>
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</table>

$^a$ 1a (0.2 mmol), 4a (0.3 mmol), and fac-Ir(ppy)$_3$ (2 mol%), in 2 ml of solvent at rt under the irradiation of 6 W blue LEDs for 15 h. $^b$ Isolated yields. $^c$ Reaction time is 24 h. DMF: N,N-dimethylformamide; DMSO: Dimethyl sulfoxide; DMA: N,N-Dimethylacetamide.

### 3.4 Unsuccessful substrate

![Diagram of the reaction between 1t and 2a with fac-Ir(ppy)$_3$ (3 mol%) in DMA (2 ml), 12 h, 6 W white LEDs, yielding 3t, complex.](image)

- 1t + 2a $\xrightarrow{\text{fac-Ir(ppy)$_3$ (3 mol%)}}$ 3t, complex

- 1t + 4a $\xrightarrow{\text{fac-Ir(ppy)$_3$ (2 mol%)}}$ 5t, no reaction

![Diagram of the reaction between 1t and 4a with fac-Ir(ppy)$_3$ (2 mol%) in DMA (2 ml), 15 h, 6 W blue LEDs, yielding 5t, no reaction.](image)
4. Spectral data of the products

2-(Cyclohexylmethyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3a)

Yield of 3a: 70% as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.29 (m, 2H), 6.90 – 6.81 (m, 2H), 3.79 (s, 3H), 2.87 – 2.58 (m, 1H), 2.38 – 2.12 (m, 2H), 2.07 – 1.72 (m, 4H), 1.69 – 1.56 (m, 2H), 1.54 – 1.40 (m, 3H), 1.27 (d, $J$ = 12.9 Hz, 1H), 1.17 – 0.96 (m, 4H), 0.96 – 0.67 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.9, 158.2, 131.1, 128.1, 113.8, 56.0, 55.1, 46.3, 36.7, 34.7, 34.4, 33.9, 26.3, 26.2, 18.6. IR (in KBr): 2923, 1734, 1510, 1251 cm$^{-1}$. HRMS (ESI) for C$_{19}$H$_{26}$O$_2$ [M+K]$^+$: calcd 325.1564, found: 325.1560.

2-(cyclohexylmethyl)-2-phenylcyclopentan-1-one (3b)

Yield of 3b: 69% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J$ = 7.8 Hz, 2H), 7.31 (t, $J$ = 7.6 Hz, 2H), 7.21 (t, $J$ = 7.2 Hz, 1H), 2.84 – 2.65 (m, 1H), 2.32 – 2.15 (m, 2H), 2.08 – 1.86 (m, 3H), 1.86 – 1.73 (m, 1H), 1.64–1.56 (m, 5H), 1.31 – 1.20 (m, 1H), 1.17 – 0.96 (m, 4H), 0.97 – 0.66 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.2, 139.5, 128.4, 126.9, 126.6, 56.6, 46.3, 36.9, 36.8, 34.7, 34.4, 33.8, 26.2, 18.6. IR (in KBr): 2923, 1736, 1402 cm$^{-1}$. HRMS (ESI) for C$_{18}$H$_{24}$O [M+K]$^+$: calcd 295.1459, found: 295.1480.

2-(cyclohexylmethyl)-2-(p-tolyl)cyclopentan-1-one (3c)

Yield of 3c: 70% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J$ = 8.1 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 2.72 – 2.69 (m, 1H), 2.31 (s, 3H), 2.28 – 2.14 (m, 2H), 2.07 – 1.73 (m, 4H), 1.69 – 1.43 (m, 5H), 1.28 (d, $J$ = 13.9 Hz, 1H), 1.19 – 0.98 (m, 4H), 0.96 – 0.69 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.8, 136.3, 136.2, 129.1, 126.8, 56.4, 46.3, 36.8, 34.7, 34.4, 33.9, 26.3, 26.2, 26.1, 20.9, 18.6. IR (in KBr): 2923, 1736, 1402 cm$^{-1}$. HRMS (ESI) for C$_{19}$H$_{26}$O [M+K]$^+$: calcd 309.1615, found: 309.1603.

2-(cyclohexylmethyl)-2-(4-fluorophenyl)cyclopentan-1-one (3d)

Yield of 3d: 68% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.30 (m, 2H), 7.09 – 6.91 (m, 2H), 2.70 – 2.65 (m, 1H), 2.31 – 2.19 (m, 2H), 2.11 – 1.71 (m, 4H), 1.68 – 1.41 (m, 5H), 1.24 (d, $J$ = 13.3 Hz, 1H), 1.14 – 1.01 (m, 4H), 0.95 – 0.65 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.5, 161.6 (d, $J=$
254.1 (d, J = 2.1 Hz), 135.1 (d, J = 7.8 Hz), 115.2 (d, J = 20.0 Hz), 56.0, 46.3, 36.8, 34.7, 34.4, 34.0, 26.2 (d, J = 4.6 Hz), 26.1, 18.6. IR (in KBr): 2923, 1736, 1508 , 1232 cm$^{-1}$. HRMS (ESI) for C$_{18}$H$_{23}$FO [M+Na]$^+$: calcd 297.1625, found: 297.1621.

2-(4-chlorophenyl)-2-(cyclohexylmethyl)cyclopentan-1-one (3e)

Yield of 3e: 75% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.9 Hz, 2H), 2.69 – 2.63 (m, 1H), 2.30 – 2.22 (m, 2H), 2.13 – 1.72 (m, 4H), 1.69 – 1.39 (m, 5H), 1.34 – 1.21 (m, 1H), 1.18 – 0.97 (m, 4H), 0.95 – 0.68 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 219.3, 138.0, 132.5, 128.5, 128.4, 56.2, 46.2, 36.8, 34.7, 34.4, 33.8, 26.2, 26.1, 18.6. IR (in KBr): 2943, 1736, 1400 cm$^{-1}$. HRMS (ESI) for C$_{18}$H$_{23}$ClO [M+Na]$^+$: calcd 313.1330, found: 313.1323.

2-(cyclohexylmethyl)-2-(m-tolyl)cyclopentan-1-one (3f)

Yield of 3f: 80% as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (d, J = 3.4 Hz, 3H), 7.03 (t, J = 4.5 Hz, 1H), 2.71 (dd, J = 12.2, 6.1 Hz, 1H), 2.33 (s, 3H), 2.29 – 2.15 (m, 2H), 2.03 – 1.75 (m, 4H), 1.60 (d, J = 11.6 Hz, 2H), 1.57 – 1.47 (m, 3H), 1.29 (d, J = 13.3 Hz, 1H), 1.19 – 0.99 (m, 4H), 0.96 – 0.69 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 219.9, 139.4, 137.9, 128.2, 127.6, 127.4, 123.8, 56.7, 46.3, 36.9, 34.7, 34.5, 34.4, 33.8, 26.3, 26.2, 26.1, 21.6, 18.6. IR (in KBr): 2923, 1735, 1401 cm$^{-1}$. HRMS (ESI) for C$_{19}$H$_{26}$O [M+Na]$^+$: calcd 293.1876, found: 293.1874.

2-(cyclohexylmethyl)-2-(2-fluorophenyl)cyclopentan-1-one (3g)

Yield of 3g: 55% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 –7.19 (m, 2H), 7.12 – 6.92 (m, 2H), 2.54 – 2.33 (m, 1H), 2.42 – 2.33 (m, 2H), 2.16 – 2.06 (m, 1H), 2.01 – 1.92 (m, 1H), 1.99 – 1.77 (m, 3H), 1.58 (t, J = 12.3 Hz, 6H), 1.19 – 1.06 (m, 3H), 0.90 (d, J = 12.5 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 219.6, 161.2 (d, J = 246.0 Hz), 129.6 (d, J = 12.3 Hz), 128.7 (d, J = 3.7 Hz), 128.5 (d, J = 8.8 Hz), 123.8 (d, J = 3.3 Hz), 116.5 (d, J = 23.5 Hz), 55.1 (d, J = 2.7 Hz), 42.3, 37.4, 36.2, 36.1, 35.1, 34.7, 34.3, 26.3 (d, J = 4.1 Hz), 26.2, 18.9. IR (in KBr): 2924, 1739, 1401, 1218 cm$^{-1}$. HRMS (ESI) for C$_{18}$H$_{23}$FO [M+Na]$^+$: calcd 297.1625, found: 297.1622.

2-([1,1'-biphenyl]-4-yl)-2-(cyclohexylmethyl)cyclopentan-1-one (3h)

Yield of 3h: 58% as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (dd, J = 16.3, 8.2 Hz, 4H), 7.44 (dd, J = 25.6, 7.8 Hz, 4H), 7.32 (t, J = 7.3 Hz, 1H), 2.82 – 2.69 (m, 1H), 2.36 – 2.16 (m, 2H), 1.19 – 0.16 (m, 3H), 1.88 –
1.80 (m, 1H), 1.69 – 1.46 (m, 5H), 1.30 (t, $J = 15.1$ Hz, 1H), 1.21 – 1.00 (m, 4H), 0.97 – 0.71 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 219.7, 140.5, 139.3, 138.5, 128.7, 127.3, 127.2, 127.0, 126.9, 56.3, 46.3, 36.9, 34.7, 34.4, 34.3, 33.7, 26.3, 26.2, 26.1, 18.7. IR (in KBr): 2923, 1734, 1402 cm$^{-1}$. HRMS (ESI) for C$_{24}$H$_{28}$O $[\text{M+K}]^+$: calcd 371.1772, found: 371.1748.

2-(cyclohexylmethyl)-2-(naphthalen-2-yl)cyclopentan-1-one (3i)

Yield of 3i : 53% as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J = 8.5$ Hz, 4H), 7.59 (dd, $J = 8.7$, 1.9 Hz, 1H), 7.51 – 7.38 (m, 2H), 2.90 – 2.85 (m, 1H), 2.43 – 2.18 (m, 2H), 2.18 – 1.94 (m, 3H), 1.88 (dd, $J = 11.5$, 7.0 Hz, 1H), 1.60 (d, $J = 8.8$ Hz, 4H), 1.48 (s, 1H), 1.29 (d, $J = 13.8$ Hz, 1H), 1.21 – 0.97 (m, 4H), 0.92 (d, $J = 2.5$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 219.7, 136.8, 133.2, 132.1, 128.1, 128.0, 127.4, 126.0, 125.8, 125.6, 125.2, 56.9, 46.2, 36.9, 34.7, 34.4, 34.3, 34.0, 26.3, 26.2, 26.1, 18.7. IR (in KBr): 2923, 1736 cm$^{-1}$. HRMS (ESI) for C$_{22}$H$_{26}$O $[\text{M+Na}]^+$: calcd 329.1876, found: 329.1857.

2-(4-methoxyphenyl)-2-(5-phenylpentyl)cyclopentan-1-one (3j)

Yield of 3j : 50% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.27 (m, 2H), 7.23 (t, $J = 7.4$ Hz, 2H), 7.18 – 7.06 (m, 3H), 6.90 – 6.81 (m, 2H), 3.76 (s, 3H), 2.58 – 2.48 (m, 3H), 2.36 – 2.09 (m, 2H), 2.02 – 1.66 (m, 4H), 1.66 – 1.39 (m, 3H), 1.34 – 0.88 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 219.9, 158.2, 142.6, 131.2, 128.3, 128.1, 127.8, 125.5, 113.7, 56.0, 55.1, 38.7, 37.3, 35.7, 33.7, 31.1, 29.5, 24.3, 18.6. IR (in KBr): 2933, 1733, 1511, 1251 cm$^{-1}$. HRMS (ESI) for C$_{23}$H$_{30}$O$_2$ $[\text{M+Na}]^+$: calcd 359.1982, found: 359.1965.

2-(4-methoxyphenyl)-2-(pent-4-yn-1-yl)cyclopentan-1-one (3k)

Yield of 3k : 40% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, $J = 8.6$ Hz, 2H), 7.03 – 6.73 (m, 2H), 3.78 (s, 3H), 2.67 – 2.54 (m, 1H), 2.37 – 2.15 (m, 2H), 2.09 – 2.05 (m, 2H), 2.01 – 1.87 (m, 4H), 1.88 – 1.75 (m, 1H), 1.72 – 1.64 (m, 1H), 1.30 (dd, $J = 12.0$, 6.2 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 219.5, 158.3, 130.6, 127.9, 113.8, 84.0, 68.4, 55.7, 55.1, 38.0, 37.2, 33.8, 23.8, 18.7, 18.5. IR (in KBr): 2953, 1732, 1511, 1252 cm$^{-1}$. HRMS (ESI) for C$_{17}$H$_{20}$O$_2$ $[\text{M+Na}]^+$: calcd 279.1356, found: 279.1367.

2-isobutyl-2-(4-methoxyphenyl)cyclopentan-1-one (3l)
Yield of 3l: 70% as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.22 (m, 2H), 6.83 – 6.73 (m, 2H), 3.71 (d, $J$ = 1.6 Hz, 3H), 2.82 – 2.51 (m, 1H), 2.33 – 1.99 (m, 2H), 1.97 – 1.80 (m, 3H), 1.80 – 1.66 (m, 1H), 1.39 – 1.26 (m, 2H), 0.82 – 0.63 (m, 3H), 0.68 – 0.49 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.7, 158.2, 130.6, 128.1, 113.7, 56.0, 55.1, 47.5, 36.6, 33.9, 24.9, 24.4, 23.7, 18.6. IR (in KBr): 2956, 1734, 1511, 1252 cm$^{-1}$. HRMS (ESI) for C$_{16}$H$_{22}$O$_2$ [M+Na]$^+$: calcd 269.1512, found: 269.1508.

2-(4-methoxyphenyl)-2-(2-methylhexyl)cyclopentan-1-one (3m)

Yield of 3m: 66% as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J$ = 8.3 Hz, 2H), 6.85 (d, $J$ = 8.8 Hz, 2H), 3.79 (s, 3H), 2.77 – 2.67 (m, 1H), 2.35 – 2.14 (m, 2H), 2.09 (dd, $J$ = 14.1, 3.7 Hz, 1H, major), 2.02 – 1.89 (m, 2H), 1.87 – 1.77 (m, 1H), 1.56 (dd, $J$ = 14.2, 4.9 Hz, 1H, minor), 1.32 (dd, $J$ = 14.1, 8.3 Hz, 1H), 1.28 – 1.15 (m, 3H), 1.13 – 0.98 (m, 4H), 0.86 (t, $J$ = 6.7 Hz, 2H), 0.78 (dd, $J$ = 10.1, 6.6 Hz, 3H), 0.51 (d, $J$ = 6.5 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.9, 219.7, 158.1, 130.9, 130.6, 128.2, 128.1, 113.7, 113.7, 56.1, 56.0, 55.1, 45.8, 45.7, 38.1, 37.7, 36.8, 36.6, 34.2, 33.7, 29.7, 29.3, 29.0, 28.8, 22.9, 22.7, 21.2, 21.0, 18.6, 18.5, 14.1, 14.0. IR (in KBr): 2958, 1734, 1511, 1252 cm$^{-1}$. HRMS (ESI): for C$_{19}$H$_{28}$O$_2$ [M+Na]$^+$: calcd 311.1982, found: 311.1987.

2-((2,3-dihydro-1H-inden-2-yl)methyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3o)

Yield of 3o: 50% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.27 (m, 2H), 7.10 (d, $J$ = 5.1 Hz, 1H), 7.07 – 7.00 (m, 3H), 6.90 – 6.82 (m, 2H), 3.78 (s, 3H), 2.89 (dd, $J$ = 15.3, 7.6 Hz, 1H), 2.77 (dd, $J$ = 11.5, 5.8 Hz, 1H), 2.62 – 2.51 (m, 2H), 2.43 – 2.12 (m, 5H), 1.98 (d, $J$ = 13.4 Hz, 1H), 1.88 – 1.77 (m, 1H), 1.73 – 1.64 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.7, 158.3, 130.4, 130.2, 129.8, 128.1, 113.8, 56.3, 55.2, 45.1, 39.9, 39.7, 36.7, 35.1, 34.0, 18.5. IR (in KBr): 2927, 1733, 1609, 1511, 1251 cm$^{-1}$. HRMS (ESI) for C$_{18}$H$_{22}$O$_2$ [M+Na]$^+$: calcd 293.1512, found: 293.1514.
8.5 Hz, 4H). 13C NMR (100 MHz, CDCl3) δ 219.4, 158.4, 143.3, 143.2, 130.2, 128.0, 126.0, 125.9, 124.0, 124.0, 113.9, 56.1, 55.2, 44.5, 40.3, 40.1, 37.5, 36.6, 34.1, 18.5. IR (in KBr): 2934, 1732, 1510, 1251 cm⁻¹. HRMS (ESI) for C22H24O2 [M+Na]⁺: calcd 343.1669, found: 343.1642.

2-((4,4-difluorocyclohexyl)methyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3p)

Yield of 3p: 70% as a yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.46 – 7.27 (m, 2H), 6.92 – 6.79 (m, 2H), 3.79 (d, J = 2.0 Hz, 3H), 2.76 – 2.69 (m, 1H), 2.22 (s, 2H), 2.09 – 1.75 (m, 6H), 1.72 – 1.39 (m, 4H), 1.41 – 0.97 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 219.2, 158.4, 130.2, 127.9, 123.3 (dd, J = 241.6, 239.5 Hz), 113.9, 55.7, 55.1, 44.4 (d, J = 2.0 Hz), 36.5, 33.5, 33.3 (d, J = 2.8 Hz), 33.0, 32.4, 30.2 (d, J = 9.2 Hz), 29.8 (d, J = 8.2 Hz), 18.5. 19F NMR (376 MHz, CDCl3) δ -91.80 (dd, J = 235.0, 167.6 Hz, 1F), -101.97 (dd, J = 234.8, 124.4 Hz, 1F). IR (in KBr): 2938, 1733, 1511, 1252, 1114 cm⁻¹. HRMS (ESI) for C19H24F2O2 [M+Na]⁺: calcd 345.1637, found: 345.1604.

2-(4-methoxyphenyl)-2-neopentylcyclopentan-1-one (3q)

Yield of 3q: 71% as a yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.51 – 7.30 (m, 2H), 6.94 – 6.76 (m, 2H), 3.79 (s, 3H), 3.14 – 2.83 (m, 1H), 2.30 – 2.06 (m, 3H), 2.05 – 1.90 (m, 2H), 1.88 – 1.75 (m, 1H), 1.44 (d, J = 14.7 Hz, 1H), 0.69 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 219.3, 158.4, 129.3, 128.8, 113.7, 56.0, 55.2, 51.6, 35.6, 34.6, 31.9, 31.3, 18.5. IR (in KBr): 2957, 1732, 1400, 1252 cm⁻¹. HRMS (ESI) for C17H24O2 [M+Na]⁺: calcd 283.1669, found: 283.1672.

Methyl-4-((1-(4-methoxyphenyl)-2-oxocyclopentyl)methyl)bicyclo[2.2.2]octane-1-carboxylate (3r)

Yield of 3r: 54% as a white solid. 1H NMR (400 MHz, CDCl3) δ 7.25 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 3.72 (s, 3H), 3.51 (s, 3H), 2.85 (dd, J = 11.9, 5.5 Hz, 1H), 2.11 (d, J = 15.2 Hz, 3H), 1.85 (dd, J = 6.6, 3.0 Hz, 3H), 1.52 (t, J = 6.5 Hz, 6H), 1.25 (d, J = 14.9 Hz, 1H), 1.22 – 1.00 (m, 6H). 13C NMR (100 MHz, CDCl3) δ 219.1, 178.5, 158.4, 129.2, 128.6, 113.7, 55.4, 55.1, 51.5, 49.8, 38.3, 35.5, 34.8, 31.8, 31.4, 28.4, 18.4. IR (in KBr): 2950, 1728, 1510, 1251, 1185 cm⁻¹. HRMS (ESI) for C23H30O4 [M+Na]⁺: calcd 393.2036, found: 393.2046.
2-(cyclohexylmethyl)-2-phenylcyclohexan-1-one (3s)

Yield of 3s: 33% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 2.75 (dd, J = 13.7, 2.9 Hz, 1H), 2.36 – 2.22 (m, 2H), 1.96 – 1.89 (m, 1H), 1.86 – 1.62 (m, 5H), 1.62 – 1.42 (m, 5H), 1.17 – 0.81 (m, 6H), 0.67 (d, J = 11.3 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 213.7, 141.3, 128.7, 126.9, 126.5, 57.6, 47.5, 40.1, 35.5, 35.2, 35.1, 33.3, 28.2, 26.5, 26.4, 26.2, 21.6. IR (in KBr): 2925, 1708, 1447 cm$^{-1}$. HRMS (ESI) for C$_{19}$H$_{26}$O$^{+}$: calcd 309.1615, found: 309.1617.

5-(1-(4-methoxyphenyl)-2-oxocyclopentyl)pentanenitrile (5a)

Yield of 5a: 92% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 3.79 (s, 3H), 2.62 (dd, J = 11.2, 6.0 Hz, 1H), 2.35 – 2.18 (m, 4H), 1.98 – 1.76 (m, 4H), 1.61 – 1.51 (m, 3H), 1.38 – 1.07 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.6, 158.4, 130.2, 127.8, 119.5, 113.9, 55.8, 55.2, 38.0, 37.1, 33.6, 25.6, 23.8, 18.5, 16.9. IR (in KBr): 2944, 2245, 1731, 1511, 1251 cm$^{-1}$. HRMS (ESI) for C$_{17}$H$_{21}$NO$_2$ [M+Na]$^{+}$: calcd 294.1465, found: 294.1439.

5-(2-oxo-1-phenylcyclopentyl)pentanenitrile (5b)

Yield of 5b: 50% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.32 (m, 4H), 7.26 (d, J = 6.9 Hz, 1H), 2.66 (dd, J = 11.0, 6.3 Hz, 1H), 2.38 – 2.15 (m, 4H), 2.06 – 1.76 (m, 4H), 1.71 – 1.46 (m, 3H), 1.26 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.5, 138.7, 128.7, 127.0, 126.7, 119.5, 56.5, 38.1, 37.3, 33.6, 25.6, 23.7, 18.6, 16.9. IR (in KBr): 2945, 2245, 1731, 1511, 1251 cm$^{-1}$. HRMS (ESI) for C$_{16}$H$_{19}$NO$^{+}$: calcd 264.1359, found: 264.1339.

5-(1-([1,1'-biphenyl]-4-yl)-2-oxocyclopentyl)pentanenitrile (5c)

Yield of 5c: 80% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (dd, J = 7.9, 5.0 Hz, 4H), 7.43 (dd, J = 11.5, 7.9 Hz, 4H), 7.35 (d, J = 7.3 Hz, 1H), 2.68 (s, 1H), 2.45 – 2.16 (m, 4H), 2.07 – 1.78 (m, 4H), 1.74 – 1.48 (m, 3H), 1.34 – 1.20 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.4, 140.4, 139.8, 137.8, 130.5, 128.7, 127.3, 127.1, 126.9, 119.5, 56.4, 38.0, 37.3, 33.6, 25.6, 23.9, 18.6, 16.9. IR (in KBr): 2944, 2245, 1732, 1402, 1154 cm$^{-1}$. HRMS (ESI) for C$_{22}$H$_{23}$NO$^{+}$: calcd 340.1672, found: 340.1648.
5-(1-(4-fluorophenyl)-2-oxocyclopentyl)pentanenitrile (5d)

Yield of 5d: 54% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 – 7.32 (m, 2H), 7.06 – 7.00 (m, 2H), 2.70 – 2.51 (m, 1H), 2.41 – 2.16 (m, 4H), 2.08 – 1.75 (m, 4H), 1.66 – 1.45 (m, 3H), 1.36 – 1.06 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.1, 161.7 (d, $J$ = 244.8 Hz), 134.5, 128.4 (d, $J$ = 7.8 Hz), 119.4, 115.4 (d, $J$ = 21.0 Hz), 55.9, 38.1, 37.3, 33.8, 25.5, 23.8, 18.5, 16.9. IR (in KBr): 2947, 2246, 1733, 1508, 1402, 1229 cm$^{-1}$. HRMS (ESI) for C$_{16}$H$_{18}$FNO $[M+Na]^+$: calcd 282.1265, found: 282.1243.

5-(2-oxo-1-(m-tolyl)cyclopentyl)pentanenitrile (5e)

Yield of 5e: 54% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 – 7.19 (m, 1H), 7.16 (d, $J$ = 6.7 Hz, 2H), 7.06 (d, $J$ = 7.3 Hz, 1H), 2.75 – 2.58 (m, 1H), 2.34 (s, 3H), 2.31 – 2.15 (m, 4H), 2.04 – 1.70 (m, 4H), 1.68 – 1.47 (m, 3H), 1.38 – 1.12 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.5, 138.7, 138.2, 128.4, 127.6, 127.3, 123.6, 119.5, 56.4, 38.0, 37.2, 33.7, 25.6, 23.8, 21.5, 18.5, 16.8. IR (in KBr): 2949, 2246, 1733, 1402 cm$^{-1}$. HRMS (ESI) for C$_{17}$H$_{21}$NO $[M+Na]^+$: calcd 278.1515, found: 278.1513.

5-(4-oxo-3-phenyltetrahydrofuran-3-yl)pentanenitrile (5f)

Yield of 5f: 83% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 – 7.33 (m, 3H), 7.33 – 7.23 (m, 2H), 4.95 (d, $J$ = 2.4 Hz, 1H), 4.71 (dd, $J$ = 13.1, 9.3 Hz, 1H), 4.27 (dd, $J$ = 30.6, 9.1 Hz, 1H), 4.05 (s, 1H), 2.34 – 2.02 (m, 2H), 1.61 (d, $J$ = 15.3 Hz, 4H), 1.28 (dd, $J$ = 13.7, 6.4 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 214.6, 136.9, 128.9, 127.5, 126.6, 119.2, 76.3, 71.0, 54.9, 35.0, 25.6, 23.7, 16.9. IR (in KBr): 3132, 2945, 2246, 1756, 1400, 1066 cm$^{-1}$. HRMS (ESI) for C$_{15}$H$_{17}$NO$_2$ $[M+Na]^+$: calcd 266.1151, found: 266.1151.

2-(2-(1-(4-methoxyphenyl)-2-oxocyclopentyl)ethoxy)acetonitrile (5g)

Yield of 5g: 54% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.3 – 7.2 (m, 2H), 6.9 (d, $J$ = 8.9 Hz, 2H), 4.1 (d, $J$ = 8.7 Hz, 2H), 3.8 (s, 3H), 3.4 (d, $J$ = 1.2 Hz, 2H), 2.8 – 2.6 (m, 1H), 2.4 – 2.1 (m, 3H), 2.0 – 1.7 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 218.8, 158.5, 129.6, 127.8, 115.9, 114.1, 68.6, 55.9, 55.1, 54.5, 37.5, 36.5, 34.3, 18.5. IR (in KBr): 3138, 2361, 1637, 1400 cm$^{-1}$. HRMS (ESI) for C$_{16}$H$_{19}$NO$_3$ $[M+Na]^+$: calcd 296.1257, found: 296.1259.
Methyl 2-(cyanomethyl)-4-(1-(4-methoxyphenyl)-2-oxocyclopentyl)butanoate (5h)

Yield of 5h: 90% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.26 (m, 2H), 6.95 – 6.74 (m, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 2.64 – 2.59 (m, 2H), 2.60 – 2.42 (m, 4H, minor), 2.38 – 2.13 (m, 4H, major), 2.04 – 1.73 (m, 4H), 1.72 – 1.27 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.0, 172.7, 172.6, 158.5, 129.7, 129.6, 127.8, 127.7, 117.5, 117.4, 114.0, 113.9, 55.5, 55.4, 55.1, 52.2, 41.3, 41.2, 36.9, 36.8, 35.3, 35.2, 33.6, 26.3, 19.1, 19.0, 18.4. IR (in KBr): 2957, 2250, 1734, 1512, 1252, 1186 cm$^{-1}$. HRMS (ESI) for C$_{19}$H$_{23}$NO$_4$ [M+Na]$^+$: calcd 352.1519, found: 352.1513.

3-(benzyloxy)-5-(1-(4-methoxyphenyl)-2-oxocyclopentyl)pentanenitrile (5i)

Yield of 5i: 43% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.26 (m, 7H), 6.86 (d, $J$ = 8.6 Hz, 2H), 4.61 – 4.28 (m, 2H), 3.78 (s, 3H), 3.58 – 3.50 (m, 1H), 2.64 – 2.56 (m, 1H), 2.51 – 2.16 (m, 4H), 1.96 – 1.86 (m, 3H), 1.82 (d, $J$ = 9.0 Hz, 2H, major), 1.71 (d, $J$ = 4.6 Hz, 2H, minor), 1.46 (dd, $J$ = 7.8, 4.9 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.4, 158.5, 137.4, 130.3, 130.1, 128.0, 127.9, 127.8, 127.7, 117.4, 117.3, 129.0, 114.0, 74.4, 71.8, 71.6, 55.6, 55.4, 55.2, 37.2, 37.1, 33.8, 33.7, 29.1, 29.0, 22.8, 22.7, 18.5. IR (in KBr): 2955, 2249, 1731, 1511, 1251 cm$^{-1}$. HRMS (ESI) for C$_{24}$H$_{27}$NO$_3$ [M+Na]$^+$: calcd 400.1883, found: 400.1883.

4-benzyl-5-(1-(4-methoxyphenyl)-2-oxocyclopentyl)pentanenitrile (5j)

Yield of 5j: 65% as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.32 (m, 1H), 7.27 – 7.24 (m, 2H), 7.22 – 7.14 (m, 2H), 7.08 – 6.98 (m, 1H), 6.93 – 6.89 (m, 2H), 6.86 – 6.79 (m, 1H), 3.79 (d, $J$ = 9.8 Hz, 3H), 2.80 – 2.59 (m, 1H), 2.50 (dd, $J$ = 13.6, 6.7 Hz, 1H, minor), 2.39 (dd, $J$ = 13.6, 7.9 Hz, 1H, major), 2.29 – 2.15 (m, 3H), 2.10 – 1.56 (m, 6H), 1.56 – 1.43 (m, 2H), 1.26 (d, $J$ = 3.6 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 219.0, 218.9, 158.7, 158.5, 139.7, 139.5, 129.6, 129.4, 129.0, 128.9, 128.4, 128.3, 128.1, 128.0, 126.2, 126.1, 119.7, 119.5, 114.2, 114.0, 55.8, 55.5, 55.2, 55.1, 41.8, 41.6, 41.2, 41.1, 36.6, 36.5, 35.8, 35.5, 34.0, 33.9, 29.8, 29.7, 18.4, 18.2, 14.5, 14.3. IR (in KBr): 2931, 2245, 1732, 1511, 1251 cm$^{-1}$. HRMS (ESI) for C$_{24}$H$_{27}$NO$_2$ [M+Na]$^+$: calcd 384.1934, found: 384.1904.

5-(2-oxo-1-phenylcyclohexyl)pentanenitrile (5k)
Yield of 5k: 69% as a colorless oil. **1H NMR** (400 MHz, CDCl₃) δ 7.36 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 3.9 Hz, 1H), 7.14 (d, J = 7.7 Hz, 2H), 2.74 (dd, J = 13.9, 3.1 Hz, 1H), 2.39 – 2.16 (m, 4H), 2.06 – 1.90 (m, 1H), 1.82 – 1.62 (m, 6H), 1.57 – 1.46 (m, 2H), 1.34 – 1.16 (m, 1H), 1.13 – 0.95 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ 213.6, 140.5, 128.9, 126.8, 119.7, 57.1, 40.1, 39.3, 35.0, 28.3, 25.8, 22.9, 21.6, 16.9. **IR** (in KBr): 2941, 2246, 1706, 1400 cm⁻¹. **HRMS (ESI)** for C₁₇H₂₁NO [M+Na]⁺: calcd 278.1515, found: 278.1503.
5. Mechanism Investigation and the Proposed Mechanism

5.1 Control Experiment with 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)

**Procedure:** To a dried Schlenk tube was treated with 1a (0.2 mmol, 1.0 equiv), 2a (0.4 mmol, 2.0 equiv), fac-Ir(ppy)$_3$ (0.006 mmol, 3 mol%) and TEMPO (62.50 mg, 0.4 mmol). Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via ‘freeze-pump-thaw’ procedure. After that, this resulting solution was stirred at room temperature under irradiation by 6 W white LEDs (distance of ~2 cm) for 12 h. 3aa can’t be detected by TLC.

5.2 Control Experiment with 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)

**Procedure:** To a dried Schlenk tube was treated with 1a (0.2 mmol, 1.0 equiv), 4a (0.3 mmol, 1.5 equiv), fac-Ir(ppy)$_3$ (0.004 mmol, 2 mol%) and TEMPO (62.50 mg, 0.4 mmol). Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via ‘freeze-pump-thaw’ procedure. After that, this resulting solution was stirred at room temperature under irradiation by 6 W blue LEDs (distance of ~2 cm) for 15 h. Product 5a was not be detected by TLC, but the radical could be captured by TEMPO, 5aa was be characterized by $^1$H NMR.

4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (5aa)

Yield of 5aa: 18% yield of a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.84 (t, $J$ = 5.8 Hz, 1H), 2.49 (t, $J$ = 7.2 Hz, 1H), 2.00 – 1.76 (m, 1H), 1.57 (s, 2H), 1.45 (dd, $J$ = 7.7, 4.2 Hz, 2H), 1.37 – 1.28 (m, 1H), 1.12 (d, $J$ = 23.3 Hz, 6H). The $^1$H NMR data are consistent with the reported literature (Angew. Chem. Int. Ed. 2018, 57, 738-743.).
5.3 A plausible mechanism involved 4a
6. X-Ray Crystal Structure Determination of 3r

<table>
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<th>3r</th>
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CCDC: 1841673
7. Copies of $^1$H, $^{13}$C and $^{19}$F NMR Spectra

$^1$H NMR Spectrum of 3a

$^{13}$C NMR Spectrum of 3a
$^1$H NMR Spectrum of 3b

$^1$C NMR Spectrum of 3b
$^1$H NMR Spectrum of 3c

$^{13}$C NMR Spectrum of 3c
$^1$H NMR Spectrum of 3d

$^{13}$C NMR Spectrum of 3d
$^1$H NMR Spectrum of 3e

$^{13}$C NMR Spectrum of 3e
$^1$H NMR Spectrum of 3f

$^{13}$C NMR Spectrum of 3f
$^1$H NMR Spectrum of 3g

$^{13}$C NMR Spectrum of 3g
\(^1\)H NMR Spectrum of 3h

\(^{13}\)C NMR Spectrum of 3h
\(^1\text{H NMR Spectrum of 3i}\)

\[^1\text{C NMR Spectrum of 3i}\]
$^1$H NMR Spectrum of 3j

$^{13}$C NMR Spectrum of 3j
$^1$H NMR Spectrum of 3k

$^{13}$C NMR Spectrum of 3k
**$^1$H NMR Spectrum of 3l**

![H NMR Spectrum of 3l](image)

**$^{13}$C NMR Spectrum of 3l**

![C NMR Spectrum of 3l](image)
$^1$H NMR Spectrum of 3m

$^{13}$C NMR Spectrum of 3m
**$^1$H NMR Spectrum of 3o**

**$^{13}$C NMR Spectrum of 3o**
$^1$H NMR Spectrum of 3p

$^{13}$C NMR Spectrum of 3p
$^{19}$F NMR Spectrum of 3p

$^1$H NMR Spectrum of 3q
**13C NMR Spectrum of 3q**

**1H NMR Spectrum of 3r**
$^{13}$C NMR Spectrum of 3r

$^1$H NMR Spectrum of 3s
$^{13}$C NMR Spectrum of 3s

$^1$H NMR Spectrum of 5a
$^{13}$C NMR Spectrum of 5a

$^1$H NMR Spectrum of 5b
**13C NMR Spectrum of 5b**

**1H NMR Spectrum of 5c**
$^{13}$C NMR Spectrum of 5c

$^{1}$H NMR Spectrum of 5d
\( ^{13}C \) NMR Spectrum of 5d

\( ^{1}H \) NMR Spectrum of 5e
$^{13}$C NMR Spectrum of 5e

$^1$H NMR Spectrum of 5f
$^{13}$C NMR Spectrum of 5f

$^1$H NMR Spectrum of 5g
$^{13}$C NMR Spectrum of 5g

$^1$H NMR Spectrum of 5h
$^{13}$C NMR Spectrum of 5h

$^1$H NMR Spectrum of 5i
$^{13}$C NMR Spectrum of 5i

$^1$H NMR Spectrum of 5j
$^{13}$C NMR Spectrum of $5j$

$^1$H NMR Spectrum of $5k$
$^{13}$C NMR Spectrum of 5k