Supporting Information

Sunlight-driven Synthesis of *γ*-Diketones via Oxidative Coupling of Enamines with Silyl Enol Ethers Catalyzed by [Ru(bpy)₃]²⁺

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Materials and methods

 $[\mathbf{Ru}(\mathbf{bpv})_3](\mathbf{PF}_6)_2$ was prepared according to the literature procedures.¹ Enamine 1a was purchased from TCI. Other enamines were prepared according to the literature procedures.² Silyl enol ether 2a was purchased from TCI. Other silvl enol ethers were prepared according to the literature procedures.³ Ketone bearing PMB group was prepared according to the literature procedures.⁴ Catalytic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Solvents were dried by standard procedures (CH₃CN, CH₂Cl₂ (P₂O₅), DMF (CaH₂)), distilled, and stored under nitrogen. NMR solvents were dried over molecular sieves, degassed and stored under N₂. Thin-layer chromatography was performed on Merck TLC plate with 60 F₂₅₄. Visible light irradiations were performed with a Soma Kogaku Xe lamp (150 W; λ > 420 nm with L42 cut-off filter). The ¹H NMR was acquired on Bruker AVANCE-400 (400 MHz). NMR chemical shifts were referenced to residual protio impurities in the deuterated solvent. UV-vis and steady-state emission spectra were obtained on JASCO V-670 and SHIMADZU RF-5300PC spectrometer, respectively. Electrochemical measurements were recorded on a Hokutodenkou HZ-5000 analyzer (observed in 0.001 M CH₃CN; [NBu₄PF₆]= 0.1 M; Ag/AgCl = electrode; reported with respect to the $[FeCp_2]/[FeCp_2]^+$ couple). HRMS (ESI-TOF Mass spectra) were obtained with a Bruker micrOTOF II. Single-crystal X-ray measurement was made on a Bruker SMART APEX II ULTRA. The crystallographic data for **5ai** are summarized in Table S1. The crystallographic data were deposited at the Cambridge Crystallographic Data Centre: CCDC 869541(5ai). Sunlight spectra were measured with EKO portable spectroradiometer MS-720.

Typical NMR experimental procedure and NMR spectra of entry 8 in Table 1



LiBF₄ (1.4 mg, 15 µmol) was weighted in an NMR tube under N₂, and [Ru(bpy)₃](PF₆)₂ (2.2 mg,

2.5 µmol), duroquinone (9.8 mg, 60 µmol), 1,4-dimethoxybenzene (2.0 mg) as an internal standard, and CD₃CN (0.50 mL) were added to the NMR tube. After enamine **1a** (8.4 mg, 50 µmol) and silyl enol ether **2a** (19.2 mg, 100 µmol) were introduced, the reaction mixture was degassed by freeze-pump-thaw cycle. Then tube was closed. The reaction was carried out at room temperarure (water bath) under irradiation of visible light (placed at a distance of 6-7 cm from Xe lamp with cut-off filter: hv > 420 nm).

In ¹H NMR spectrum of the reaction mixture under visible light for 12 h, complete conversion of enamine (**1a**) and appearance of new signal at 4.84 ppm were observed (Figure S1). In addition, HMBC spectrum gave a correlation between characteristic ¹H peak at 4.84 ppm and ¹³C signal at 150.7 ppm assignable to iminium carbon (Figure S2). These results suggest formation of iminium ion **4aa** under these reaction conditions.



Figure S1. ¹H NMR spectra.



Figure S2. HMBC spectrum.

Synthesis of enol silane bearing PMB group (2i).



50 mL-Schlenk tube was charged with ketone (1.9 g, 7.4 mmol) and dry CH_2Cl_2 (18 mL) under N_2 atmosphere at room temperature. Then, ^{*i*}Pr₂NEt (2.70 g, 21.0 mmol, 3.0 eq) was added and the reaction mixture was cooled to 0 °C. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (2.5 g, 8.2 mmol, 1.1 eq) was added dropwise to the reaction solution during 10 min under N_2 . The resulting mixtures were stirred at room temperature for overnight. Saturated NH_4Cl aq (100 mL) was added to the pale pink solution, and organic layer was washed with NH_4Cl aq (200 mL) and dried over Na_2SO_4 . The residue was concentrated in *vacuo* to afford **2i** as a white solid (2.9 g, 99% yield).

¹H NMR (400 MHz, CDCl₃, rt): δ 7.53 (d, J = 8.8 Hz, 2 H), 7.35 (d, J = 8.8 Hz, 2 H), 6.95-6.90 (m,

4 H), 5.00 (s, 2 H), 4.77 (s, 1 H), 4.32 (s, 1 H), 3.82 (s, 3 H), 1.00 (s, 9H), 0.21 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃, rt): δ 159.6, 159.1, 155.9, 130.8, 129.4, 129.1, 126.7, 114.5 114.2, 89.4,
69.9, 55.4, 26.0, 25.8, 18.5, -4.46.

HRMS (ESI-TOF): calculated for $[C_{22}H_{30}O_3Si+Na]^+$ requires 393.1856, found 393.1859.

General procedure for the preparation of *γ*-diketones.

20 mL-Schlenk tube was charged activated MS 4A pellet (100 mg), duroquinone (49 mg, 0.30 mmol, 1.2 eq), [**Ru(bpy)**₃](PF₆)₂ (11 mg, 13 µmol) and CH₃CN (2.0 mL) under N₂. Silyl enol ether (0.50 mmol, 2.0 eq), enamine (0.25 mmol, 1.0 eq) and solution of LiBF₄ in CH₃CN (7.0 mg, 0.075 mmol, 0.5 mL) were added to the reaction mixture, and the solution was degassed by the freeze-pump-thaw method with three times. The tube was placed at a distance of 5–6 cm from Xe lamp with cut-off filter: $h\nu > 420$ nm. The orange solution was stirred at room temperature under visible light irradiation for 12 h. After, the reaction mixture was poured into saturated aqueous NH₄Cl and stirred for another 1 h. The resulting mixture was extracted with CH₂Cl₂. Combined organic layers were dried (Na₂SO₄), and filtered. The filtrate was concentrated in *vacuo* and the residue was purified by preparative TLC (PTLC) to afford *y*-diketones.

2-Phenacylcyclohexanone (5aa)⁵



According to general procedure, duroquinone (50 mg, 0.31 mmol), [**Ru(bpy)**₃](PF₆)₂ (11 mg, 13 μ mol), enamine (42 mg, 0.25 mmol) and silyl enol ether (100 mg, 0.52 mmol) afford **5aa** as a colorless oil (36 mg, 67% yield) after purification with silica PTLC (hexane/EtOAc = 4:1). ¹H NMR (400 MHz, CDCl₃, rt): δ 7.98 (dd, *J* = 6.8, 1.4 Hz, 2 H), 7.54 (dd, *J* = 6.8, 1.4 Hz, 1 H),

7.45 (dd, J = 6.8, 1.4 Hz, 2 H), 3.57 (dd, J = 17.6, 6.4 Hz, 1 H), 3.18-3.13 (m, 1 H), 2.67 (dd, J =

17.6, 5.6 Hz, 1 H), 2.46-2.40 (m, 2 H), 2.41(s, 3H), 2.23-2.11 (m, 2 H), 1.91-1.61 (m, 4 H),

1.47-1.38 (m, 1 H).

¹³C NMR (100 MHz, CDCl₃, rt): δ 211.6, 198.8, 137.2, 133.1, 128.6, 128.2, 46.6, 42.1, 38.5, 34.5,

28.1, 25.5.

HRMS (ESI-TOF): calculated for $[C_{14}H_{16}O_2+Na]^+$ requires 239.1045, found 239.1043.

2-Phenacyl-4-methylcyclohexanone (5da)⁶



According to general procedure, duroquinone (50.0 mg, 0.31 mmol), $[\mathbf{Ru}(\mathbf{bpy})_3](\mathbf{PF}_6)_2$ (11 mg, 13 μ mol), enamine (43 mg, 0.24 mmol) and silvl enol ether (93 mg, 0.48 mmol) afford **5da** as a colorless oil (29 mg, 54% yield) after purification with silica PTLC (hexane/EtOAc = 4:1).

¹H NMR (400 MHz, CDCl₃, rt): δ 7.98 (dd, J = 7.2, 1.4 Hz, 2 H), 7.54 (dd, J = 6.4, 1.4 Hz, 1 H), 7.45 (m, 2 H), 3.58-3.50 (m, 1 H), 3.18-3.13 (m, 1 H), 3.34-3.32 (m, 1 H), 2.73-2.12 (m, 5 H), 1.96-1.86 (m, 2H), 1.77-1.31 (m, 1 H), 1.28-0.98 (m, 3 H).

¹³C NMR (100 MHz, CDCl₃, rt): δ 212.4, 211.9, 198.7, 137.2, 133.2, 128.7, 128.2, 45.6, 42.5, 41.8, 41.3, 39.6, 38.6, 38.4, 37.6, 36.0, 33.3, 32.2, 27.3, 21.4, 18.2.

HRMS (ESI-TOF): calculated for $[C_{15}H_{18}O_2+Na]^+$ requires 253.1210, found 253.1199.

2-Phenacyl-1,4-dioxaspiro[4.5]decan-8-one (5ea)⁸



According to general procedure, enamine (62 mg, 0.25 mmol), duroquinone (54.0 mg, 0.33 mmol),

[**Ru(bpy)**₃](PF₆)₂ (12 mg, 14 μmol) and silyl enol ether (96 mg, 0.50 mmol) afford **5ea** as a pale yellow solid (34 mg, 50% yield) after purification with silica PTLC (hexane/EtOAc = 7:3). ¹H NMR (400 MHz, CDCl₃, rt): δ 7.97 (dd, J = 8.4, 1.2 Hz, 2 H), 7.54 (dd, J = 8.8, 1.2 Hz, 1 H), 7.45 (dd, J = 8.8, 1.2 Hz, 2 H), 4.12-3.99 (m, 4 H), 3.59-3.48 (m, 2 H), 2.80-2.72 (m, 2 H), 2.46-2.40 (m, 2 H), 2.46-2.41 (m, 1 H), 2.20-2.02 (m, 2 H), 1.88-1.80 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃, rt): δ 210.4, 198.0, 137.0, 133.1, 128.6, 128.1, 107.3, 64.9, 64.7, 42.5, 40.5, 38.0, 34.8.

HRMS (ESI-TOF): calculated for $[C_{16}H_{18}O_4+Na]^+$ requires 297.1097, found 297.1097.

2-(4-Methylphenacyl)cyclohexanone (5ab)^{6,7}



According to general procedure, duroquinone (49 mg, 0.30 mmol), [**Ru(bpy)**₃](PF₆)₂ (12 mg, 14 μ mol), enamine (42 mg, 0.25 mmol) and silyl enol ether (124 mg, 0.50 mmol) afford **5ab** as a white solid (40 mg, 69% yield) after purification with silica PTLC (hexane/EtOAc = 4:1). ¹H NMR (400 MHz, CDCl₃, rt): δ 7.88 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 3.60 (dd, *J* =

17.6, 6.8 Hz, 1 H), 3.19-3.14 (m, 1 H), 2.67 (dd, J = 17.6, 5.6 Hz, 1 H), 2.46-2.41 (m, 2 H), 2.23-2.12 (m, 2 H), 1.90-1.66 (m, 4 H), 1.48-1.32 (m, 1 H).

¹³C NMR (100 MHz, CDCl₃, rt): δ 211.7, 198.4, 143.9, 134.8, 129.3, 128.3, 46.6, 42.1, 38.3, 34.5, 28.1, 25.5, 21.7.

HRMS (ESI-TOF): calculated for $[C_{15}H_{18}O_2+Na]^+$ requires 253.1210, found 253.1199.

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2-(4-Methoxylphenacyl)cyclohexanone (5ac)⁵



According to general procedure, duroquinone (49.0 mg, 0.30 mmol), [**Ru(bpy)**₃](PF₆)₂ (10 mg, 12 μ mol), enamine (40 mg, 0.24 mmol) and silyl enol ether (130 mg, 0.49 mmol) afford **5ac** as a pale yellow solid (37 mg, 63% yield) after purification with silica PTLC (hexane/EtOAc = 4:1). ¹H NMR (400 MHz, CDCl₃, rt): δ 7.97 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.59 (dd, *J* = 17.2, 6.0 Hz, 1 H), 3.18-3.12 (m, 1 H), 2.67 (dd, *J* = 17.6, 6.0 Hz, 1 H), 2.46-2.41 (m, 2 H), 2.22-2.11 (m, 2 H), 1.91-1.55 (m, 4 H), 1.46-1.38 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃, rt): δ 211.8, 197.3, 163.6, 130.5, 130.4, 113.8, 55.6, 46.7, 42.2, 38.1, 34.6, 28.2, 25.6.

HRMS (ESI-TOF): calculated for $[C_{15}H_{18}O_3+Na]^+$ requires 269.1149, found 269.1148.

2-(4-Fluorophenacyl)cyclohexanone (5ad)⁶



According to general procedure, duroquinone (49 mg, 0.30 mmol), $[\mathbf{Ru}(\mathbf{bpy})_3](\mathbf{PF}_6)_2$ (11 mg, 13 μ mol), enamine (44 mg, 0.26 mmol) and silvl enol ether (126 mg, 0.54 mmol) afford **5ad** as a pale yellow oil (12 mg, 19% yield) after purification with silica PTLC (hexane/EtOAc = 4:1).

¹H NMR (400 MHz, CDCl₃, rt): δ 8.01 (dd, *J* = 9.2, 5.2 Hz, 2 H), 6.93 (dd, *J* = 7.2, 5.2 Hz, 2 H), 3.56 (dd, *J* = 17.6, 6.2 Hz, 1 H), 3.19-3.13 (m, 1 H), 2.66 (dd, *J* = 17.6, 5.6 Hz, 1 H), 2.46-2.41 (m, 2 H), 2.22-2.13 (m, 2 H), 1.93-1.52 (m, 4 H), 1.51-1.38 (m, 1 H).

¹³C NMR (100 MHz, CDCl₃, rt): δ 211.6, 197.2, 166.5 (d, J_{HF} = 252.9 Hz), 133.6, 130.8 (d, J_{HF} = 9.3

Hz), 115.7 (d, *J*_{HF} = 21.8 Hz), 46.6, 42.1, 38.4, 34.5, 28.1, 25.5.

HRMS (ESI-TOF): calculated for $[C_{14}H_{15}O_2F+Na]^+$ requires 257.0948, found 257.0951.

2-(4-Bromophenacyl)cyclohexanone (5ae)⁵



According to general procedure, duroquinone (50.0 mg, 0.31 mmol), $[\mathbf{Ru}(\mathbf{bpy})_3](\mathbf{PF}_6)_2$ (10 mg, 12 μ mol), enamine (42 mg, 0.25 mmol) and silvl enol ether (150 mg, 0.48 mmol) afford **5ae** as a pale brown solid (24 mg, 33% yield) after purification with silica PTLC (hexane/EtOAc = 4:1).

¹H NMR (400 MHz, CDCl₃, rt): δ 7.85 (dd, *J* = 9.0, 1.8 Hz, 2 H), 7.61 (dd, *J* = 9.0, 1.8 Hz, 2 H), 3.55 (dd, *J* = 17.6, 6.8 Hz, 1 H), 3.19-3.13 (m, 1 H), 2.61 (dd, *J* = 17.6, 5.6 Hz, 1 H), 2.46-2.41 (m, 2 H), 2.22-2.03 (m, 2 H), 1.93-1.66 (m, 4 H), 1.51-1.38 (m, 1 H).

¹³C NMR (100 MHz, CDCl₃, rt): δ 211.5, 197.8, 136.0, 132.0, 129.8, 128.3, 46.7, 42.1, 38.5, 34.4, 28.1, 25.5.

HRMS (ESI-TOF): calculated for $[C_{14}H_{15}O_2Br+Na]^+$ requires 317.0148, found 317.0140.

2-[2-Oxo-2-(2-furyl)ethyl]cyclohexanone (5ag)



According to general procedure, duroquinone (53.0 mg, 0.32 mmol), $[\mathbf{Ru}(\mathbf{bpy})_3](\mathbf{PF}_6)_2$ (11 mg, 13 µmol), enamine (48 mg, 0.29 mmol) and silyl enol ether (119 mg, 0.53 mmol) afford **5ag** as a white solid (32 mg, 55% yield) after purification with silica PTLC (hexane/EtOAc = 4:1).

¹H NMR (400 MHz, CDCl₃, rt): δ 7.85 (dd, J = 1.6, 0.8 Hz, 1 H), 7.21 (dd, J = 3.6, 0.8 Hz, 1 H),

6.53 (dd, J = 3.6, 1.6 Hz, 1 H), 3.45 (dd, J = 17.2, 6.8 Hz, 1 H), 3.15-3.10 (m, 1 H), 2.58 (dd, J = 17.6, 6.0 Hz, 1 H), 2.44-2.39 (m, 2 H), 2.21-2.10 (m, 2 H), 1.91-1.54 (m, 4 H), 1.50-1.40 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃, rt): δ 211.3, 187.9, 152.9, 146.4, 117.1, 112.3, 46.4, 42.0, 38.3, 34.3, 28.0, 25.4.

HRMS (ESI-TOF): calculated for $[C_{12}H_{14}O_3+Na]^+$ requires 229.0835, found 229.0835.

2-[2-Oxo-2-(2-thienyl)ethyl]cyclohexanone (5ah)^{6,7}



According to general procedure, duroquinone (50.0 mg, 0.31 mmol), $[\mathbf{Ru}(\mathbf{bpy})_3](\mathbf{PF}_6)_2$ (12 mg, 14 µmol), enamine (42 mg, 0.25 mmol) and silvl enol ether (122 mg, 0.51 mmol) afford **5ah** as a pale yellow oil (32 mg, 58% yield) after purification with silica PTLC (hexane/EtOAc = 4:1).

¹H NMR (400 MHz, CDCl₃, rt): δ 7.77 (dd, J = 4.0, 1.2 Hz, 1 H), 7.63 (dd, J = 5.2, 1.2 Hz, 1 H), 7.12 (dd, J = 5.2, 4.0 Hz, 1 H), 3.51 (dd, J = 17.2, 6.4 Hz, 1 H), 3.16-3.11 (m, 1 H), 2.66 (dd, J = 17.2, 6.0 Hz, 1 H), 2.45-2.40 (m, 2 H), 2.23-2.15 (m, 2 H), 1.89-1.55 (m, 4 H), 1.50-1.42 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃, rt): δ 211.4, 191.7, 144.4, 133.5, 132.0, 128.1, 46.6, 42.0, 39.1, 34.3, 28.0, 25.4.

HRMS (ESI-TOF): calculated for $[C_{12}H_{14}O_2S+Na]^+$ requires 245.0607, found 245.0602.

2-(4-p-Methoxybenzyloxyphenacyl)cyclohexanone (5ai)



According to general procedure, duroquinone (36 mg, 0.22 mmol), [Ru(bpy)₃](PF₆)₂ (8.6 mg, 10

 μ mol), enamine (30 mg, 0.18 mmol) and silvl enol ether (136 mg, 0.37 mmol) afford **5ai** as a pale yellow solid (33 mg, 52% yield) after purification with silica PTLC (hexane/EtOAc = 7:3).

¹H NMR (400 MHz, CDCl₃, rt): δ 7.96 (dd, J = 7.0, 2.4 Hz, 2 H), 7.35 (dd, J = 7.0, 1.6 Hz, 2 H),

7.00 (dd, *J* = 6.8, 2.4 Hz, 2 H), 6.92 (dd, *J* = 6.8, 2.0 Hz, 2 H), 5.05 (s, 2 H), 3.82 (s, 3 H), 3.55 (dd, *J*

= 17.6, 6.4 Hz, 1 H), 3.18-3.12 (m, 1 H), 2.64 (dd, J = 17.6, 6.0 Hz, 1 H), 2.45-2.41 (m, 2 H),

2.22-2.12 (m, 2 H), 1.88-1.55 (m, 4 H), 1.46-1.41 (m, 1 H).

¹³C NMR (100 MHz, CDCl₃, rt): δ 211.8, 197.3, 162.8, 159.7, 130.5, 130.4, 129.4, 128.3, 114.6, 114.2, 70.1, 55.4, 46.6, 42.1, 38.1, 34.5, 28.1, 25.5.

HRMS (ESI-TOF): calculated for $[C_{22}H_{24}O_4+Na]^+$ requires 375.1567, found 375.1563.

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Sunlight-driven reaction

Cylindrical vessel was used for photoreaction under sunlight (right). The vessel was charged activated MS 4A pellet (100 mg), duroquinone (50 mg, 0.31 mmol), [**Ru(bpy)**₃](PF₆)₂ (11 mg, 13 µmol), then **1a** (42 mg, 0.25 mmol), **2a** (103 mg, 0.54 mmol), LiBF₄ in CH₃CN (7.0 mg, 0.075 mmol, 0.5 mL) and



CH₃CN (2.0 mL) were added. The reaction mixture was exposed to sunlight for 11 h (in February 21st, 22nd, and 24th, 2012) below 15 °C. After workup, **5aa** was obtained as oil (33 mg, 61% yield). Sunlight spectrum was measured in the 300–1150 nm region as shown in Figure S3.



Figure S3. Typical solar spectrum (14:07, 21st, February, 2012).

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Cyclic voltammogram

Cyclic voltammetry experiments were performed using Hokutodenkou HZ-5000 analyzer under N_2 at room temperature.



Figure S5.

Stern-Volmer studies

Emission spectra for the Ru catalyst in a deaerated solution whose concentration was adjusted so as to show the absorbance 0.1 at excitation wavelength were recorded at room temperature by SHIMADZU RF-5300PC spectrometer. ($[Ru(bpy)_3](PF_6)_2$ excited at 450 nm in CH₃CN exhibited emission band at 610 nm.)

General experimental procedure: A solution of the Ru catalyst was prepared and degassed three times via freeze-pump-thaw cycle in a 1 cm quartz cell equipped with an sphere moiety for freeze. The solution of quencher was added to the solution of the Ru catalyst before measurement of emission intensities.



Figure S6.

Crystallographic Data for 5ai

Diffraction measurements were made on a Bruker SMART APEX II ULTRA/CCD. Intensity measurements were performed using monochromated (doubly curved silicon crystal) Mo-K α -radiation (0.71073 Å) from a sealed microfocus tube. Data collection temperature was –183 °C for **5ai**. Data were acquired using three sets of Omega scans at different Phi settings. The frame width was 0.5 °. The crystallographic data are summarized in Table S1.

The structural analysis was performed on an APEX2 software for preliminary determination of the unit cell. Determination of integrated intensities and unit cell refinement were performed using SAINT. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically by full-matrix least-square techniques based on F^2 . All hydrogen atoms were fixed at the calculated positions.

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Table S1. Crystal data and structure refinement for 5ai.

Identification code	1234	
Empirical formula	C22 H24 O4	
Formula weight	352.41	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.9714(17) Å	$\alpha = 75.680(4)^{\circ}$
	b = 9.360(3) Å	$\beta = 82.150(3)^{\circ}$
	c = 15.546(4) Å	$\gamma = 68.441(3)^{\circ}$
Volume	913.0(4) Å ³	
Z	2	
Density (calculated)	1.282 Mg/cm ³	
Absorption coefficient	0.087 mm^{-1}	
F(000)	376	
Theta range for data collection	2.40 to 28.71°	
Index ranges	-9<=h<=7, -11<=k<=12, -19<=l<=20	
Reflections collected	5292	
Independent reflections	4074 [R(int) = 0.1356]	
Completeness to theta = 28.71°	86.1%	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4074 / 0 / 237	
Goodness-of-fit on F ²	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0826, $wR2 = 0.2177$	
R indices (all data)	R1 = 0.1130, wR2 = 0.2402	
Largest diff. peak and hole	1.346 and -0.508	

 $\begin{aligned} \mathbf{R}_{\text{int}} &= \Sigma |F_{o}^{2} - F_{o}^{2}(\text{mean})| / \Sigma [F_{o}^{2}] \\ \mathbf{R}_{1} &= \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}| \\ \text{GOOF} &= \mathbf{S} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / (\mathbf{n} - \mathbf{p})\}^{1/2} \\ w\mathbf{R}_{2} &= \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]\}^{1/2} \\ w &= 1 / [\sigma(F_{o}^{2}) + (\mathbf{a}P)^{2} + \mathbf{b}P] \text{ where } P \text{ is } [2F_{c}^{2} + \text{Max}(F_{o}^{2}, 0)] / 3 \end{aligned}$

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Table S2. Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters (\mathring{A}^2x10^3) for 5ai.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	Х	У	Z	U(eq)
C1	-6693(5)	-2936(4)	6732(2)	34(1)
C2	-3964(4)	-3173(3)	5602(2)	23(1)
C3	-3166(4)	-2258(3)	5933(2)	28(1)
C4	-1480(4)	-1906(3)	5478(2)	28(1)
C5	-594(4)	-2420(3)	4703(2)	22(1)
C6	1229(4)	-2031(3)	4229(2)	24(1)
C7	1939(4)	-378(3)	2874(2)	19(1)
C8	1193(4)	662(3)	2077(2)	22(1)
C9	2544(4)	1115(3)	1437(2)	22(1)
C10	4662(4)	545(3)	1560(2)	20(1)
C11	6197(4)	914(3)	855(2)	21(1)
C12	5406(4)	2134(3)	24(2)	22(1)
C13	7097(4)	2481(3)	-617(2)	22(1)
C14	8200(4)	3351(3)	-275(2)	25(1)
C15	9856(5)	3737(4)	-897(2)	31(1)
C16	9041(5)	4640(4)	-1816(2)	34(1)
C17	-3080(4)	-3709(3)	4833(2)	23(1)
C18	-1416(4)	-3332(3)	4390(2)	22(1)
C19	5368(4)	-459(3)	2367(2)	24(1)
C20	4036(4)	-919(3)	3020(2)	25(1)
C21	6278(4)	3436(3)	-1531(2)	27(1)
C22	7975(5)	3769(3)	-2179(2)	28(1)
01	-5598(3)	-3620(2)	6001(1)	28(1)
02	482(3)	-787(2)	3459(1)	23(1)
03	8033(3)	211(2)	942(1)	28(1)
O4	7741(4)	3704(3)	450(1)	44(1)

Table S3. Bond lengths (Å) and angles (°) for 5ai.

C1-O1	1.431(3)
C2-O1	1.373(3)
C2-C17	1.390(4)
C2-C3	1.398(4)
C3-C4	1.390(4)
C4-C5	1.390(4)
C5-C18	1.391(4)
C5-C6	1.497(4)
C6-O2	1.448(3)
C7-O2	1.366(3)
C7-C20	1.391(4)
C7-C8	1.400(3)
C8-C9	1.373(4)
C9-C10	1.396(4)
C10-C19	1.394(3)
C10-C11	1.494(4)
C11-O3	1.214(3)
C11-C12	1.509(4)
C12-C13	1.513(4)
C13-C14	1.524(3)
C13-C21	1.537(3)
C14-O4	1.221(3)
C14-C15	1.493(4)
C15-C16	1.533(4)
C16-C22	1.524(4)
C17-C18	1.380(4)
C19-C20	1.379(4)
C21-C22	1.517(4)
O1-C2-C17	115.9(2)
01-C2-C3	124.0(2)
C17-C2-C3	120.1(2)
C4-C3-C2	118.7(2)
C5-C4-C3	121.8(2)

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C4-C5-C18	118.3(2)
C4-C5-C6	120.7(2)
C18-C5-C6	121.0(2)
O2-C6-C5	107.2(2)
O2-C7-C20	124.8(2)
O2-C7-C8	115.3(2)
C20-C7-C8	119.8(2)
C9-C8-C7	119.7(2)
C8-C9-C10	121.3(2)
C19-C10-C9	118.1(2)
C19-C10-C11	119.0(2)
C9-C10-C11	122.9(2)
O3-C11-C10	120.3(2)
O3-C11-C12	121.2(2)
C10-C11-C12	118.4(2)
C11-C12-C13	113.7(2)
C12-C13-C14	113.1(2)
C12-C13-C21	111.9(2)
C14-C13-C21	108.5(2)
O4-C14-C15	123.3(3)
O4-C14-C13	122.0(3)
C15-C14-C13	114.7(2)
C14-C15-C16	111.4(2)
C22-C16-C15	111.0(2)
C18-C17-C2	120.1(2)
C17-C18-C5	121.1(2)
C20-C19-C10	121.5(2)
C19-C20-C7	119.5(2)
C22-C21-C13	112.0(2)
C21-C22-C16	111.1(2)
C2-O1-C1	117.1(2)
C7-O2-C6	116.77(19)

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Table S4. Anisotropic displacement parameters $(\text{\AA}^2 x 10^3)$ for 5ai.

The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h² a^{*2} U¹¹ + ... + 2 h k a^{*} b^{*} U¹²]

	U^{11}	U^{22}	U ³³	U ²³	U ¹³	U^{12}
C1	33(2)	39(2)	30(2)	-6(1)	-6(1)	-17(1)
C2	27(1)	24(1)	18(1)	4(1)	4(1)	-15(1)
C3	40(2)	31(2)	18(1)	-5(1)	-5(1)	-21(1)
C4	40(2)	31(2)	21(1)	-4(1)	-4(1)	-23(1)
C5	28(1)	22(1)	17(1)	3(1)	3(1)	-13(1)
C6	30(2)	28(1)	17(1)	4(1)	4(1)	-17(1)
C7	28(1)	21(1)	15(1)	-4(1)	-4(1)	-15(1)
C8	24(1)	25(1)	20(1)	-3(1)	-3(1)	-13(1)
C9	30(1)	25(1)	14(1)	-0(1)	-0(1)	-14(1)
C10	29(1)	21(1)	18(1)	-5(1)	-5(1)	-15(1)
C11	27(1)	22(1)	21(1)	-7(1)	-7(1)	-14(1)
C12	25(1)	24(1)	19(1)	-3(1)	-3(1)	-13(1)
C13	29(1)	25(1)	18(1)	-4(1)	-4(1)	-15(1)
C14	33(2)	25(1)	21(1)	-6(1)	-6(1)	-12(1)
C15	39(2)	34(2)	33(2)	-7(1)	-7(1)	-24(1)
C16	46(2)	32(2)	30(2)	-5(1)	-5(1)	-27(1)
C17	30(1)	24(1)	20(1)	-1(1)	-1(1)	-14(1)
C18	29(1)	25(1)	15(1)	0(1)	0(1)	-13(1)
C19	24(1)	30(1)	20(1)	-3(1)	-3(1)	-13(1)
C20	32(2)	27(1)	18(1)	1(1)	1(1)	-16(1)
C21	33(2)	33(2)	19(1)	-3(1)	-3(1)	-17(1)
C22	43(2)	28(1)	17(1)	-0(1)	-0(1)	-20(1)
01	30(1)	34(1)	25(1)	-3(1)	-3(1)	-20(1)
O2	27(1)	27(1)	17(1)	2(1)	2(1)	-16(1)
03	27(1)	33(1)	25(1)	-2(1)	-2(1)	-13(1)
O4	58(2)	51(1)	37(1)	-15(1)	-15(1)	-29(1)

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Table S5. Hydrogen coordinates $(x10^4)$ and isotropic displacement parameters $(\text{\AA}^2 x10^3)$ for 5ai.

	X	У	Z	U(eq)
H24	-5794	-3275	7216	51
Н3	-7864	-3264	6922	51
H1	-7154	-1811	6550	51
H4	-3750	-1893	6447	33
Н5	-929	-1309	5699	33
H21	1865	-1686	4618	29
H20	2249	-2950	4047	29
H19	-212	1045	1981	26
H18	2039	1816	912	26
H17	4495	3101	193	26
H16	4598	1773	-277	26
H15	8125	1472	-703	27
H8	10983	2772	-956	38
H9	10390	4368	-653	38
H10	8071	5677	-1773	40
H2	10180	4772	-2222	40
H23	-3610	-4321	4615	28
H22	-835	-3695	3875	27
H7	6770	-827	2466	28
H6	4535	-1586	3555	30
H21A	5654	2859	-1773	32
H21B	5215	4424	-1460	32
H12	7389	4397	-2740	33
H11	8984	2785	-2288	33

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X-ray Data of 5ai

Figure S7. ORTEP plot of the molecular structure



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