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Supporting Information

Experimental Procedures and Characterization Data

Photoinduced Rearrangement of α -(2-Nitrophenyl)ketones

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General Remarks

Dehydrated tetrahydrofuran and dichloromethane were purchased from FUJIFILM Wako Pure Chemical Co. *N*,*N*-dimethylformamide and toluene was purchased from FUJIFILM Wako Pure Chemical Co. and stored over activated MS4A. Acetonitrile was purchased from FUJIFILM Wako Pure Chemical Co. and stored over activated MS3A. All non-aqueous reactions were carried out in oven-dried glass tubes under a slight positive pressure of argon unless otherwise noted. Reactions that require heating were conducted in an oil bath unless otherwise noted.

Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F254. Preparative TLC separations were performed on Merck analytical plates (0.25 or 0.50 mm thick) precoated with silica gel 60 F254. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical, 40-100 mesh) unless otherwise noted. Reagents were commercial grades and were used without any purification.

Nuclear magnetic resonance (¹H NMR (400 MHz), ¹³C NMR (100 MHz), ¹⁹F NMR (376 MHz)) spectra were determined on JEOL-ECS400 or JEOL-ECZ400 instrument unless otherwise noted. Chemical shifts were reported in δ (ppm) using residual solvent as the internal standard (δ 7.26 for CDCl₃ in ¹H NMR, δ 77.00 for CDCl₃ in ¹³C NMR) or α,α,α -trifluorotoluene as the external standard (δ –63.7 in ¹⁹F NMR). Coupling constants were reported as *J* values in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad.

Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrophotometer and are reported in wavenumbers (cm⁻¹). High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics compact in positive electrospray ionization (ESI) method using ESI tuning mix as the internal standard.

Methyl 3-oxo-3-phenylpropanoate,¹ 3,3-dimethyl-1-phenylbutan-2-one,² 4-(2-nitrophenyl)octan-3-one,³ and 2-(2-nitrophenyl)cyclohexane-1,3-dione⁴ were prepared according to the literatures. Photoirradiation was carried out with Techno Sigma PER-365 and AMP-N4.

$\begin{array}{c c} & LED (wavelength) \\ \hline \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$					
entry	wavelength (nm)	temperature (°C)	solvent	time $(h)^b$	yield of 18 (%)
1	365	rt	MeOH	2.5	64
2	365	0	MeOH	2.5	65
3	365	-78	MeOH	4	83
4	405	-78	MeOH	6	58
5	448	-78	MeOH	6^c	5
6	365	-78	<i>i</i> -PrOH	3	76
7	365	-40	MeCN	3	49
8	365	-78	CH_2Cl_2	3	14^{f}
9	365	-78	toluene	6.5	9 ^f
10	365	-78	hexane	3^d	6^{f}
11	-	-78	MeOH	4 ^e	-

Table S1. Optimization of the Conditions for Photoinduced Rearrangement^a

^{*a*}Conditions: a solution of **17** was irradiated with LED at the designated temperature. ^{*b*}The time required for consumption of the starting material (compound **17**) is given unless otherwise noted. ^{*c*}85% of the starting material (compound **17**) was recovered. ^{*d*}30% of the starting material (compound **17**) was recovered. ^{*d*}Without irradiation, 99% of the starting material (compound **17**) was recovered. ^{*f*}Formation of many byproducts was observed on TLC.

General Procedure A: S_NAr reaction: A solution of 2-fluoronitrobenzene (1 equiv.), a ketoester (1.0 equiv.) and potassium carbonate (2.0 equiv.) in DMSO (1.0 M) was heated at 80 °C for the indicated time. After cooling to room temperature, the resulting mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography to give a ketoester.

Methyl 4,4-dimethyl-2-(2-nitrophenyl)-3-oxopentanoate (15)



A reaction of 2-fluoronitrobenzene (0.749 mL, 7.10 mmol) with methyl 4,4-dimethyl-3-oxovalerate (1.13 mL, 7.07 mmol) and potassium carbonate (1.97 g, 14.3 mmol) in DMSO (7.1 mL, 1.0 M) for 13 hours, followed by purification with flash silica gel column chromatography (0-25% ethyl acetate-hexane), gave **15** (1.46 g, 5.24 mmol, 74% yield, yellow amorphous solid). **¹H NMR** (CDCl₃, 400 MHz) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.6, 1.2 Hz, 1H), 5.92 (s, 1H), 3.75 (s, 3H), 1.15 (s, 9H) **¹³C NMR** (CDCl₃, 100 MHz) δ 208.1 (C), 168.4 (C), 148.8 (C), 133.2 (CH), 131.2 (CH), 129.0 (CH), 127.7 (C), 125.2 (CH), 53.5 (CH), 53.0 (CH₃), 45.8 (C), 26.4 (CH₃) **IR** (film, cm⁻¹) 1748, 1711, 1528, 1478, 1349, 1267, 1203, 1000, 787, 716 **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₁₇NNaO₅ 302.0999; Found 302.0998

Methyl 2-(2-nitrophenyl)-3-oxo-3-phenylpropanoate (S1)



keto:enol = 3:4

A reaction of 2-fluoronitrobenzene (0.820 mL, 7.78 mmol) with methyl 3-oxo-3-phenylpropanoate¹ (1.39 g, 7.80 mmol) and potassium carbonate (2.16 g, 15.6 mmol) in DMSO (7.8 mL, 1.0 M) for 5 hours, followed by purification with flash silica gel column chromatography (0-25% ethyl acetate-hexane), gave **S1** (1.97 g, 6.59 mmol, 85% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) keto form: δ 8.09 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.62 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.58 (dt, J = 7.6, 1.6 Hz, 1H), 7.51 (dt, J = 7.8, 1.2 Hz, 1H), 7.49 (dd, J = 7.8, 1.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.40 (s, 1H), 3.80 (s, 3H) enol form: δ 7.98 (dd, J = 7.6, 2.0 Hz, 1H), 7.37 (dt, J = 7.6, 1.2 Hz, 1H), 7.33 (dt, J = 7.6, 2.0 Hz, 1H), 7.30-7.26 (m, 3H), 7.18 (t, J = 7.4 Hz, 2H), 6.99 (dd, J = 7.6, 1.2 Hz, 1H), 3.70 (s, 3H) ¹³C NMR (CDCl₃, 100 MHz) keto form: δ 192.6 (C), 168.5 (C), 148.4 (C), 135.3 (C), 133.9 (CH), 133.6 (CH), 131.7 (CH), 129.2 (CH), 128.9 (CH), 128.7 (CH), 128.2 (C), 125.3 (CH), 55.6 (CH), 53.0 (CH₃) enol form: δ 171.8 (C), 171.0 (C), 149.9 (C), 134.9 (CH), 134.1 (C), 132.6 (CH), 130.3 (C), 130.1 (CH), 128.7 (CH), 128.2 (CH), 127.9 (CH), 124.3 (CH), 101.3 (C), 52.1 (CH₃) IR (film, cm⁻¹) 1743, 1688, 1652, 1612, 1526, 1446, 1350, 1257, 1134, 698 HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₆H₁₃NNaO₅ 322.0686; Found 322.0686

Methyl 2-(5-methoxy-2-nitrophenyl)-4,4-dimethyl-3-oxopentanoate (S2)



A reaction of 2-fluoro-4-methoxy-1-nitrobenzene (1.00 g, 5.85 mmol) with methyl 4,4-dimethyl-3-oxovalerate (0.93 mL, 5.82 mmol) and potassium carbonate (1.62 g, 11.7 mmol) in DMSO (5.8 mL, 1.0 M) for 2 hours, followed by purification with flash silica gel column chromatography (0-33% ethyl acetate-hexane), gave **S2** (1.20 g, 3.89 mmol, 67% yield, yellow oil).

¹**H** NMR (CDCl₃, 400 MHz) δ 8.11 (d, *J* = 9.2 Hz, 1H), 6.96 (d, *J* = 2.8 Hz, 1H), 6.92 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.11 (s, 1H), 3.87 (s, 3H), 3.75 (s, 3H), 1.16 (s, 9H) ¹³**C** NMR (CDCl₃, 100 MHz) δ 208.5 (C), 168.5 (C), 163.2 (C), 141.4 (C), 130.7 (C), 128.1 (CH), 116.3 (CH), 113.7 (CH), 55.9 (CH₃), 53.9 (CH), 52.9 (CH₃), 45.8 (C), 26.4 (CH₃) **IR** (film, cm⁻¹) 1749, 1710, 1581, 1518, 1340, 1296, 1254, 1200, 1173, 1084 **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₉NNaO₆ 332.1105; Found 332.1105

Methyl 4,4-dimethyl-2-(2-nitro-4-(trifluoromethyl)phenyl)-3-oxopentanoate (S3)



A reaction of 4-fluoro-3-nitrobenzotrifluoride (0.650 mL, 4.76 mmol) with methyl 4,4-dimethyl-3-oxovalerate (0.760 mL, 4.76 mmol) and potassium carbonate (1.32 g, 9.58 mmol) in

DMSO (4.8 mL, 1.0 M) for 3 hours, followed by purification with flash silica gel column chromatography (0-7% ethyl acetate-hexane), gave **S3** (1.04 g, 3.01 mmol, 63% yield, yellow amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 8.24 (d, J = 1.2 Hz, 1H), 7.87 (dd, J = 8.4, 1.2 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 5.98 (s, 1H), 3.77 (s, 3H), 1.18 (s, 9H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 207.2 (C), 167.7 (C), 148.7 (C), 132.5 (CH), 131.6 (C, J = 34.3 Hz), 131.5 (C), 129.5 (CH, J = 3.8 Hz), 122.6 (C, J = 270.8 Hz), 122.3 (CH, J = 3.8 Hz), 53.3 (CH₃), 53.1 (CH), 45.9 (C), 26.3 (CH₃) ¹⁹**F NMR** (CDCl₃, 376 MHz) δ -63.4 (s, 3F) **IR** (film, cm⁻¹) 1749, 1713, 1543, 1329, 1272, 1205, 1178, 1139, 1090, 1000 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₅H₁₆F₃NNaO₅ 370.0873; Found 370.0873

General Procedure B: Krapcho decarboxylation: A solution of a ketoester (1 equiv.), lithium chloride (1.1 equiv.) and water (2.2 equiv.) in DMSO (0.3 M) was heated at 140 °C for the indicated time. After cooling to room temperature, the resulting mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography to give a ketone.

3,3-Dimethyl-1-(2-nitrophenyl)butan-2-one (16)



A reaction of methyl 4,4-dimethyl-2-(2-nitrophenyl)-3-oxopentanoate (**15**, 2.55g, 9.14 mmol) with lithium chloride (427 mg, 10.1 mmol) and water (0.36 mL, 20 mmol) in DMSO (31 mL, 0.29 M) for 5 hours, followed by purification with flash silica gel column chromatography (0-33% ethyl acetate-hexane), gave **16** (1.66 g, 7.51 mmol, 82% yield, orange oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 8.09 (dd, J = 7.6, 1.2 Hz, 1H), 7.56 (dt, J = 7.6, 1.2 Hz, 1H), 7.43 (dt, J = 7.6, 1.2 Hz, 1H), 7.22 (dd, J = 7.6, 1.2 Hz, 1H), 4.29 (s, 2H), 1.27 (s, 9H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 210.8 (C), 149.1 (C), 133.4 (CH), 133.2 (CH), 130.9 (C), 128.1 (CH), 125.1 (CH), 44.2 (C), 42.6 (CH₂), 26.7 (CH₃) **IR** (film, cm⁻¹) 2971, 1710, 1525, 1478, 1405, 1349, 1062, 1008, 788, 725 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₂H₁₅NNaO₃ 244.0944; Found 244.0944

2-(2-Nitrophenyl)-1-phenylethan-1-one (S4)



A reaction of methyl 2-(2-nitrophenyl)-3-oxo-3-phenylpropanoate (**S1**, 1.97g, 6.59 mmol) with lithium chloride (314 mg, 7.42 mmol) and water (0.26 mL, 14 mmol) in DMSO (13 mL, 0.51 M) for 1 hour, followed by purification with flash silica gel column chromatography (0-33% ethyl acetate-hexane), gave **S4** (1.37 g, 5.68 mmol, 86% yield, white amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 8.16 (dd, J = 7.6, 1.6 Hz, 1H), 8.04 (dd, J = 7.6, 1.2 Hz, 2H), 7.63-7.59 (m, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.49 (dt, J = 7.6, 1.6 Hz, 1H), 7.35 (dd, J = 7.6, 1.6 Hz, 1H), 4.74 (s, 2H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 195.3 (C), 149.0 (C), 136.4 (C), 133.6 (CH), 133.5 (CH), 133.4 (CH), 130.6 (C), 128.7 (CH), 128.4 (CH), 128.2 (CH), 125.2 (CH), 44.1 (CH₂) **IR** (film, cm⁻¹) 3066, 1688, 1524, 1347, 1216, 993, 757, 729, 691, 577 **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₁₁NNaO₃ 264.0631; Found 264.0631

1-(5-Methoxy-2-nitrophenyl)-3,3-dimethylbutan-2-one (S5)



A reaction of methyl 2-(5-methoxy-2-nitrophenyl)-4,4-dimethyl-3-oxopentanoate (**S2**, 2.07 g, 6.68 mmol) with lithium chloride (313 mg, 7.37 mmol) and water (0.27 mL, 15 mmol) in DMSO (22 mL, 0.30 M) for 2 hours, followed by purification with flash silica gel column chromatography (0-33% ethyl acetate-hexane), gave **S5** (1.53 g, 6.10 mmol, 91% yield, yellow amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 8.17 (d, J = 9.0 Hz, 1H), 6.87 (dd, J = 9.0, 3.2 Hz, 1H), 6.66 (d, J = 3.2 Hz, 1H), 4.27 (s, 2H), 3.87 (s, 3H), 1.27 (s, 9H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 211.0 (C), 163.2 (C), 142.0 (C), 134.1 (C), 127.9 (CH), 118.6 (CH), 112.6 (CH), 55.8 (CH₃), 44.2 (C), 43.5 (CH₂), 26.8 (CH₃) **IR** (film, cm⁻¹) 2970, 1709, 1586, 1514, 1484, 1339, 1292, 1263, 1082, 840 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₃H₁₇NNaO₄ 274.1050; Found 274.1050

3,3-Dimethyl-1-(2-nitro-4-(trifluoromethyl)phenyl)butan-2-one (S6)



A reaction of methyl 4,4-dimethyl-2-(2-nitro-4-(trifluoromethyl)phenyl)-3-oxopentanoate (**S3**, 2.03 g, 5.85 mmol) with lithium chloride (280 mg, 6.60 mmol) and water (0.23 mL, 13 mmol) in DMSO (20 mL, 0.29 M) for 2 hours, followed by purification with flash silica gel column chromatography (0-10% ethyl acetate-hexane), gave **S6** (728 mg, 2.52 mmol, 43% yield, yellow amorphous solid).

¹H NMR (CDCl₃, 400 MHz) δ 8.37 (s, 1H), 7.81 (dd, J = 8.2, 1.6 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 4.36 (s, 2H), 1.27 (s, 9H) ¹³C NMR (CDCl₃, 100 MHz) δ 210.0 (C), 149.2 (C), 134.9 (C), 134.3 (CH), 130.9 (C, J = 34.3 Hz), 129.6 (CH, J = 3.8 Hz), 122.8 (C, J = 270.8 Hz), 122.4 (CH, J = 3.8 Hz), 44.3 (C), 42.6 (CH₂), 26.6 (CH₃) ¹⁹F NMR (CDCl₃, 376 MHz) δ -63.5 (s, 3F) IR (film, cm⁻¹) 2972, 1710, 1630, 1542, 1403, 1325, 1139, 1091, 1061, 905 HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₃H₁₄F₃NNaO₃ 312.0818; Found 312.0818

General Procedure C: Alkylation at the benzyl position: To a solution of a ketone (1 equiv.) in DMSO (2.0 M) was added potassium carbonate (1.5 equiv.) and alkyl iodide (1.5 equiv.) at room temperature. After stirring for the indicated time, the mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography to give a ketone.

2,2-Dimethyl-4-(2-nitrophenyl)octan-3-one (17)



A reaction of 3,3-dimethyl-1-(2-nitrophenyl)butan-2-one (**16**, 802 mg, 3.62 mmol) with 1-iodobutane (0.62 mL, 5.4 mmol) and potassium carbonate (751 mg, 5.43 mmol) in DMSO (1.8 mL, 2.0 M) for 31 hours, followed by purification with flash silica gel column chromatography (0-10% ethyl acetate-hexane), gave **17** (881 mg, 3.18 mmol, 88% yield, yellow oil).

¹**H** NMR (CDCl₃, 400 MHz) δ 7.78 (d, J = 8.0 Hz, 1H), 7.51-7.50 (m, 2H), 7.35 (ddd, J = 8.0, 5.2,

3.2 Hz, 1H), 4.74 (dd, *J* = 8.6, 5.2 Hz, 1H), 2.02 (dddd, *J* = 16.2, 10.2, 8.6, 5.2 Hz, 1H), 1.66 (dddd, *J* = 16.2, 10.8, 5.6, 5.2 Hz, 1H), 1.30 (dq, *J* = 7.4, 7.2 Hz, 1H), 1.26 (dq, *J* = 7.4, 7.2 Hz, 1H), 1.23-1.10 (m, 2H), 1.03 (s, 9H), 0.85 (t, *J* = 7.4 Hz, 3H) ¹³C NMR (CDCl₃, 100 MHz) δ 214.6 (C), 149.5 (C), 133.9 (C), 132.7 (CH), 129.1 (CH), 127.5 (CH), 124.5 (CH), 45.5 (CH), 45.1 (C), 35.3 (CH₂), 30.1 (CH₂), 26.2 (CH₃), 22.6 (CH₂), 13.8 (CH₃)

IR (film, cm⁻¹) 3070, 2961, 2868, 1706, 1528, 1472, 1356, 1061, 788, 740

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for C₁₆H₂₃NNaO₃ 300.1570; Found 300.1570

2,2,5-Trimethyl-4-(2-nitrophenyl)hexan-3-one (S7)



A reaction of 3,3-dimethyl-1-(2-nitrophenyl)butan-2-one (16, 299 mg, 1.35 mmol) with 2-iodopropane (0.200 mL, 2.01 mmol) and potassium carbonate (286 mg, 2.07 mmol) in DMSO (0.68 mL, 2.0 M) for 140 hours, followed by purification with flash silica gel column chromatography (0-2% ethyl acetate-hexane), gave **S7** (149 mg, 0.565 mmol, 42% yield, yellow amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.78 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.50 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.35 (dt, *J* = 7.8, 1.6 Hz, 1H), 4.64 (d, *J* = 10.4 Hz, 1H), 2.37 (dsep, *J* = 10.4, 6.8 Hz, 1H), 1.03 (s, 9H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.67 (d, *J* = 6.8 Hz, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 215.1 (C), 150.3 (C), 133.1 (C), 132.8 (CH), 129.0 (CH), 127.6 (CH), 124.5 (CH), 51.6 (CH), 45.4 (C), 34.2 (CH), 26.1 (CH₃), 22.0 (CH₃), 19.4 (CH₃) **IR** (film, cm⁻¹) 2967, 2873, 1702, 1529, 1473, 1352, 1235, 1055, 787, 739 **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₅H₂₁NNaO₃ 286.1414; Found 286.1414

2,2-Dimethyl-4-(2-nitrophenyl)pentan-3-one (S8)



A reaction of 3,3-dimethyl-1-(2-nitrophenyl)butan-2-one (16, 229 mg, 1.03 mmol) with iodomethane (94 μ L, 1.5 mmol) and potassium carbonate (209 mg, 1.51 mmol) in DMSO (0.50 mL, 2.1 M) for 8 hours, followed by purification with flash silica gel column chromatography (0-2% ethyl acetate-hexane), gave **S8** (204 mg, 0.867 mmol, 84% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.80 (d, J = 8.2 Hz, 1H), 7.53-7.51 (m, 2H), 7.37 (ddd, J = 8.2, 5.2, 3.6 Hz, 1H), 4.82 (q, J = 6.8 Hz, 1H), 1.43 (d, J = 6.8 Hz, 3H), 1.06 (s, 9H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 215.2 (C), 149.1 (C), 135.1 (C), 132.8 (CH), 129.2 (CH), 127.7 (CH), 124.5 (CH), 45.0 (C), 40.4 (CH), 26.5 (CH₃), 20.2 (CH₃) **IR** (film, cm⁻¹) 2972, 2935, 1706, 1527, 1479, 1353, 991, 856, 786, 745 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₃H₁₇NNaO₃ 258.1101; Found 258.1101

2-(2-Nitrophenyl)-1-phenylhexan-1-one (S9)



A reaction of 2-(2-nitrophenyl)-1-phenylethan-1-one (S4, 1.37 g, 5.68 mmol) with 1-iodobutane (0.97 mL, 8.5 mmol) and potassium carbonate (1.18 g, 8.55 mmol) in DMSO (2.8 mL, 2.0 M) for 24 hours, followed by purification with flash silica gel column chromatography (0-10% ethyl acetate-hexane), gave S9 (1.32 g, 4.43 mmol, 78% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.96 (dd, J = 8.0, 1.2 Hz, 2H), 7.86 (dd, J = 8.2, 1.2 Hz, 1H), 7.54-7.51 (m, 2H), 7.48 (dd, J = 8.2, 1.6 Hz, 1H), 7.42 (dt, J = 8.0, 1.6 Hz, 2H), 7.36 (dt, J = 8.2, 1.6 Hz, 1H), 5.31 (t, J = 7.0 Hz, 1H), 2.20 (dddd, J = 13.4, 10.0, 7.6, 4.8 Hz, 1H), 1.83 (dddd, J = 13.4, 10.0, 6.8, 5.2 Hz, 1H), 1.36-1.20 (m, 4H), 0.86 (t, J = 7.2 Hz, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 199.1 (C), 149.4 (C), 136.3 (C), 133.9 (C), 133.3 (CH), 133.1 (CH), 129.9 (CH), 128.7 (CH), 128.5 (CH), 127.8 (CH), 124.7 (CH), 47.0 (CH), 33.7 (CH₂), 29.8 (CH₂), 22.6 (CH₂), 13.8 (CH₃) **IR** (film, cm⁻¹) 2957, 2866, 1685, 1601, 1542, 1448, 1351, 1235, 740, 704

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{19}NNaO_3$ 320.1257; Found 320.1257

4-(5-Methoxy-2-nitrophenyl)-2,2-dimethyloctan-3-one (S10)



A reaction of 1-(5-methoxy-2-nitrophenyl)-3,3-dimethylbutan-2-one (**S5**, 1.53 g, 6.10 mmol) with 1-iodobutane (1.04 mL, 9.14 mmol) and potassium carbonate (1.27 g, 9.19 mmol) in DMSO (3.1 mL, 2.0 M) for 40 hours, followed by purification with flash silica gel column chromatography

(0-4% ethyl acetate-hexane), gave S10 (1.32 g, 4.29 mmol, 70% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.94 (d, *J* = 8.8 Hz, 1H), 6.94 (d, *J* = 2.8 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.03 (dd, *J* = 8.6, 5.2 Hz, 1H), 3.84 (s, 3H), 2.00 (dddd, *J* = 13.4, 10.4, 8.6, 5.2 Hz, 1H), 1.65 (dddd, *J* = 16.0, 10.4, 5.4, 5.2 Hz, 1H), 1.30 (dq, *J* = 7.2, 7.2 Hz, 1H), 1.27 (dq, *J* = 7.2, 7.2 Hz, 1H), 1.24-1.12 (m, 2H), 1.04 (s, 9H), 0.85 (t, *J* = 7.4 Hz, 3H)

¹³C NMR (CDCl₃, 100 MHz) δ 214.9 (C), 162.9 (C), 142.0 (C), 137.4 (C), 127.7 (CH), 113.6 (CH), 112.7 (CH), 55.8 (CH₃), 45.6 (CH), 45.1 (C), 35.3 (CH₂), 30.1 (CH₂), 26.2 (CH₂), 22.6 (CH₃), 13.8 (CH₃)

IR (film, cm⁻¹) 2961, 2869, 1705, 1605, 1581, 1482, 1343, 1288, 1258, 1076 HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₇H₂₅NNaO₄ 330.1676; Found 330.1676

2,2-Dimethyl-4-(2-nitro-4-(trifluoromethyl)phenyl)octan-3-one (S11)



A reaction of 3,3-dimethyl-1-(2-nitro-4-(trifluoromethyl)phenyl)butan-2-one (**86**, 728 mg, 2.52 mmol) with 1-iodobutane (0.43 mL, 3.8 mmol) and potassium carbonate (522 mg, 3.78 mmol) in DMSO (1.3 mL, 1.9 M) for 24 hours, followed by purification with flash silica gel column chromatography (0-10% ethyl acetate-hexane), gave **S11** (775 mg, 2.24 mmol, 89% yield, yellow amorphous solid).

¹**H** NMR (CDCl₃, 400 MHz) δ 8.04 (s, 1H), 7.76 (m, 2H), 4.80 (dd, J = 8.2, 6.0 Hz, 1H), 2.03 (dddd, J = 13.4, 10.4, 8.2, 5.2 Hz, 1H), 1.68 (dddd, J = 13.4, 13.4, 6.0, 5.8 Hz, 1H), 1.30 (dq, J = 7.2, 7.0 Hz, 1H), 1.27 (dq, J = 7.2, 7.0 Hz, 1H), 1.23-1.11 (m, 2H), 1.06 (s, 9H), 0.85 (t, J = 7.2 Hz, 3H)

¹³C NMR (CDCl₃, 100 MHz) δ 213.9 (C), 149.4 (C), 137.7 (C), 130.3 (CH), 130.2 (C, *J* = 34.3 Hz), 129.1 (CH, *J* = 3.8 Hz), 122.7 (C, *J* = 270.8 Hz), 121.7 (CH, *J* = 3.8 Hz), 45.3 (CH), 45.3 (C), 35.5 (CH₂), 30.0 (CH₂), 26.0 (CH₃), 22.5 (CH₂), 13.7 (CH₃)

¹⁹**F NMR** (CDCl₃, 376 MHz) δ –63.5 (s, 3F)

IR (film, cm⁻¹) 2964, 2871, 1708, 1626, 1540, 1471, 1359, 1327, 1142, 1084

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}F_3NNaO_3$ 368.1444; Found 368.1444

Synthesis of 1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one (S12b)



To a solution of 2-(4-methoxyphenyl)acetic acid (1.67 g, 10.0 mmol) and DMF (7.7 μ L, 0.1 mmol) in dichloromethane (50 mL, 0.2 M) was added dropwise thionyl chloride (1.44 mL, 20.0 mmol), and the reaction mixture stirred at room temperature for 1.5 hours. The solvent was concentrated *in vacuo*, and the residue was used without further purification. To the residue and CuCl (993 mg, 10.0 mmol) in THF (10 mL, 1.0 M) was added dropwise a solution of *t*-BuMgCl in THF (11 mL, 11 mmol) at -20 °C. The reaction mixture was allowed to warm to room temperature and stir at this temperature. After stirring for 2.5 hours, the resulting mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography (0-2% ethyl acetate-hexane), gave **S12b** (1.11 g, 5.38 mmol, 54% yield, colorless oil).

¹**H** NMR (CDCl₃, 400 MHz) δ 7.09 (dd, *J* = 6.4, 2.0 Hz, 2H), 6.85 (dd, *J* = 6.4, 2.0 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 2H), 1.20 (s, 9H) ¹³**C** NMR (CDCl₃, 100 MHz) δ 213.2 (C), 158.3 (C), 130.5 (CH), 126.9 (C), 113.8 (CH), 55.2 (CH₃), 44.5 (C), 42.3 (CH₂), 26.4 (CH₃) **IR** (film, cm⁻¹) 2968, 1710, 1477, 1465, 1301, 1178, 1062, 1036, 818, 786 **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₃H₁₈NaO₂ 229.1199; Found 229.1199

Preparation of 3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butan-2-one (S12c)



To a solution of 2-(4-(trifluoromethyl)phenyl)acetic acid (2.05 g, 10.0 mmol) and DMF (7.6 μ L, 99 μ mol) in dichloromethane (50 mL, 0.2 M) was added dropwise thionyl chloride (1.44 mL, 20.0 mmol), and the reaction mixture stirred at room temperature for 1 hour. The solvent was concentrated *in vacuo*, and the residue was used without further purification. To the residue and CuCl (991 mg, 10.0 mmol) in THF (10 mL, 1.0 M) was added dropwise a solution of *t*-BuMgCl in

THF (11 mL, 11 mmol) at -20 °C. The reaction mixture was allowed to warm to room temperature and stir at this temperature. After stirring for 1.5 hours, the resulting mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography (0-2% ethyl acetate-hexane), gave **S12c** (1.08 g, 4.42 mmol, 44% yield, white amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.57 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 3.86 (s, 2H), 1.22 (s, 9H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 211.9 (C), 139.0 (C), 130.0 (CH), 129.0 (C, J = 32.4 Hz), 125.3 (CH, J = 3.8 Hz), 124.2 (C, J = 270.4 Hz), 44.7 (C), 42.9 (CH₂), 26.3 (CH₃) ¹⁹**F NMR** (CDCl₃, 376 MHz) δ -63.9 (s, 3F) **IR** (film, cm⁻¹) 2977, 1704, 1468, 1416, 1326, 1166, 1121, 1064, 870, 816 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₃H₁₅F₃NaO 267.0967; Found 267.0968

Synthesis of 3,3-dimethyl-1-(2-nitrophenyl)-1-phenylbutan-2-one (S13a)



A solution of 2-fluoronitrobenzene (0.35 mL, 3.3 mmol), 3,3-dimethyl-1-phenylbutan-2-one² (871 mg, 4.94 mmol) and potassium carbonate (911 mg, 6.59 mmol) in DMSO (3.3 mL) was heated at 80 °C for 10 hours. After cooling to room temperature, the resulting mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography (0-3% ethyl acetate-hexane; 0-50% dichloromethane-hexane), gave **S13a** (544 mg, 1.83 mmol, 55% yield, yellow amorphous solid).

¹H NMR (CDCl₃, 400 MHz) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.40-7.31 (m, 4H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.26 (s, 1H), 1.16 (s, 9H)
¹³C NMR (CDCl₃, 100 MHz) δ 212.8 (C), 148.6 (C), 136.2 (C), 134.4 (C), 132.8 (CH), 131.9 (CH), 130.0 (CH), 129.1 (CH), 127.9 (CH), 127.7 (CH), 124.7 (CH), 54.5 (CH), 45.2 (C), 27.5 (CH₃)

IR (film, cm⁻¹) 2972, 2872, 1694, 1521, 1449, 1349, 1300, 1271, 1060, 713 HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₈H₁₉NNaO₃ 320.1257; Found 320.1257 Synthesis of 1-(4-methoxyphenyl)-3,3-dimethyl-1-(2-nitrophenyl)butan-2-one (S13b)



A solution of 2-fluoronitrobenzene (0.35 mL, 3.3 mmol), 1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one (**S12b**, 1.02g, 4.94 mmol) and potassium carbonate (906 mg, 6.56 mmol) in DMSO (3.3 mL) was heated at 80 °C for 10 hours. After cooling to room temperature, the resulting mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography (0-10% ethyl acetate-hexane; 0-50% dichloromethane-hexane), gave **S13b** (518 mg, 1.58 mmol, 48% yield, yellow amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.36 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.19-7.15 (m, 3H), 6.91 (dd, *J* = 7.0, 1.6 Hz, 2H), 6.19 (s, 1H), 3.82 (s, 3H), 1.15 (s, 9H)

¹³C NMR (CDCl₃, 100 MHz) δ 213.1 (C), 159.2 (C), 148.6 (C), 135.0 (C), 132.7 (CH), 131.9 (CH), 131.2 (CH), 127.8 (C), 127.6 (CH), 124.6 (CH), 114.5 (CH), 55.3 (CH₃), 54.0 (CH), 45.0 (C), 27.6 (CH₃)

IR (film, cm⁻¹) 2967, 1699, 1518, 1351, 1302, 1254, 1180, 1032, 790, 733 HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₉H₂₁NNaO₄ 350.1363; Found 350.1363

Synthesis of 3,3-dimethyl-1-(2-nitrophenyl)-1-(4-(trifluoromethyl)phenyl)butan-2-one (S13c)



A solution of 2-fluoronitrobenzene (0.30 mL, 2.8 mmol), 3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butan-2-one (**S12c**, 1.02 g, 4.18 mmol) and potassium carbonate (779 mg, 5.64 mmol) in DMSO (2.8 mL) was heated at 80 °C for 5 hours. After cooling to room temperature, the resulting mixture was quenched with aqueous ammonium chloride and

extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography (0-2% ethyl acetate-hexane), gave **S13c** (935 mg, 2.56 mmol, 91% yield, yellow amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.94 (dd, J = 8.0, 1.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.53 (dt, J = 8.0, 1.6 Hz, 1H), 7.44-7.38 (m, 3H), 7.27 (dd, J = 8.0, 1.6 Hz, 1H), 6.35 (s, 1H), 1.15 (s, 9H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 212.1 (C), 148.7 (C), 140.7 (C), 133.0 (CH), 132.9 (C), 131.3 (CH), 130.1 (C, J = 32.8 Hz), 130.0 (CH), 128.2 (CH), 125.9 (CH, J = 2.8 Hz), 125.0 (CH), 123.9 (C, J = 271.0 Hz), 53.1 (CH), 45.5 (C), 27.1 (CH₃) ¹⁹**F NMR** (CDCl₃, 376 MHz) δ -63.8 (s, 3F) **IR** (film, cm⁻¹) 2972, 1706, 1529, 1327, 1168, 1125, 1064, 1014, 789, 734 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₉H₁₈F₃NNaO₃ 388.1131; Found 388.1131 General Procedure D: Photo-induced rearrangement of ketones: A stirred solution of a ketone in MeOH was irradiated with 365 nm LED at -78 °C for the indicated time with Ar bubbling. After adding Na₂CO₃ at -78 °C, the resulting mixture was warmed up to room temperature and then concentrated under reduced pressure. Purification of the residue by preparative TLC gave a hydroxamate.



Pictures of the photoreactor

1-(3-Butyl-3-hydroxybenzo[c]isoxazol-1(3H)-yl)-2,2-dimethylpropan-1-one (18)



2,2-Dimethyl-4-(2-nitrophenyl)octan-3-one (**17**, 23.6 mg, 85.1 μ mol) was irradiated in MeOH (2.0 mL, 43 mM) for 4 hours at -78 °C before adding Na₂CO₃ (2.4 mg, 23 μ mol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave **18** (19.6 mg, 70.7 μ mol, 83% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.88 (d, J = 7.8 Hz, 1H), 7.38 (dt, J = 7.8, 0.8 Hz, 1H), 7.30 (dd, J = 7.8, 0.8 Hz, 1H), 7.16 (dt, J = 7.8, 0.8 Hz, 1H), 3.50 (brs, 1H), 2.24 (ddd, J = 14.4, 11.2, 4.8 Hz, 1H), 2.13 (ddd, J = 14.4, 11.2, 4.8 Hz, 1H), 1.52-1.23 (m, 4H), 1.37 (s, 9H), 0.89 (t, J = 7.2 Hz, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 173.7 (C), 137.9 (C), 130.3 (CH), 128.7 (C), 124.7 (CH), 121.8 (CH), 115.1 (CH), 108.5 (C), 40.0 (C), 37.1 (CH₂), 26.3 (CH₃), 26.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃) **IR** (film, cm⁻¹) 3361, 2958, 2871, 1631, 1462, 1405, 1363, 951, 907, 753 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₆H₂₃NNaO₃ 300.1570; Found 300.1570



¹³C NMR, Selected H-H COSY and HMBC of compound **18**

1-(3-Hydroxy-3-isopropylbenzo[c]isoxazol-1(3H)-yl)-2,2-dimethylpropan-1-one (25)



2,2,5-Trimethyl-4-(2-nitrophenyl)hexan-3-one (**S7**, 26.2 mg, 99.5 μ mol) was irradiated with in MeOH (2.0 mL, 50 mM) for 3 hours at -78 °C before adding Na₂CO₃ (2.7 mg, 25 μ mol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave **25** (20.3 mg, 77.1 μ mol, 77% yield, yellow amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.93 (d, J = 7.6 Hz, 1H), 7.39 (dt, J = 7.6, 1.2 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.17 (dt, J = 7.6, 0.8 Hz, 1H), 3.24 (brs, 1H), 2.48 (sep, J = 6.8 Hz, 1H), 1.39 (s, 9H), 1.20 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 173.5 (C), 138.1 (C), 130.4 (CH), 128.0 (C), 124.6 (CH), 122.1 (CH), 115.0 (CH), 110.6 (C), 40.1 (C), 35.6 (CH), 26.3 (CH₃), 17.8 (CH₃), 16.1 (CH₃) **IR** (film, cm⁻¹) 3357, 2970, 1632, 1462, 1406, 1363, 1286, 1085, 910, 750 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₅H₂₁NNaO₃ 286.1414; Found 286.1414

1-(3-Hydroxy-3-methylbenzo[c]isoxazol-1(3H)-yl)-2,2-dimethylpropan-1-one (26)



2,2-Dimethyl-4-(2-nitrophenyl)pentan-3-one (S8, 24.9 mg, 0.106 mmol) was reacted in MeOH (2.0 mL, 53 mM). After stirring for 5.5 hours at -78 °C, the solution was added to Na₂CO₃ (2.3 mg, 22

 μ mol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave **26** (20.1 mg, 85.4 μ mol, 81% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.88 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 3.43 (brs, 1H), 1.91 (s, 3H), 1.37 (s, 9H). ¹³**C NMR** (CDCl₃, 100 MHz) δ 173.9 (C), 137.7 (C), 130.3 (CH), 129.7 (C), 124.8 (CH), 121.5 (CH), 115.2 (CH), 106.5 (C), 40.1 (C), 26.3 (CH₃), 24.2 (CH₃) **IR** (film, cm⁻¹) 3360, 1631, 1602, 1483, 1405, 1363, 1156, 1034, 847, 757 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₃H₁₇NNaO₃ 258.1101; Found 258.1101

1-(3-Hydroxybenzo[*c*]isoxazol-1(3*H*)-yl)-2,2-dimethylpropan-1-one (27)



3,3-Dimethyl-1-(2-nitrophenyl)butan-2-one (**16**, 23.5 mg, 0.106 mmol) was irradiated in MeOH (4.8 mL, 5.0 mM) with 365 nm LED (×2) at -78 °C with Ar bubbling for 16.5 hours before adding Na₂CO₃ (2.2 mg, 21 µmol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave **27** (3.8 mg, 17 µmol, 16% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.92 (dd, J = 7.6, 0.8 Hz, 1H), 7.43 (dt, J = 7.6, 0.8 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.19 (dt, J = 7.6, 0.8 Hz, 1H), 6.64 (s, 1H), 3.39 (brs, 1H), 1.39 (s, 9H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 174.1 (C), 137.6 (C), 130.8 (CH), 126.6 (C), 124.7 (CH), 122.9 (CH), 115.1 (CH), 99.0 (CH), 40.1 (C), 26.3 (CH₃) **IR** (film, cm⁻¹) 3357, 2968, 1632, 1469, 1407, 1023, 913, 754, 676, 579 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₂H₁₅NNaO₃ 244.0944; Found 244.0944





28a keto:hemiacetal = 1:2

3,3-Dimethyl-1-(2-nitrophenyl)-1-phenylbutan-2-one (**S13a**, 30.3 mg, 0.102 mmol) was irradiated in MeOH (10 mL, 10 mM) for 5 hours at -78 °C before adding Na₂CO₃ (2.3 mg, 22 µmol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 8) gave **28a** (22.6 mg, 76.0 µmol, 75% yield, white amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz)

hemiacetal form: δ 7.97 (dd, J = 8.4, 2.8 Hz, 1H), 7.68-7.65 (m, 2H), 7.45-7.38 (m, 4H), 7.12-7.11 (m, 2H), 3.69 (brs, 1H), 1.40 (s, 9H) keto form: δ 8.86 (brs, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.65-7.61 (m, 2H), 7.55-7.53 (m, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.45-7.40 (m, 1H), 1.33 (s, 9H) ¹³C NMR (CDCl₃, 100 MHz) hemiacetal form: δ 174.1 (C), 138.7 (C), 137.4 (C), 130.3 (C), 130.0 (CH), 129.2 (CH), 128.4 (CH), 126.6 (CH), 124.9 (CH), 122.7 (CH), 115.1 (CH), 107.2 (C), 40.1 (C), 26.3 (CH₃) keto form: δ 198.3 (C), 178.0 (C), 141.9 (C), 137.0 (C), 135.2 (C), 133.6 (CH), 133.1 (CH), 132.0 (CH), 130.7 (CH), 130.4 (CH), 128.4 (CH), 127.8 (CH), 39.1 (C), 26.9 (CH₃) **IR** (film, cm⁻¹) 3309, 1631, 1467, 1404, 1286, 1204, 1061, 934, 753, 699 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₈H₁₉NNaO₃ 320.1257; Found 320.1257

1-(3-Hydroxy-3-(4-methoxyphenyl)benzo[*c*]isoxazol-1(3*H*)-yl)-2,2-dimethylpropan-1-one (28b)



28b keto:hemiacetal = 3:1

1-(4-Methoxyphenyl)-3,3-dimethyl-1-(2-nitrophenyl)butan-2-one (**S13b**, 33.0 mg, 0.101 mmol) was irradiated in MeOH (10 mL, 10 mM) for 5 hours at -78 °C before adding Na₂CO₃ (2.3 mg, 22 µmol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 8) gave **28b** (20.1 mg, 61.4 µmol, 61% yield, white amorphous solid).

¹H NMR (CDCl₃, 400 MHz)

hemiacetal form: δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.41-7.37 (m, 1H), 7.14-7.08 (m, 2H), 6.94-6.92 (m, 2H), 3.83 (s, 3H), 1.39 (s, 9H) keto form: δ 8.97 (brs, 1H), 7.81 (dd, *J* = 7.0, 2.0 Hz, 2H), 7.62 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.54-7.51 (m, 2H), 7.44-7.41 (m, 1H), 6.96-6.94 (m, 2H), 3.89 (s, 3H), 1.32 (s, 9H) ¹³C NMR (CDCl₃, 100 MHz) hemiacetal form: δ 174.1 (C), 160.3 (C), 137.4 (C), 131.6 (C), 130.8 (C), 130.2 (CH), 128.0 (CH), 124.9 (CH), 122.7 (CH), 115.0 (CH), 113.7 (CH), 107.3 (C), 55.3 (CH₃), 40.1 (C), 26.4 (CH₃) keto form: δ 196.8 (C), 178.0 (C), 164.2 (C), 141.8 (C), 135.9 (C), 133.4 (CH), 132.7 (CH), 131.6 (CH), 130.3 (CH), 129.6 (C), 127.7 (CH), 113.8 (CH), 55.6 (CH₃), 39.0 (C), 26.9 (CH₃) **IR** (film, cm⁻¹) 3254, 1601, 1467, 1403, 1302, 1256, 1176, 1030, 932, 741 **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₁9H₂₁NNaO₄ 350.1363; Found 350.1363



¹³C NMR, Selected H-H COSY and HMBC of compound **28b**

1-(3-Hydroxy-3-(4-(trifluoromethyl)phenyl)benzo[*c*]isoxazol-1(3*H*)-yl)-2,2-dimethylpropan-1one (28c)



28c

3,3-Dimethyl-1-(2-nitrophenyl)-1-(4-(trifluoromethyl)phenyl)butan-2-one (S13c, 36.7 mg, 0.100 mmol) was irradiated in MeOH (10 mL, 10 mM) for 2 hours at -78 °C before adding Na₂CO₃ (2.9 mg, 27 µmol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 8) gave **28c** (25.3 mg, 69.2 µmol, 69% yield, white amorphous solid).

¹**H** NMR (CDCl₃, 400 MHz) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 3.96 (brs, 1H), 1.38 (s, 9H). A small amount of the keto form was detected on ¹H NMR.

¹³C NMR (CDCl₃, 100 MHz) δ 174.2 (C), 142.4 (C), 137.4 (C), 131.4 (C, *J* = 33.2 Hz), 130.8 (CH), 129.0 (C), 127.2 (CH), 125.4 (CH, *J* = 3.8 Hz), 125.1 (CH), 123.9 (C, *J* = 270.0 Hz), 122.7 (CH), 115.2 (CH), 106.7 (C), 40.2 (C), 26.3 (CH₃)

¹⁹**F NMR** (CDCl₃, 376 MHz) δ –64.1 (s, 3F)

IR (film, cm⁻¹) 3313, 1630, 1468, 1407, 1326, 1130, 1069, 934, 842, 749 HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}F_3NNaO_3$ 388.1131; Found 388.1131

1-(3-Butyl-3-hydroxybenzo[c]isoxazol-1(3H)-yl)propan-1-one (29)



4-(2-Nitrophenyl)octan-3-one³ (23.5 mg, 94.2 μ mol) was irradiated in MeOH (2.0 mL, 47 mM) for 6 hours at -78 °C before adding Na₂CO₃ (2.3 mg, 22 μ mol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave **29** (17.8 mg, 71.4 μ mol, 76% yield, yellow amorphous solid).

¹**H** NMR (CDCl₃, 400 MHz) δ 7.76 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.37 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.17 (dt, *J* = 7.6, 0.8 Hz, 1H), 4.69 (brs, 1H), 2.50 (dq, *J* = 16.8, 7.2 Hz, 1H), 2.25 (dq, *J* = 16.8, 7.2 Hz, 1H), 2.21 (ddd, *J* = 14.2, 11.0, 4.8 Hz, 1H), 2.11 (ddd, *J* = 14.2, 11.0, 4.8 Hz, 1H), 1.48-1.15 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). A small amount of the keto form was detected on ¹H NMR.

¹³C NMR (CDCl₃, 100 MHz) δ 170.1 (C), 136.5 (C), 130.2 (CH), 129.4 (C), 124.9 (CH), 122.2 (CH), 114.1 (CH), 108.6 (C), 37.2 (CH₂), 27.1 (CH₂), 26.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃), 7.9 (CH₃)

IR (film, cm⁻¹) 3350, 2950, 1646, 1469, 1419, 1295, 1019, 951, 862, 754 HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₄H₁₉NNaO₃ 272.1257; Found 272.1257

(3-Butyl-3-hydroxybenzo[c]isoxazol-1(3H)-yl)(phenyl)methanone (30)



2-(2-Nitrophenyl)-1-phenylhexan-1-one (**S9**, 28.2 mg, 94.8 μ mol) was irradiated in MeOH (2.0 mL, 47 mM) for 6 hours at -78 °C before adding Na₂CO₃ (2.9 mg, 27 μ mol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave **30** (18.8 mg, 63.2 μ mol, 67% yield, white amorphous solid).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.50 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.42 (dt, *J* = 7.2, 1.2 Hz, 2H), 7.38 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.19 (dt, *J* = 7.6, 0.8 Hz, 1H), 3.92 (brs, 1H), 2.22 (ddd, *J* = 14.4, 11.2, 4.8 Hz, 1H), 2.13 (ddd, *J* = 14.4, 11.2, 4.8 Hz, 1H), 1.52-1.19 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 3H)

¹³C NMR (CDCl₃, 100 MHz) δ 164.5 (C), 137.5 (C), 132.9 (C), 131.6 (CH), 130.3 (CH), 129.5 (C), 129.5 (CH), 127.9 (CH), 125.3 (CH), 122.0 (CH), 115.3 (CH), 109.0 (C), 37.2 (CH₂), 26.0 (CH₂), 22.5 (CH₂), 13.8 (CH₃)

IR (film, cm⁻¹) 3330, 2954, 1630, 1471, 1413, 1291, 948, 875, 755, 697

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for C₁₈H₁₉NNaO₃ 320.1257; Found 320.1257

1-(3-Butyl-3-hydroxy-5-methoxybenzo[c]isoxazol-1(3H)-yl)-2,2-dimethylpropan-1-one (31)



4-(5-Methoxy-2-nitrophenyl)-2,2-dimethyloctan-3-one (**S10**, 30.5 mg, 99.2 μ mol) was irradiated in MeOH (2.0 mL, 50 mM) for 5 hours at -78 °C before adding Na₂CO₃ (3.1 mg, 29 μ mol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave **31** (22.3 mg, 72.5 μ mol, 73% yield, yellow oil).

¹**H** NMR (CDCl₃, 400 MHz) δ 7.79 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.79 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 2.22 (ddd, *J* = 14.2, 11.2, 4.8 Hz, 1H), 2.10 (ddd, *J* = 14.2, 11.2, 4.8 Hz, 1H), 1.54-1.24 (m, 4H), 1.35 (s, 9H), 0.89 (t, *J* = 7.2 Hz, 3H). A small amount of the keto form was detected on ¹H NMR.

¹³C NMR (CDCl₃, 100 MHz) δ 173.1 (C), 157.1 (C), 131.9 (C), 130.2 (C), 116.1 (CH), 115.8 (CH), 108.4 (C), 107.1 (CH), 55.8 (CH₃), 39.8 (C), 37.0 (CH₂), 26.3 (CH₃), 25.9 (CH₂), 22.6 (CH₂), 13.9 (CH₃)

IR (film, cm⁻¹) 3350, 2958, 2934, 1621, 1486, 1405, 1364, 1278, 1239, 1035 HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₇H₂₅NNaO₄ 330.1676; Found 330.1676 1-(3-Butyl-3-hydroxy-6-(trifluoromethyl)benzo[c]isoxazol-1(3H)-yl)-2,2-dimethylpropan-1-on e (32)



2,2-Dimethyl-4-(2-nitro-4-(trifluoromethyl)phenyl)octan-3-one (S11, 31.3 mg, 90.6 μ mol) was irradiated in MeOH (2.0 mL, 45 mM) for 3 hours at -78 °C before adding Na₂CO₃ (2.7 mg, 25 μ mol). Purification by preparative TLC (dichloromethane: ethyl acetate: hexane = 1: 1: 10) gave 32 (23.4 mg, 67.8 μ mol, 75% yield, yellow oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 8.22 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 3.59 (brs, 1H), 2.27 (ddd, *J* = 14.4, 11.2, 4.8 Hz, 1H), 2.16 (ddd, *J* = 14.4, 11.2, 4.8 Hz, 1H), 1.54-1.23 (m, 4H), 1.36 (s, 9H), 0.90 (t, *J* = 7.2 Hz, 3H)

¹³C NMR (CDCl₃, 100 MHz) δ 174.2 (C), 138.3 (C), 132.8 (C, *J* = 32.4 Hz), 131.8 (C), 123.6 (C, *J* = 270.8 Hz), 122.5 (CH), 121.7 (CH, *J* = 3.8 Hz), 112.5 (CH, *J* = 3.8 Hz), 108.4 (C), 40.1 (C), 37.1 (CH₂), 26.1 (CH₃), 25.9 (CH₂), 22.5 (CH₂), 13.8 (CH₃)

¹⁹**F NMR** (CDCl₃, 376 MHz) δ –64.0 (s, 3F)

IR (film, cm⁻¹) 3382, 2961, 1640, 1437, 1402, 1323, 1247, 1170, 1132, 1059

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}F_3NNaO_3$ 368.1444; Found 368.1444

Synthesis of 6-hydroxy-3,4,5,6-tetrahydro-1,6-epoxybenzo[b]azonine-2,7-dione (37)



A stirred solution of 2-(2-nitrophenyl)cyclohexane-1,3-dione⁴ (**33**, 5.6 mg, 24 μ mol) in MeOH (4.8 mL, 5.0 mM) was irradiated with 365 nm LED at -78 °C for 9 hours with Ar bubbling. The resulting mixture was warmed up to room temperature and then concentrated under reduced pressure. Purification of the residue by preparative TLC (dichloromethane: MeOH = 15: 1) gave **37** (1.2 mg, 5.1 μ mol, 21% yield, white amorphous solid).

¹**H** NMR (CDCl₃, 400 MHz) δ 8.03 (dd, J = 7.8, 1.6 Hz, 1H), 7.67 (dt, J = 7.8, 1.6 Hz, 1H), 7.62 (dd, J = 7.8, 1.2 Hz, 1H), 7.35 (dt, J = 7.8, 1.2 Hz, 1H), 4.32 (brs, 1H), 3.46 (ddd, J = 13.2, 12.0, 6.4 Hz, 1H), 2.58 (ddd, J = 13.2, 10.4, 2.0 Hz, 1H), 2.40-2.27 (m, 1H), 2.04-1.93 (m, 3H)

¹³C NMR (CDCl₃, 100 MHz) δ 191.7 (C), 175.5 (C), 142.6 (C), 135.4 (CH), 127.8 (CH), 126.2 (CH), 122.7 (CH), 119.4 (C), 101.4 (C), 32.8 (CH₂), 30.6 (CH₂), 15.0 (CH₂)
IR (film, cm⁻¹) 3188, 1703, 1668, 1474, 1363, 1282, 1251, 1219, 1007, 735
HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₂H₁₁NNaO₄ 256.0580; Found 256.0580



¹³C NMR, Selected H-H COSY and HMBC of compound **37**

Photo-induced rearrangement of ketone 17 in a 1 mmol scale



A stirred solution of 2,2-dimethyl-4-(2-nitrophenyl)octan-3-one (17, 293 mg, 1.06 mmol) in MeOH (20 mL, 53 mM) was irradiated with 365 nm LED (×2) at -78 °C with Ar bubbling for 5 hours. After addition of Na₂CO₃ (22 mg, 0.21 mmol), the resulting mixture was warmed up to room temperature and then concentrated under reduced pressure. Purification of the residue by flash silica gel column chromatography (dichloromethane: ethyl acetate: hexane = 1: 1: 20) gave **18** (228 mg, 0.822 mmol, 78% yield, yellow amorphous solid).

Transformation of 18 into 3-butylbenzo[c]isoxazole (19)



To a solution of 1-(3-butyl-3-hydroxybenzo[c]isoxazol-1(3H)-yl)-2,2-dimethylpropan-1-one (**18**, 20.5 mg, 73.9 µmol) in MeOH (2.8 mL, 40 mM) was added sodium hydroxide (637 mg, 15.9 mmol) at room temperature. After stirring for 10 minutes, the mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was

washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by preparative TLC with (dichloromethane: ethyl acetate: hexane = 1: 1: 10) to give **19** (9.8 mg, 56 μ mol, 76% yield, colorless oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.51 (d, J = 9.2 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.26 (dd, J = 9.2, 6.2 Hz, 1H), 6.91 (dd, J = 8.8, 6.2 Hz, 1H), 3.15 (t, J = 7.4 Hz, 2H), 1.85 (tt, J = 7.4, 7.4 Hz, 2H), 1.41 (tq, J = 7.4, 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 169.7 (C), 157.0 (C), 130.7 (CH), 122.7 (CH), 119.9 (CH), 115.2 (C), 114.9 (CH), 29.8 (CH₂), 26.4 (CH₂), 22.3 (CH₂), 13.6 (CH₃) **IR** (film, cm⁻¹) 2957, 2865, 1642, 1525, 1461, 1355, 1261, 1022, 801, 746 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₁H₁₃NNaO 198.0889; Found 198.0889

Transformation of 17 into 3-butylbenzo[c]isoxazole (19)



To a solution of 2,2-dimethyl-4-(2-nitrophenyl)octan-3-one (**17**, 32.8 mg, 0.118 mmol) in MeOH (2.0 mL, 59 mM) was added sodium hydroxide (80.7 mg, 2.02 mmol) at 80 °C. After stirring for 53 hours, the mixture was quenched with hydrochloric acid (2 M) and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by preparative TLC with (dichloromethane: ethyl acetate: hexane = 1: 1: 10) to give **19** (9.8 mg, 56 μ mol, 47% yield, colorless oil).

Synthesis of methyl 2-(2-nitrophenyl)hexanoate (S14)



To a solution of nitrobenzene (0.51 mL, 5.0 mmol) and *t*-BuOK (1.0 M solution in THF, 12.0 mL, 12.0 mmol) in THF (8.0 mL, 0.63 M) was added dropwise methyl 2-bromohexanoate (1.0 mL, 6.2 mmol) at -78 °C for 1 hour. After warming to room temperature, the resulting mixture was quenched with hydrochloric acid (2 M) and extracted three times with ethyl acetate. The combined

organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by MPLC (ULTRA PACK, SI-40C, 0-7% THF-hexane) to give **S14** (280 mg, 1.11 mmol, 22% yield, colorless oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.85 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.6, 1.2 Hz, 1H), 7.55 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.41 (ddd, *J* = 8.2, 6.6, 2.0 Hz, 1H), 4.17 (t, *J* = 7.4 Hz, 1H), 3.66 (s, 3H), 2.15 (dddd, *J* = 13.1, 10.2, 7.4, 4.8 Hz, 1H), 1.83 (dddd, *J* = 13.1, 10.0, 7.4, 5.6 Hz, 1H), 1.37-1.15 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 173.3 (C), 149.6 (C), 133.6 (C), 132.9 (CH), 129.8 (CH), 127.9 (CH), 124.5 (CH), 52.2 (CH₃), 45.9 (CH), 32.8 (CH₂), 29.8 (CH₂), 22.4 (CH₂), 13.8 (CH₃) **IR** (film, cm⁻¹) 2956, 2869, 1739, 1527, 1353, 1222, 1169, 851, 779, 735 **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₃H₁₇NNaO₄ 274.1050; Found 274.1050

Synthesis of 2-(2-nitrophenyl)hexanoic acid (S15)



To a solution of methyl 2-(2-nitrophenyl)hexanoate (S14, 223 mg, 0.887 mmol) and water (33 μ L, 1.8 mmol) in EtOH (1.77 mL, 0.501 M) was added potassium hydroxide (101 mg, 1.80 mmol) at room temperature. After stirring for 30 minutes, the mixture was quenched with hydrochloric acid (2 M) and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography (0-50% ethyl acetate-hexane) to give S15 (90.8 mg, 0.383 mmol, 43% yield, colorless oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.89 (dd, J = 7.8, 1.2 Hz, 1H), 7.60 (dt, J = 7.8, 1.2 Hz, 1H), 7.54 (dd, J = 7.8, 1.2 Hz, 1H), 7.43 (dt, J = 7.8, 1.2 Hz, 1H), 4.19 (t, J = 7.6 Hz, 1H), 2.22-2.13 (m, 1H), 1.90-1.81 (m, 1H), 1.38-1.19 (m, 4H), 0.88-0.85 (t, J = 7.2 Hz, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 178.8 (C), 149.5 (C), 133.1 (CH), 133.0 (C), 130.1 (CH), 128.2 (CH), 124.7 (CH), 46.2 (CH), 32.2 (CH₂), 29.7 (CH₂), 22.4 (CH₂), 13.8 (CH₃) **IR** (film, cm⁻¹) 3076, 2959, 2933, 2870, 1710, 1528, 1413, 1352, 1289, 734 **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₂H₁₅NNaO₄ 260.0893; Found 260.0893

Synthesis of 1-nitro-2-pentylbenzene (23)



To a solution of 2-(2-nitrophenyl)hexanoic acid (S15, 64.4 mg, 0.271 mmol) in N,N-dimethylformamide (2.7 mL, 0.10 M) was added potassium carbonate (40.5 mg, 0.293 mmol) at 50 °C. After stirring for 30 minutes, the mixture was quenched with aqueous ammonium chloride and extracted three times with ethyl acetate. The combined organic layer was washed with water and brine, and dried over sodium sulfate. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by flash silica gel column chromatography (0-10% ethyl acetate-hexane), gave 23 (32.0 mg, 0.166 mmol, 61% yield, colorless oil).

¹**H NMR** (CDCl₃, 400 MHz) δ 7.86 (dd, J = 7.8, 1.6 Hz, 1H), 7.50 (dt, J = 7.8, 1.6 Hz, 1H), 7.34 (dd, J = 7.8, 1.6 Hz, 1H), 7.32 (dt, J = 7.8, 1.6 Hz, 1H), 2.89-2.85 (m, 2H), 1.67-1.60 (m, 2H), 1.40-1.30 (m, 4H), 0.92-0.88 (m, 3H) ¹³**C NMR** (CDCl₃, 100 MHz) δ 149.4 (C), 137.7 (C), 132.7 (CH), 131.8 (CH), 126.7 (CH), 124.5 (CH), 32.9 (CH₂), 31.7 (CH₂), 30.4 (CH₂), 22.4 (CH₂), 13.9 (CH₃) **IR** (film, cm⁻¹) 2957, 2930, 2863, 1609, 1526, 1462, 1349, 855, 785, 741

IK (IIIII, CIII) 2357, 2350, 2005, 1009, 1520, 1402, 1549, 855, 765, 741

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{15}NNaO_2$ 216.0995; Found 216.0995

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Procedure for calculations. The geometries of the transition state were optimized using B3LYP and the 6-31+G(d) basis set with Spartan '16. The vibrational frequencies were calculated at the same level of theory. Intrinsic reaction coordinate (IRC) calculations from the transition state were performed at the same level of theory, and the resulting geometries were optimized.





structure	Gibbs free energy at 195.15 K (hartree)	Number of imaginary frequency
Α	-783.564179	0
TS _{A-B}	-783.536240	1
В	-783.542154	0
TS _{B−C}	-783.537103	1
С	-783.567086	0
D	-667.917777	0
E	-667.921895	0
TS _{A-B'}	-783.564695	1
B'	-783.556937	0
methanol	-115.687626	0

Cartesia	an coordinates			0	-1.083982	-1.924385	0.547390
Α				С	-0.117332	-3.784575	-2.529529
Н	1.813087	1.778315	-0.789647	Н	-1.103361	-3.491641	-2.917150
С	1.141792	2.115739	-0.009016	Н	-0.191600	-4.782214	-2.077477
С	-0.582063	2.995549	2.016568	Н	0.592928	-3.826763	-3.359962
С	0.133533	1.250505	0.433320	Н	0.956140	-1.140282	-1.655905
С	1.281353	3.390799	0.543720	0	0.384145	-2.835674	-1.592554
С	0.418902	3.838413	1.555879	н	-0.209174	-2.772014	-0.803681
C	-0.721674	1.712384	1.460212				
H	2 071963	4 043475	0 181606	В			
н	0 538913	4 832069	1 978915	н	2 059693	2 448516	-0 769827
н	-1 263323	3 2032005	2 807370	C	1 318736	2.440310	0.023818
C C	-0.061/06	-0 111208	-0.222728	C	-0 672346	2.470352	2 0667/1
C C	1 244071	-0.111298	-0.232720	C	-0.072340	2.336060	0.112055
	-1.544971	-0.100400	-1.079515	C	0.540451	1.451209	0.112955
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С	0.900287	-1.250187	1.952735	С	-1.253949	0.181320	-1.466253
Н	1.820654	-0.713726	1.699653	Н	-1.216266	0.592345	-2.486374
Н	1.132683	-2.265386	2.282949	Н	-2.049435	0.684684	-0.916837
Н	0.418451	-0.716499	2.779674	Н	-1.504364	-0.882349	-1.537051
0	-0.635582	-2.340204	0.485247	С	-0.463990	-1.002667	1.102760
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Н	-1.007738	-3.109366	-3.425490	0	-2.393906	0.159868	1.821648
Н	-0.082878	-4.610442	-3.110581	0	1.150274	-0.153501	-1.438794
Н	0.663646	-3.277409	-4.025568	С	0.968050	-1.115688	1.602558
н	0.949346	-1.176179	-1.561377	Н	1.588355	-1.607481	0.847550
0	0.545425	-2.938022	-2.024298	Н	0.934135	-1.765732	2.486030
н	-0.028287	-3.117594	-1.255707	н	1.422759	-0.166649	1.884463
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TSAR				C	-0.102460	-3.784606	-2.484375
Н	1 908288	2 471170	-0 863342	н	-1 165886	-3 699535	-2 743882
C	1 210629	2 500435	-0.032230	н	0.078668	-4 757684	-2 011494
C C	-0 647751	2.500455	2 13/168	н	0.070000	-3 718753	-3 307110
C C	0.216201	1 /20705	0 179666	н Ц	0.494820	-1.012071	-1 850824
C C	1 1 2 2 1 6 5	2 612659	0.179000	0	0.003013	-1.013571	1 621770
C C	1.125105	2.012030	1.800021	0	0.515127	-2.717057	-1.051//9
C C	0.100215	5.070280	1.000557	п	-0.190718	-2.755045	-0.787902
	-0.521921	1.409071	1.309114	тс			
н	1.768301	4.468316	0.618682	IS _{B-C}	4 702 474	2 660 402	4 4 2 2 4 6 7
н	0.142129	4.560459	2.481653	H	1.792471	2.668492	-1.123167
Н	-1.340700	2.596471	2.969198	С	1.161196	2.5/356/	-0.243518
С	0.078250	0.233991	-0.620424	С	-0.496028	2.329742	2.035100
С	-1.193048	0.201800	-1.456584	С	0.361055	1.440481	-0.064204
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c c	0.207426	2.704324	2 102690	с Ц	1 565101	2 22012	1 609022
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ĉ	-0 300332	2 879691	-0 467407	н	1 657172	3 642162	2 061062
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ц	-2 456827	-2.026501	1 220880
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U U	2 260056	-0.062644	-2.229420
п С	070220 2 01000	-2.030321 1.026164	0.245018
с u	2.340002		-0.4103/0
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п О	3.100485	-0.8/3593	0.085/94
0	1.579414	-2.0155/5	-0.785987
н	0.992141	-2.003105	0.01/024
Н	0.762845	-1.134992	-1./39411



¹H NMR (400 MHz, CDCl₃)







S1 (keto:enol = 3:4)

¹H NMR (400 MHz, CDCl₃)





¹³C NMR (100 MHz, CDCl₃)

S1 (keto:enol = 3:4)



X : parts per Million : Carbon13
































210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 X : parts per Million : Carbon13











































X : parts per Million : Carbon13


























S73

























X : parts per Million : Carbon13























S92















X : parts per Million : Carbon13





S101






















¹³C NMR (100 MHz, CDCl₃)

