

Supplementary Information

Metal-free visible-light-induced aerobic oxidation of α -diazoesters leading to α -ketoesters in air

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1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Energy Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz ^1H , 125 MHz ^{13}C /400 MHz ^1H , 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). We use RLH-18 8-position Photo Reaction System, which manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This Photo reactor has equipped 8 blue light 3W LED,

other LEDs could be selected and replaced each position. This blue light 3W LED's energy peak wavelength is 452.6nm, peak width at half-height is 19.8nm. Irradiation vessel is borosilicate glass test tube, LED irradiate through a high-reflection channel to the test tube, path length is 2cm. No filter between LED and test tube. α -Diazoesters were prepared according to the literature.¹

产品标识

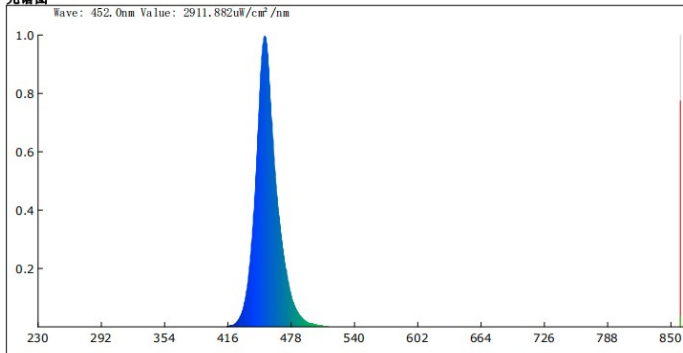
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 环境温度: 23°C
 测试员: WU

制造厂商: 诺植科技
 环境湿度: 20%
 测试日期: 2021-01-25,09:59:25

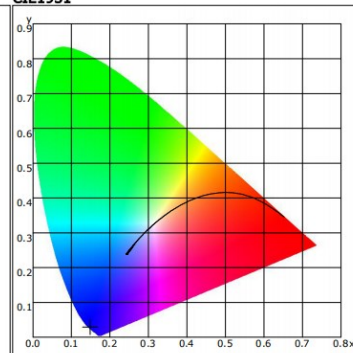
参数列表

参数名称	参数值	参数名称	参数值	参数名称	参数值
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UVC辐照度mW/cm ²	0.0000	坐标u',v'	0.1952,0.0850	CIE1931 Z	1122548.375
UVB辐照度mW/cm ²	0.0000	色容差	100.00	TLCI-2012	0
UVA辐照度mW/cm ²	0.0000	显色指数Ra	-70.0	积分时间(ms)	0.2
Euv辐照度mW/cm ²	0.00	辐照度Ee(mW/cm ²)	69.70213	峰值信号	50817
Eb蓝光辐照度mW/cm ²	69.49	明暗视觉比S/P	22.771	暗信号	2354
Eg绿光辐照度mW/cm ²	0.21	主波长(nm)	457.80	补偿电平	2892
Er红光辐照度mW/cm ²	0.00	色纯度(%)	99.2		
Eir红外辐照度mW/cm ²	0.00	半宽度(nm)	19.8		
照度E(lx)	26832.26	峰值波长(nm)	452.6		
烛光E(fc)	2492.78	中心波长(nm)	453.8		
相关色温(K)	100000	质心波长(nm)	455.6		
黑体偏离Duv	-0.06598	光通量色比(RGB)	0.0,5.6,94.4		
坐标x,y	0.1487,0.0288	CIE1931 X	203008.422		

光谱图



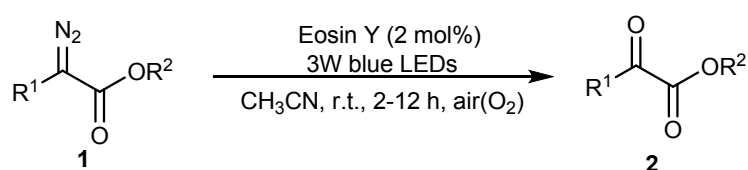
CIE1931





Picture of reaction setup

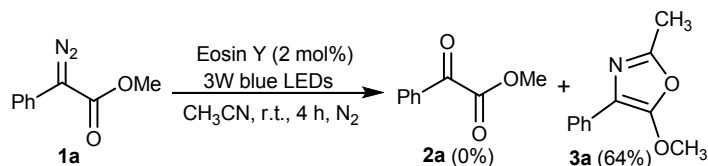
2. The general procedure for visible-light-induced aerobic oxidation of α -diazoesters leading to α -ketoesters in air



To a mixture of α -diazoesters **1** (0.2 mmol) and Eosin Y (2 mol%) was added CH_3CN (2 mL). The reaction mixture was open to air and stirred under the irradiation of 3W blue LEDs at room temperature for 2-12 h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2**.

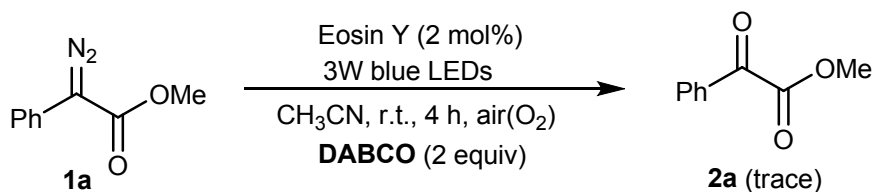
3. Preliminary mechanistic studies

3.1 The model reaction was conducted under nitrogen



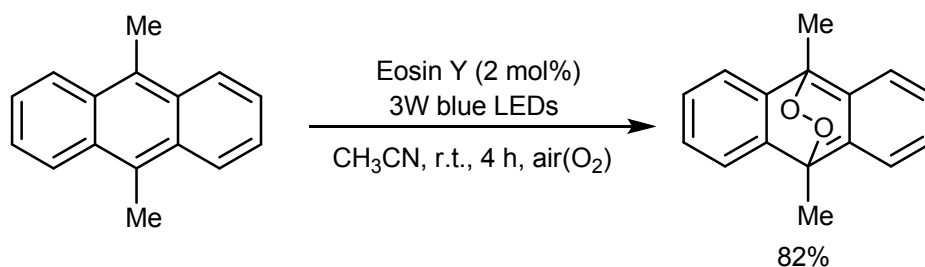
To a mixture of α -diazoester **1a** (0.2 mmol, 35.2 mg), Eosin Y (2 mol%) and DABCO (0.4 mmol, 44.8 mg) was added CH_3CN (2 mL) under N_2 . The reaction was stirred under the irradiation of 3W blue LEDs at room temperature. When the reaction was conducted for 4h, the reaction was stopped, oxazole **3a** was isolated in 64% yield and none of the desired product **2a** was detected.

3.2 The addition of DABCO in the model reaction system.



To a mixture of α -diazoester **1a** (0.2 mmol, 35.2 mg), Eosin Y (2mol%) and DABCO (0.4 mmol, 44.8 mg) was added CH_3CN (2 mL). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature. After completion of the reaction, the organic solution was concentrated in vacuum. None of the desired product **2a** was detected, which indicated that this transformation should involve $^1\text{O}_2$ -mediated process.

3.3 The trapping experiments of $^1\text{O}_2$

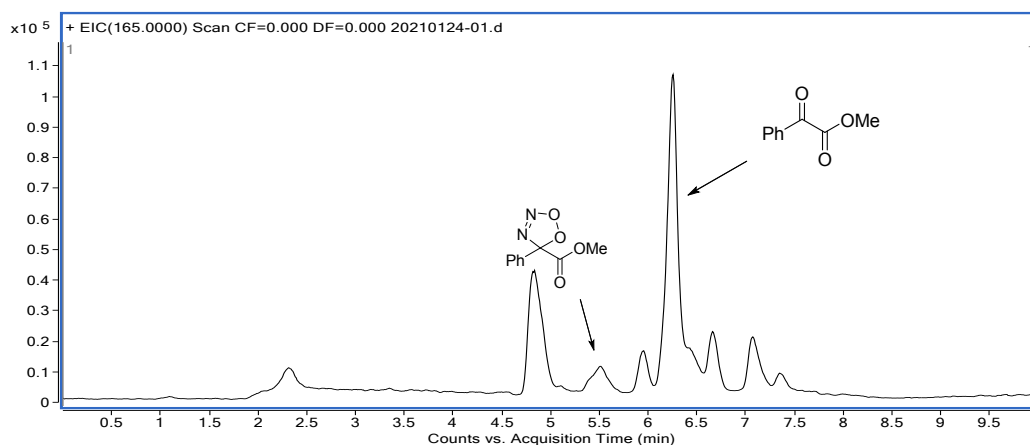


To a mixture of 9,10-dimethylanthracene (0.2 mmol, 41.2mg) and Eosin Y

(2mol%, 2.6mg) was added CH₃CN (2 mL). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired endoperoxide product in 82% yield.

3.3 The LC-MS analysis

To a mixture of α -diazoester **1a** (0.2 mmol, 35.2 mg) and Eosin Y (2mol%) was added CH₃CN (2 mL). The reaction mixture was open to the air and stirred under the irradiation of 3W blue LEDs at room temperature. When the reaction was conducted at 1h, the reaction mixture was detected by LC-MS analysis. As shown in Figure S1, in addition to the desired product **2a**, the key intermediate **A** was also detected.



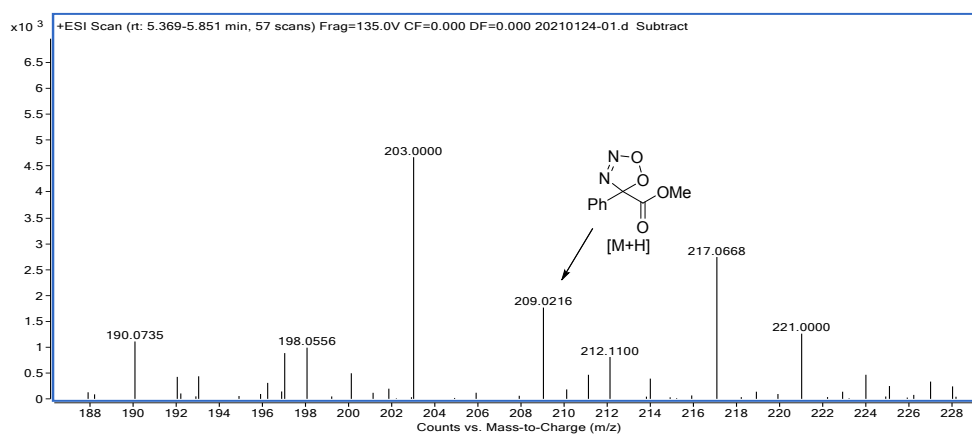
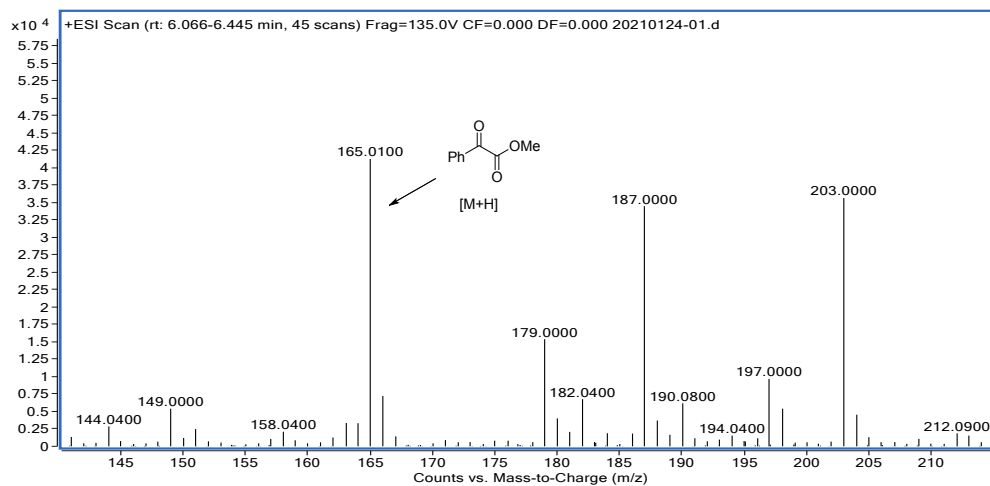
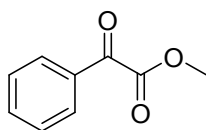
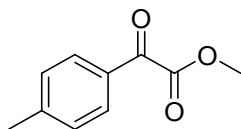


Figure S1.

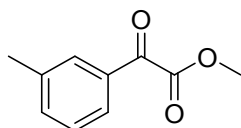
4. Characterization data of products 2a-2x, oxazole 3a, endoperoxide product,



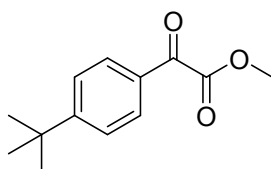
Methyl 2-oxo-2-phenylacetate^[1], Compound **2a** was obtained in 82% yield (26.9mg) according to the general procedure (4h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 8.03 - 8.01 (m, 2H), 7.68 - 7.64 (m, 1H), 7.53 - 7.50 (m, 2H), 3.98 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 186.1, 164.1, 135.0, 132.4, 130.1, 128.9, 52.8. ESI HRMS: calculated for C₉H₉O₃ [M+H]⁺: 165.0552; found 165.0526.



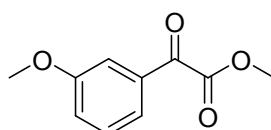
Methyl 2-oxo-2-(p-tolyl)acetate^[3], Compound **2b** was obtained in 74% yield (26.4mg) according to the general procedure (7h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 3H), 2.44 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 185.7, 164.3, 146.4, 130.2, 130.0, 129.7, 52.7, 21.9. ESI HRMS: calculated for C₁₀H₁₁O₃ [M+H]⁺: 179.0708; found 179.0700.



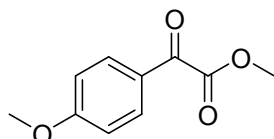
Methyl 2-oxo-2-(m-tolyl)acetate^[3], Compound **2c** was obtained in 71% yield (25.2mg) according to the general procedure (10h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.81 (s, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 3.98 (s, 3H), 2.42 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 186.3, 164.2, 138.9, 135.9, 132.4, 130.4, 128.8, 127.4, 52.7, 21.3. ESI HRMS: calculated for C₁₀H₁₁O₃ [M+H]⁺: 179.0708; found 179.0701.



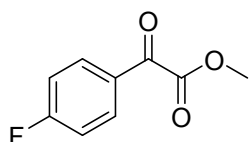
Methyl 2-(4-(tert-butyl)phenyl)-2-oxoacetate^[1], Compound **2d** was obtained in 67% yield (29.3mg) according to the general procedure (11h). Brown oil. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 8.52 Hz, 2H), 7.53 (d, *J* = 8.52 Hz, 2H), 3.97 (s, 3H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 185.7, 164.3, 159.2, 130.1, 129.9, 126.0, 52.7, 35.4, 31.0. ESI HRMS: calculated for C₁₃H₁₇O₃ [M+H]⁺: 221.1178; found 221.1175.



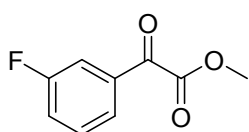
Methyl 2-(3-methoxyphenyl)-2-oxoacetate^[4], Compound **2e** was obtained in 67% yield (28.2mg) according to the general procedure(2h). Brown oil. ¹H NMR (500 MHz, CDCl₃): δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.42(t, *J* = 8.0 Hz, 1H), 7.22-7.20 (m, 1H), 3.98 (s, 3H), 3.86 (s, 3H); ¹³C NMR (125 MHz,CDCl₃): δ 186.0, 164.1, 160.0, 133.6, 129.9, 123.2, 121.9, 113.3, 55.5, 52.8. ESI HRMS: calculated for C₁₀H₁₁O₄ [M+H]⁺: 195.0657; found 195.0650.



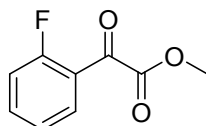
Methyl 2-(4-methoxyphenyl)-2-oxoacetate^[1], Compound **2f** was obtained in 55% yield (21.3mg) according to the general procedure(4h). White solid. 47 - 48°C. ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 9.3 Hz, 2H), 3.96 (s, 3H), 3.90 (s, 3H); ¹³C NMR (125 MHz,CDCl₃): δ 184.5, 165.1, 164.4, 132.7, 125.5, 114.3, 55.7,52.7. ESI HRMS: calculated for C₁₀H₁₁O₄ [M+H]⁺: 195.0657; found 195.0645.



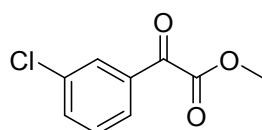
Methyl 2-(4-fluorophenyl)-2-oxoacetate^[1], Compound **2g** was obtained in 60% yield (21.6mg) according to the general procedure(4h). White solid. 54 - 55°C. ¹H NMR (500 MHz, CDCl₃): δ 8.11 - 8.08 (m, 2H), 7.19 (t, *J* = 8.6 Hz, 2H), 3.98 (s, 3H); ¹³C NMR (125 MHz,CDCl₃): δ 184.1,166.9(d, *J* = 256.9 Hz), 163.6, 133.1(d, *J* = 9.8 Hz), 129.0(d, *J* = 2.9 Hz), 116.3(d, *J* = 22.1Hz), 52.9. ESI HRMS: calculated for C₉H₈FO₃ [M+H]⁺: 183.0457, found 183.0443.



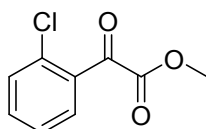
Methyl 2-(3-fluorophenyl)-2-oxoacetate^[2], Compound **2h** was obtained in 66% yield (24.5mg) according to the general procedure(4h). Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 7.76 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.47 -7.41 (m, 1H), 7.33 – 7.28 (m, 1H) 3.93 (s, 3H); ¹³C NMR (100 MHz,CDCl₃): δ 184.5, 163.3, 162.7 (d, *J* = 247.65 Hz), 134.4 (d, *J* = 6.66 Hz), 130.7 (d, *J* = 7.59 Hz), 126.1 (d, *J* = 3.11 Hz), 122.2 (d, *J* = 21.36 Hz), 116.6 (d, *J* = 22.86 Hz), 53.0. ESI HRMS: calculated for C₉H₈FO₃ [M+H]⁺: 183.0457, found 183.0435.



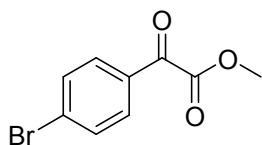
Methyl 2-(2-fluorophenyl)-2-oxoacetate^[2], Compound **2i** was obtained in 83% yield (30.3mg) according to the general procedure(4h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.94 – 7.91 (m, 1H), 7.67-7.63 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.15 (m, 1H), 3.97 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 183.8, 164.4, 162.7 (d, *J* = 256.4 Hz), 136.8 (d, *J* = 9.22 Hz), 130.9 (d, *J* = 1.22 Hz), 124.9 (d, *J* = 3.46 Hz), 121.7 (d, *J* = 10.3 Hz), 116.6 (d, *J* = 21.4 Hz), 53.0. ESI HRMS: calculated for C₉H₈FO₃ [M+H]⁺: 183.0457, found 183.04385.



Methyl 2-(3-chlorophenyl)-2-oxoacetate^[3], Compound **2j** was obtained in 77% yield (30.5mg) according to the general procedure(4h). White solid. 44 - 45°C. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (t, *J* = 1.88 Hz, 1H), 7.92 (d, *J* = 7.80 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.46 (t, *J* = 7.92 Hz, 1H), 3.98 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 184.5, 163.2, 135.3, 134.9, 134.0, 130.3, 129.9, 128.3, 53.1. ESI HRMS: calculated for C₉H₈ClO₃ [M+H]⁺: 199.0162; found 199.0148.

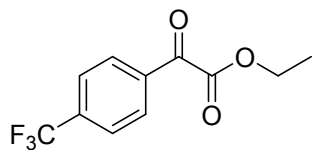


Methyl 2-(2-chlorophenyl)-2-oxoacetate^[5], Compound **2k** was obtained in 77% yield (30.5mg) according to the general procedure(4h). Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.78 – 7.75 (m, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.39 (m, 2H), 3.96 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 186.3, 163.5, 134.4, 134.0, 133.3, 131.6, 130.6, 127.3, 53.3. ESI HRMS: calculated for C₉H₈ClO₃ [M+H]⁺: 199.0162; found 199.0148.

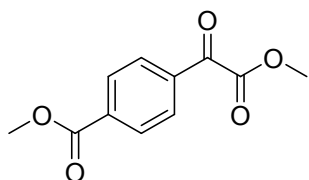


Methyl 2-(4-bromophenyl)-2-oxoacetate^[1], Compound **2l** was obtained in 72% yield (33.0mg) according to the general procedure(4h). White solid. 55 - 56°C. ¹H NMR (500 MHz, CDCl₃): δ 7.91 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 3.98 (s,

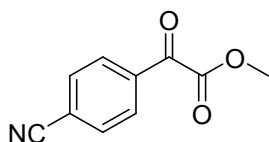
3H); ^{13}C NMR (125 MHz, CDCl_3): δ 184.7, 163.4, 132.3, 131.5, 131.3, 130.7, 53.0. ESI HRMS: calculated for $\text{C}_9\text{H}_8\text{BrO}_3$ $[\text{M}+\text{H}]^+$: 242.9657, found 242.9648.



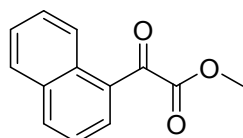
Ethyl 2-oxo-2-(4-(trifluoromethyl)phenyl)acetate^[4], Compound **2m** was obtained in 76% yield (35.1mg) according to the general procedure(6h). Yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 8.17 (d, J = 8.00 Hz, 2H), 7.8 (d, J = 8.25 Hz, 2H), 4.50 – 4.46 (m, 2H), 1.44 (t, J = 7.15 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 185.0, 162.8, 135.9 (q, J = 26.18 Hz), 135.28, 130.4, 125.9 (q, J = 2.93 Hz), 123.3 (d, J = 271.26 Hz), 62.8, 14.1. ESI HRMS: calculated for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 247.0582, found 247.0579.



Methyl 4-(2-methoxy-2-oxoacetyl)benzoate^[5], Compound **2n** was obtained in 61% yield (26.9mg) according to the general procedure(6h). White solid. 99 - 100°C. ^1H NMR (500 MHz, CDCl_3): δ 8.16 (d, J = 8.5 Hz, 2H), 8.1 (d, J = 8.6 Hz, 2H), 4.00 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 185.2, 165.9, 163.3, 135.6, 135.4, 130.0, 129.9, 53.0, 52.6. ESI HRMS: calculated for $\text{C}_{11}\text{H}_{11}\text{O}_5$ $[\text{M}+\text{H}]^+$: 223.0606; found 223.0594.

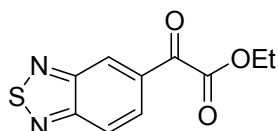


Methyl 2-(4-cyanophenyl)-2-oxoacetate^[7], Compound **2o** was obtained in 54% yield (20.7mg) according to the general procedure(4h). White solid. 42 - 43°C. ^1H NMR (400 MHz, CDCl_3): δ 8.17 (d, J = 8.52 Hz, 2H), 7.82 (d, J = 8.52 Hz, 2H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 184.0, 162.6, 135.5, 132.6, 130.5, 118.0, 117.6, 53.3. ESI HRMS: calculated for $\text{C}_{10}\text{H}_8\text{NO}_3$ $[\text{M}+\text{H}]^+$: 190.0504, found 190.0512.

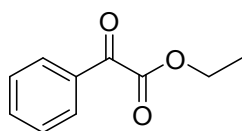


Methyl 2-(naphthalen-1-yl)-2-oxoacetate^[1], Compound **2qp** was obtained in 70% yield (29.8mg) according to the general procedure (4h). Yellow solid. 73 -74°C. ^1H

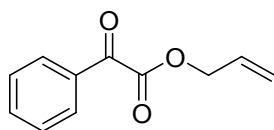
NMR (500 MHz, CDCl₃): δ 9.02 (d, J = 8.7 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 7.3 Hz, 1H), 7.90 (d, J = 8.1, 1H), 7.70 - 7.66 (m, 1H), 7.58 (t, J = 7.5 Hz, 1H), 4.00 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 188.5, 164.9, 135.9, 134.1, 133.9, 131.0, 129.3, 128.8, 128.2, 127.1, 125.6, 124.3, 52.9. ESI HRMS: calculated for C₁₃H₁₀O₃ [M+H]⁺: 215.0708; found 215.0721.



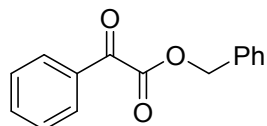
Ethyl 2-(benzo[c][1,2,5]thiadiazol-5-yl)-2-oxoacetate, Compound **2q** was obtained in 42% yield (21.2mg) according to the general procedure (2 h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 8.77 (d, J = 0.65 Hz, 1H), 8.23 - 8.21 (m, 1H), 8.12 (d, J = 9.2 Hz, 1H), 4.55 - 4.51 (m, 2H), 1.48 (t, J = 7.15 Hz, 3H); ¹³C NMR (125MHz, CDCl₃): δ 185.5, 162.9, 157.0, 154.1, 133.0, 127.4, 126.8, 122.5, 62.9, 14.1. ESI HRMS: calculated for C₁₀H₈N₂O₃S [M+H]⁺: 237.0334; found 237.0321.



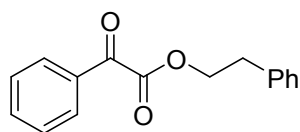
Ethyl 2-oxo-2-phenylacetate^[1], Compound **2r** was obtained in 63% yield (22.4mg) according to the general procedure(4h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 8.02 - 8.00 (m, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 4.48 - 4.44 (m, 2H), 1.43 (t, J = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 186.4, 163.9, 134.9, 132.5, 130.0, 128.9, 62.4, 14.1. ESI HRMS: calculated for C₁₀H₁₀O₃ [M+H]⁺: 179.0708; found 179.0686.



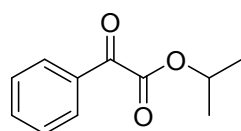
Allyl 2-oxo-2-phenylacetate^[1], Compound **2s** was obtained in 63% yield (24.0mg) according to the general procedure(6h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, J = 9.0 Hz, 2H), 7.66 (t, J = 7.45 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 6.06 - 5.99 (m, 1H), 5.47 - 5.43 (m, 1H), 5.37 - 5.34 (m, 1H), 4.88 (d, J = 6.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 186.1, 163.5, 135.0, 132.4, 130.8, 130.1, 128.9, 120.1, 66.6. ESI HRMS: calculated for C₁₁H₁₀O₃ [M+H]⁺: 191.0708; found 191.0702.



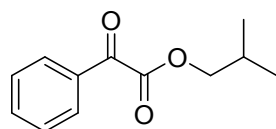
Benzyl 2-oxo-2-phenylacetate^[1], Compound **2t** was obtained in 56% yield (26.9mg) according to the general procedure(4h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.45 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.41 – 7.36 (m, 3H), 5.42 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 186.1, 163.7, 135.0, 134.6, 132.4, 130.1, 128.9, 128.9, 128.8, 128.6, 67.8. ESI HRMS: calculated for C₁₅H₁₃O₃ [M+H]⁺: 241.0865, found 241.0867.



Phenethyl 2-oxo-2-phenylacetate^[3], Compound **2u** was obtained in 80% yield (40.8mg) according to the general procedure(8h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.86 – 7.85 (m, 2H), 7.63 (t, *J* = 7.45 Hz, 1H), 7.45 (t, *J* = 7.90 Hz 2H), 7.33 - 7.30 (m, 2H), 7.27 – 7.25 (m, 3H), 4.62 (t, *J* = 7.00 Hz, 2H), 3.09 (t, *J* = 7.00 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 186.3, 163.7, 137.0, 134.9, 132.4, 130.1, 129.0, 128.9, 128.7, 126.9, 66.4, 35.0. ESI HRMS: calculated for C₁₆H₁₄O₃ [M+H]⁺: 255.1021; found 255.0998.

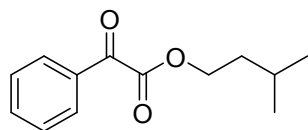


Isopropyl 2-oxo-2-phenylacetate^[6], Compound **2v** was obtained in 63% yield (22.4mg) according to the general procedure(4h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.4Hz, 1H), 7.51(t, *J* = 7.8Hz, 2H), 5.37 – 5.29 (m, 1H), 1.42 (s, 3H), 1.41 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 186.7, 163.6, 134.8, 132.6, 130.0, 128.9, 70.7, 21.7. ESI HRMS: calculated for C₁₁H₁₂O₃ [M+H]⁺ : 193.0865; found 193.0858.

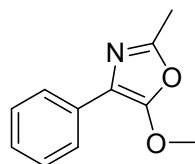


Methyl 2-(4-fluorophenyl)-2-oxoacetate^[3], Compound **2w** was obtained in 75% yield (28.8mg) according to the general procedure(4h). Yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 8.01 - 7.99 (m, 2H), 7.67 (t, *J* = 7.45 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H),

4.18 (d, $J = 6.7$ Hz, 2H), 2.38 (s, 3H), 2.13 - 2.05 (m, 1H), 1.01(s, 3H), 1.00(s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 186.6, 164.1, 134.9, 132.5, 130.0, 128.9, 72.1, 27.8, 19.0. ESI HRMS: calculated for $\text{C}_{12}\text{H}_{14}\text{O}_3$ $[\text{M}+\text{Na}]^+$: 229.0841; found 229.0830.

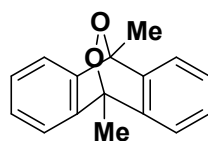


Isopentyl 2-oxo-2-phenylacetate^[6], Compound **2x** was obtained in 71% yield (31.3mg) according to the general procedure(7h). Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 8.00 (d, $J = 7.2$ Hz, 2H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.52 (t, $J = 7.9$ Hz, 2H), 4.42 (t, $J = 6.9$ Hz, 2H), 1.79 – 1.72 (m, 1H), 1.70 – 1.65 (m, 2H), 0.96 (d, $J = 6.485$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 186.5, 164.0, 134.9, 132.5, 130.0, 128.9, 65.0, 37.1, 25.0, 22.4. ESI HRMS: calculated for $\text{C}_{13}\text{H}_{16}\text{O}_3$ $[\text{M}+\text{H}]^+$: 221.1178; found 221.1174.



5-methoxy-2-methyl-4-phenyloxazole^[8]

Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 4.02 (s, 3H) 2.1341 (s, 3H), ^{13}C NMR (100MHz, CDCl_3): δ 154.3, 151.9, 131.4, 128.5, 126.3, 124.8, 114.5, 60.1, 14.3. Ms $[\text{M}+\text{H}]$ 190.1.



(9s,10s)-9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene,^[9] White solid. ^1H NMR (500 MHz, CDCl_3): δ 7.39 – 7.35 (m, 4H), 7.27 – 7.24 (m, 4H), 2.13 (s, 6H), ^{13}C NMR (125 MHz, CDCl_3): δ 186.3, 163.7, 137.0, 134.9, 132.4, 130.1, 129.0, 128.9, 128.7, 126.9, 66.4, 35.0. Ms $[\text{M}+\text{H}]$ 239.1.

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6. Copies of NMR spectra for 2a-2x, 3a, endoperoxide product

