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. $^1$H NMR and $^{13}$C NMR were recorded in CDCl$_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz $^1$H, 125 MHz $^{13}$C/400 MHz $^1$H, 100 MHz $^{13}$C) at room temperature, the chemical shifts ($\delta$) 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.\(^1\)
2. The general procedure for visible-light-induced aerobic oxidation of α-diazoesters leading to α-ketoesters in air

![Picture of reaction setup](image.png)

To a mixture of α-diazoesters 1 (0.2 mmol) and Eosin Y (2 mol%) was added CH₃CN (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$_3$CN (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 (2 mol%) and DABCO (0.4 mmol, 44.8 mg) was added CH$_3$CN (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 $^1$O$_2$-mediated process.

3.3 The trapping experiments of $^1$O$_2$

To a mixture of 9,10-dimethylanthracene (0.2 mmol, 41.2 mg) 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.
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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.03 - 8.01 (m, 2H), 7.68 - 7.64 (m, 1H), 7.53 - 7.50 (m, 2H), 3.98 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 186.1, 164.1, 135.0, 132.4, 130.1, 128.9, 52.8. ESI HRMS: calculated for C$_9$H$_9$O$_3$ [M+H]$^+$: 165.0552; found 165.0526.

![Methyl 2-oxo-2-phenylacetate](image)

**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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 3.97 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 185.7, 164.3, 146.4, 130.2, 130.0, 129.7, 52.7, 21.9. ESI HRMS: calculated for C$_{10}$H$_{11}$O$_3$ [M+H]$^+$: 179.0708; found 179.0700.

![Methyl 2-oxo-2-(p-tolyl)acetate](image)

**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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 186.3, 164.2, 138.9, 135.9, 132.4, 130.4, 128.8, 127.4, 52.7, 21.3. ESI HRMS: calculated for C$_{10}$H$_{11}$O$_3$ [M+H]$^+$: 179.0708; found 179.0701.

![Methyl 2-oxo-2-(m-tolyl)acetate](image)

**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. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95 (d, $J = 8.52$ Hz, 2H), 7.53 (d, $J = 8.52$ Hz, 2H), 3.97 (s, 3H), 1.35 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 185.7, 164.3, 159.2, 130.1, 129.9, 126.0, 52.7, 35.4, 31.0. ESI HRMS: calculated for C$_{13}$H$_{17}$O$_3$ [M+H]$^+$: 221.1178; found 221.1175.

![Methyl 2-(4-(tert-butyl)phenyl)-2-oxoacetate](image)
Methyl 2-(3-methoxyphenyl)-2-oxoacetate\[^{[4]}\], Compound \(\text{2e}\) was obtained in 67% yield (28.2mg) according to the general procedure(2h). Brown oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 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); \(^{13}\)C NMR (125 MHz,CDCl\(_3\)): \(\delta\) 186.0, 164.1, 160.0, 133.6, 129.9, 123.2, 121.9, 113.3, 55.5, 52.8. ESI HRMS: calculated for C\(_{10}\)H\(_{11}\)O\(_4\) [M+H]\(^+\): 195.0657; found 195.0650.

[Image of methyl 2-(3-methoxyphenyl)-2-oxoacetate]

Methyl 2-(4-methoxyphenyl)-2-oxoacetate\[^{[1]}\], Compound \(\text{2f}\) was obtained in 55% yield (21.3mg) according to the general procedure(4h). White solid. 47 - 48°C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.01 (d, \(J = 9.0\) Hz, 2H), 6.98 (d, \(J = 9.3\) Hz, 2H), 3.96 (s, 3H), 3.90 (s, 3H); \(^{13}\)C NMR (125 MHz,CDCl\(_3\)): \(\delta\) 184.5, 165.1, 164.4, 132.7, 125.5, 114.3, 55.7,52.7. ESI HRMS: calculated for C\(_{10}\)H\(_{11}\)O\(_4\) [M+H]\(^+\): 195.0657; found 195.0645.

[Image of methyl 2-(4-methoxyphenyl)-2-oxoacetate]

Methyl 2-(4-fluorophenyl)-2-oxoacetate\[^{[1]}\], Compound \(\text{2g}\) was obtained in 60% yield (21.6mg) according to the general procedure(4h). White solid. 54 - 55°C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.11 - 8.08 (m, 2H), 7.19 (t, \(J = 8.6\) Hz, 2H), 3.98 (s, 3H); \(^{13}\)C NMR (125 MHz,CDCl\(_3\)): \(\delta\) 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, \(J = 22.1\)Hz ), 52.9. ESI HRMS: calculated for C\(_9\)H\(_8\)FO\(_3\) [M+H]\(^+\): 183.0457, found 183.0443.

[Image of methyl 2-(4-fluorophenyl)-2-oxoacetate]

Methyl 2-(3-fluorophenyl)-2-oxoacetate\[^{[2]}\], Compound \(\text{2h}\) was obtained in 66% yield (24.5mg) according to the general procedure(4h). Yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 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); \(^{13}\)C NMR (100 MHz,CDCl\(_3\)): \(\delta\) 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 C\(_9\)H\(_8\)FO\(_3\) [M+H]\(^+\): 183.0457, found 183.0435.
Methyl 2-(2-fluorophenyl)-2-oxoacetate$^{[2]}$, Compound 2i was obtained in 83% yield (30.3 mg) according to the general procedure (4h). Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 183.8, 164.4, 162.7 (d, $J$ = 256.4 Hz), 136.8 (d, $J$ = 9.2 Hz), 130.9 (d, $J$ = 1.2 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 C$_9$H$_8$FO$_3$ [M+H]$^+$: 183.0457, found 183.04385.

Methyl 2-(3-chlorophenyl)-2-oxoacetate$^{[3]}$, Compound 2j was obtained in 77% yield (30.5 mg) according to the general procedure (4h). White solid. 44 - 45 $^\circ$C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 (t, $J$ = 1.88 Hz, 1H), 7.92 (d, $J$ = 7.8 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.46 (t, $J$ = 7.92 Hz, 1H), 3.98 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 184.5, 163.2, 135.3, 134.9, 134.0, 130.3, 129.9, 128.3, 53.1. ESI HRMS: calculated for C$_9$H$_8$ClO$_3$ [M+H]$^+$: 199.0162; found 199.0148.

Methyl 2-(2-chlorophenyl)-2-oxoacetate$^{[5]}$, Compound 2k was obtained in 77% yield (30.5 mg) according to the general procedure (4h). Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.78 – 7.75 (m, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.39 (m, 2H), 3.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 186.3, 163.5, 134.4, 134.0, 133.3, 131.6, 130.6, 127.3, 53.3. ESI HRMS: calculated for C$_9$H$_8$ClO$_3$ [M+H]$^+$: 199.0162; found 199.0148.

Methyl 2-(4-bromophenyl)-2-oxoacetate$^{[1]}$, Compound 2l was obtained in 72% yield (33.0 mg) according to the general procedure (4h). White solid. 55 - 56 $^\circ$C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J$ = 8.7 Hz, 2H), 7.66 (d, $J$ = 8.7 Hz, 2H), 3.98 (s,
3H); $^1^3$C NMR (125 MHz,CDCl$_3$): $\delta$ 184.7, 163.4, 132.3, 131.5, 131.3, 130.7, 53.0. ESI HRMS: calculated for C$_9$H$_8$BrO$_3$ [M+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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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); $^1^3$C NMR (125 MHz,CDCl$_3$): $\delta$ 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 C$_{11}$H$_{10}$F$_3$O$_3$ [M+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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.16 (d, $J$ = 8.5 Hz, 2H), 8.1 (d, $J$ = 8.6 Hz, 2H), 4.00 (s, 3H), 3.97 (s, 3H); $^1^3$C NMR (125 MHz,CDCl$_3$): $\delta$ 185.2, 165.9, 163.3, 135.6, 135.4, 130.0, 129.9, 53.0, 52.6. ESI HRMS: calculated for C$_{11}$H$_{11}$O$_5$ [M+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. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.17 (d, $J$ = 8.52 Hz, 2H), 7.82 (d, $J$ = 8.52 Hz, 2H), 4.00 (s, 3H); $^1^3$C NMR (100 MHz,CDCl$_3$): $\delta$ 184.0, 162.6, 135.5, 132.6, 130.5, 118.0, 117.6, 53.3. ESI HRMS: calculated for C$_{10}$H$_8$NO$_3$ [M+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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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); $^1^3$C NMR (125 MHz,CDCl$_3$): $\delta$ 184.7, 163.4, 132.3, 131.5, 131.3, 130.7, 53.0. ESI HRMS: calculated for C$_{12}$H$_{10}$BrO$_3$ [M+H]$^+$: 242.9657, found 242.9648.

[^1]: Methyl 2-(naphthalen-1-yl)-2-oxoacetate
[^2]: Ethyl 2-oxo-2-(4-(trifluoromethyl)phenyl)acetate
[^3]: Methyl 4-(2-methoxy-2-oxoacetyl)benzoate
[^4]: Methyl 2-(4-cyanophenyl)-2-oxoacetate
[^5]: Methyl 2-(naphthalen-1-yl)-2-oxoacetate
NMR (500 MHz, CDCl\(_3\)): 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, CDCl\(_3\)): 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 C\(_{13}\)H\(_{10}\)O\(_3\) [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. \(^1\)H NMR (500 MHz, CDCl\(_3\)): 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 (125 MHz, CDCl\(_3\)): 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 C\(_{10}\)H\(_8\)N\(_2\)O\(_3\)S [M+H]\(^+\): 237.0334; found 237.0321.

**Ethyl 2-oxo-2-phenylacetate**, Compound 2r was obtained in 63% yield (22.4mg) according to the general procedure (4h). Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): 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, CDCl\(_3\)): δ 186.4, 163.9, 134.9, 132.5, 130.0, 128.9, 62.4, 14.1. ESI HRMS: calculated for C\(_{10}\)H\(_{10}\)O\(_3\) [M+H]\(^+\): 179.0708; found 179.0686.

**Allyl 2-oxo-2-phenylacetate**, Compound 2s was obtained in 63% yield (24.0mg) according to the general procedure (6h). Yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)): 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, CDCl\(_3\)): δ 186.1, 163.5, 135.0, 132.4, 130.8, 130.1, 128.9, 120.1, 66.6. ESI HRMS: calculated for C\(_{11}\)H\(_{10}\)O\(_3\) [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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 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 C$_{15}$H$_{13}$O$_3$ [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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 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 C$_{16}$H$_{14}$O$_3$ [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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.00 (d, $J = 7.2$ Hz, 2H), 7.66 (t, $J = 7.4$Hz, 1H), 7.51 (t, $J = 7.8$Hz, 2H), 5.37 – 5.29 (m, 1H), 1.42 (s, 3H), 1.41 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 186.7, 163.6, 134.8, 132.6, 130.0, 128.9, 70.7, 21.7. ESI HRMS: calculated for C$_{11}$H$_{12}$O$_3$ [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. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 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 C$_{12}$H$_{14}$O$_3$ [M+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. $^1$H 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 C$_{13}$H$_{16}$O$_3$ [M+H]$^+$: 221.1178; found 221.1174.

5-methoxy-2-methyl-4-phenyloxazole$[^{8}]$

Yellow oil. $^1$H 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 (100 MHz, CDCl$_3$): δ 154.3, 151.9, 131.4, 128.5, 126.3, 124.8, 114.5, 60.1, 14.3. Ms [M+H] 190.1.

(9s,10s)-9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene,$[^{9}]$ White solid. $^1$H 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 [M+H] 239.1.

5. References


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