Supporting Information

Selective C(sp3)-H bond Aerobic Oxidation Enabled by π -Conjugated Small Molecule-Oxygen Charge Transfer State

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1. General consideration

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. The NMR spectra were recorded on a Bruker Avance 400 or 600 spectrometer at 400 MHz or 600MHz in CDCl₃ using tetramethylsilane as the internal standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) in hertz (Hz). ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were acquired at various field strengths as indicated and were referenced to CHCl₃ (7.27 and 77.16 ppm for ¹H and ¹³C respectively). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet, ddd = doublet of doublet. High-resolution mass spectra were obtained using a Bruker Impact II UHR-QTOF mass spectrometer. Spectra were obtained using electron impact ionization (EI) and chemical ionization (CI) techniques, or positive electrospray (ES). UV-Vis absorption spectra were recorded on Mapada P6. Column chromatography was performed on silica gel (200-300 mesh). All mixed solvent eluents are reported as v/v solutions. The LEDs used are Kessil PR160L-370 nm Gen 2, Kessil PR160L-390 nm, Kessil PR160L-427 nm.



Figure S1 (Photographed by author Panyi Huang)



Figure S2 Spectral range of Kessil PR160L-370 nm Gen 2

2.General procedures of starting materials.



The π -conjugated compounds, which were used in the synthesis of products **3a-3aa**, **3ag-3am**, **3as-3aaa**, **4a-4i** were purchased from commercial sources and used without further purification. The ester and amide derivatives **1ae**, **1am**, **1an**, **1ap**, and **1aq** were prepared according to the literature.1. **1ab** ^[2a], **1ac** ^[2b], **1ad**, ^[2c], **1af** ^[2d], **1ao**

Complex precursors containing benzyl sp³ C-H bonds

^[2e],1bb ^[2f], 1bc, ^[2g], 1bd ^[2h] were prepared following the literature procedures.

3. General Procedures

3.1 General procedure A for Selective C(sp³)-H bond Aerobic Oxidation



A mixture of arenes 1 (0.3 mmol) or alkenes 2 (0.2 mmol), and acetone (1.5 mL) were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 1-24 h until the reaction was completed as monitored by TLC. After completion of the reaction, the resulting mixture was diluted with water and then extracted with CH_2Cl_2 . The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

3.2 The Sun Light Experiment



A mixture of ethylbenzene **1a** (0.3 mmol), and acetone (1.5 mL) were added to a reaction tube. The reaction mixture was exposed to air and stirred under sunlight for 8h. After completion of the reaction, the resulting mixture was diluted with water and then extracted with CH_2Cl_2 . The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3a** with 61% yield.

3.3 The Gram Scale Reaction



A mixture of ethylbenzene **1a** (10 mmol), and acetone (5 mL) were added to a 100 mL reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 45 h. After completion of the reaction, the resulting mixture was diluted with water and then extracted with CH_2Cl_2 . The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3a** with 73% yield.

3.4 Optimizations of the Reaction Conditions

\square	Solvent, air, rt	
1a		3a
Entry	solvent	Yield (%) ^b
1	cyclohexane	NR
2	EA	17
3	THF	10
4	(CH ₂) ₄ CO	18
5	(CH ₃) ₂ CO	79
6	$(CD_3)_2CO$	81 ^{8h}
7	(CH ₃) ₂ CHCN	78
8	ACN	63
9	DMSO	16

Table S1. Optimization of solvent.^a

^aReaction conditions: 1a (0.3 mmol), solvent (1.5 mL), air, rt, 24 h irradiated under 370 nm. [b] Isolated

yield.

Table S2. Light source experiment.^a

		ght source	
	1a	3a	
Entry	Light source	additive	Yield (%) ^b
1	390 nm	cyclohexane	NR
2	390 nm	EA	trace
3	390 nm	(CH ₃) ₂ CO	16%
4	390 nm	(CH ₃) ₂ CHCN	16%
5	390 nm	ACN	12%
6	390 nm	DMSO	trace
7	427 nm	cyclohexane	NR
8	427 nm	EA	NR
9	427 nm	(CH ₃) ₂ CO	trace
10	427 nm	(CH ₃) ₂ CHCN	trace
11	427 nm	ACN	trace
12	427 nm	DMSO	trace

aReaction conditions: 1a (0.3 mmol), solvent (1.5 mL), air, rt, 24 h irradiated under 390 nm or 427 nm.[b] Isolated yield.

4. Mechanistic Studies

4.1 Oxygen concentration experiments

A mixture of ethylbenzene **1a** (0.3 mmol), inhibitor (0.45 mmol), and acetone (1.5 mL) were added to a reaction tube. Three tubes of reaction mixtures were collapsed with balloons containing different oxygen concentrations (0%, 20%, 100%) and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 12 h. After completion of the reaction, the resulting mixture was diluted with water and then extracted with CH_2Cl_2 . The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of

petroleum ether and ethyl acetate as eluent to give the desired product. The results showed that oxygen was necessary and the rate of oxidation accelerated in an oxygen atmosphere (Figure S3).



Figure S3. Oxygen concentration experiments

4.2 Exploring Active Oxygen Experiments

A mixture of ethylbenzene **1a** (0.3 mmol), inhibitor (0.45 mmol), and acetone (1.5 mL) were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 24 h. After completion of the reaction, the resulting mixture was diluted with water and then extracted with CH_2Cl_2 . The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

Table S3. Active oxygen inhibitor experiment.^a

	+ inhibitor 1a 1.5 equiv	370 nm ►	3a
Entry	inhibitor	Active oxygen	Yield (%) ^b
1	<i>t</i> -BuOH	•OH	79
2	<i>p</i> -benzoquinon	e O₂∸	79
3	DPBF	${}^{1}O_{2}$	18 + 5a
4	DPA	$^{1}O_{2}$	0
5	carotenoids	${}^{1}O_{2}$	0

^aReaction conditions: **1a** (0.3 mmol), inhibitor (0.45 mmol), acetone (1.5 mL), air, rt, 24 h irradiated under 370 nm. ^[b] Isolated yield.

Entry 3



(400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 4H), 7.65 (s, 4H), 7.57 – 7.51 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 196.63, 140.02, 137.18, 133.03, 130.39, 129.84, 129.69, 128.35.

7.77.77 7.77.56 7.77.56 7.77.56 7.77.56 7.77.55 7.77.53 7.40 7.33



Figure S4. ¹H NMR spectra of the adduct 5a.



Figure S5. ¹³C NMR spectra of the adduct 5a.

4.3 EPR spectra (Capture of singlet oxygen)

For further explore the active species of singlet oxygen involved in the reaction, 2,2,6,6-tetramethylpiperidine (TEMP) were used to trap ${}^{1}O_{2}$ (g = 2.0065). Irradiation of the reaction solution of TEMP with ethylbenzene **1a** in acetone under air with 370 nm resulted in the formation of a strong characteristic signal ${}^{1}O_{2}$ adduct with TEMP (Figure S6), implying that ${}^{1}O_{2}$ is also present during the reaction.



Figure S6. Electron spin resonance (ESR) spectra of TEMP with ¹O₂

(a) A solution of TEMP (0.20 mol/L) with ethylbenzene **1a** in air-saturated acetone without light irradiation.

(b) A solution of TEMP (0.20 mol/L) with ethylbenzene **1a** in air-saturated acetone under purple LEDs irradiation for 30 min.

4.4 UV/Vis Studies

UV/vis absorption spectra were measured in a 10 cm quartz cuvette using a P6 The UV-Vis absorption spectra of toluene (1M, in ACN) after a 5 min nitrogen bubble were recorded (Figure S7 blue line). Subsequent oxygen bubbling of the solution for 5 min resulted in a red shift in the tail of the absorption peak, which was attributed to the toluene- O_2 CT band (red line). After introducing nitrogen into the solution again for 5 min, the absorption peaks match well with solution of the first nitrogen bubble (green line), indicating that the additional absorption is not caused by oxidation products or impurities. Additional absorption peaks were also observed in acetone (red line) and cyclohexane (green line), and the tail of the absorption band extended to 420 nm in polar solvents (Figure S8).



Figure S7 Absorption spectra: toluene (1M, in ACN)



Figure S8. Absorption spectra: toluene (1M, in cyclohexane and acetone)

The absorption spectroscopy experiments of olefin 2c were carried out, and the results are presented in As shown in Figure 9. It can be observed that the absorption tail extended to 390 nm after a 5-min oxygen bubbling process (solid yellow line), providing evidence for the formation of a charge transfer (CT) state between olefin 2c and oxygen. In addition, the absorption curve of pure acetone solvents was measured. The absorption curves of pure acetone after oxygen bubbling remained consistent with those after nitrogen bubbling operations, thereby confirming that the red shift of the absorption curves (solid yellow line) is attributed to the interaction between 2c and oxygen.



Figure S9. Absorption spectra: pure acetone solvent and 2c (1M, in acetone)

4.5 $E \rightarrow Z$ isomerization (Demonstration of triplet excited states)

A. trans-stilbene $E \rightarrow Z$ isomerization



A mixture of trans-stilbene (0.3 mmol), and acetone (1.5 mL) were added to a reaction tube. One tube was open to the air and stirred at room temperature. Another tube was evacuated and backfilled with N_2 for three times. After irradiation of an LED lamp (Kessil PR160L-390 nm) for 9 h, the resulting mixture was diluted with water and then extracted with CH₂Cl₂. The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product. The trans-stilbene provides a 91:9 Z/E in an air atmosphere. While only trace cis-stilbene was observed under nitrogen atmosphere.

cis-stilbene^{3a}: ¹**H NMR (400 MHz, CDCl₃)** δ 7.33 – 7.22 (m, 10H), 6.66 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 137.29, 130.29, 128.91, 128.25, 127.13.







-7.32 -7.728 -7.728 -7.728 -7.728 -7.25 -7.25 -7.25 -7.25 -7.26 -7.26 -7.26 -7.26 -7.26 -7.26 -7.28 -7.28 -7.28 -7.28 -7.28 -7.28 -7.28 -7.729 -7.728 -7.729



Figure S11. ¹³C NMR spectra of the adduct 5a.





A mixture of (E)-3-phenylpentyl-2-enoate (0.3 mmol), and acetone (1.5 mL) were added to a reaction tube. One tube was open to the air and stirred at room temperature. Another tube was evacuated and backfilled with N_2 for three times. After irradiation of an LED lamp (Kessil PR160L-390 nm) for 8 h, the resulting mixture was diluted with water and then extracted with CH₂Cl₂. The obtained organic phase was removed under a vacuum, and the he residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product. The (E)-3phenylpentyl-2-enoate provides a 69:31 Z/E in an air atmosphere. While only trace (Z)-3-phenylpentyl-2-enoate was observed under nitrogen atmosphere.

OEt (Z)-3-phenylpentyl-2-enoate^{3b}: ¹H NMR (400 MHz, CDCl₃) δ 7.40 –
7.31 (m, 3H), 7.25 – 7.20 (m, 2H), 5.93 (s, 1H), 4.02 (q, J = 7.1 Hz, 2H), 2.20 (s, 3H),
1.10 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.94, 155.34, 140.88,
127.89, 127.72, 126.82, 117.80, 59.76, 27.16, 13.97.





Figure S12. ¹H NMR spectra of (*Z*)-3-phenylpentyl-2-enoate.



Figure S13. ¹³C NMR spectra of (Z)-3-phenylpentyl-2-enoate.



4.6 The catalytic investigation of aromatic ketone products

A mixture of tetralin **1s** (0.3 mmol), acetophenone **3a** (10 mol%), and acetone (1.5 mL) were added to a reaction tube. Another reaction tube was added with tetralin **1s** (0.3 mmol) and acetone (1.5 ml). Two reaction tubes were opened to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) until the reaction was completed as monitored by TLC. The results indicate that the addition of acetophenone accelerates the completion of the reaction. After completion of the reaction, the resulting mixture was diluted with water and then extracted with CH_2Cl_2 . The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

4.7 Radical trapped experiment using TEMPO as radical scavenger



An oven-dried reaction tube equipped with a magnetic stirrer bar was charged with ethylbenzene (1a) (0.3 mmol), TEMPO (0.9 mmol) and acetone (1.5 mL). The reaction mixture was open to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 24 h. After

completion of the reaction, no **3a** was detected and the adduct **TEMPO-Bn** was detected by ESI-HRMS shown in Figure S14, MS (ESI) $m/z C_{17}H_{28} NO [M+H]^-$: found 262.2167.



Figure S14. Mass spectra of TEMPO-Bn

4.8 Hydrogen donor competition experiment



A mixture of ethylbenzene **1a** (0.3 mmol), Ph_3SiH (0.6 mmol), and acetone (1.5 mL) were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 24 h. After completion of the reaction, the resulting mixture was diluted with water and then extracted with CH_2Cl_2 . The obtained organic phase was removed under a vacuum, and the residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3a** with 38% yield.

4.9 Determination of the kinetic isotope effect (KIE)

A mixture of toluene (0.3 mmol), toluene-d6 (0.3 mmol), and acetone (1.5 mL)

were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 24 h. After completion of the reaction, benzaldehyde-h6 and benzaldehyde-d6 were detected by GC-MS shown in Figure S15. The kinetic isotope effect was estimated by comparing the sum of the isotope fragments of benzaldehyde-h6 and benzaldehyde-d6. Hereby, a KIE of ~3.1 could be determined.



Figure S15: Estimation of the kinetic isotope effect by GC-MS

4.10 Obtained intermediates by reaction monitoring with ¹H-NMR

In an oven-dried reaction tube equipped with a magnetic stirrer bar was charged with ethylbenzene (0.2 mmol), and acetone-*d6* (0.6 mL). Then the tube was exposed to an LED lamp (Kessil PR160L-370 nm Gen 2) for 0 h and 0.5 h. After completion of the reaction, ¹H NMR analysis of the solvent (Figure S16)



Figure S16 ¹H NMR spectra of the reaction (acetone-d6).

4.11 Determination of the Quantum Yield

4.11.1 Determination of the light intensity at 370 nm

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry.⁴ A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H₂SO₄. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H₂SO₄. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 370$ nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

mol
$$\mathbf{F}\mathbf{e}^{2+} = (\mathbf{V} \times \Delta \mathbf{A})/(\mathbf{I} \times \varepsilon)$$
 (S1)

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, 1 is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol₋₁ cm₋₁).5 The photon flux can be calculated using eq 2.

photo flux = mol Fe²⁺/ (
$$\Phi \times t \times f$$
) (S2)

Where Φ is the quantum yield for the ferrioxalate actinometer (1.21 for a 0.15 M solution at $\lambda = 370$ nm),⁵ t is the time (90.0 s), and f is the fraction of light absorbed at $\lambda = 510$ nm (0.99955, *vide infra*). The photon flux was calculated (average of three experiments) to be 2.13×10^{-9} einstein s⁻¹.

	Non-irrad	Irrad 1	Irrad 2	Irrad 3
A _{510nm}	0.050	1.921	1.356	1.523
Average A_{510nm} of irradiation samples		1.600		

Determination of fraction of light absorbed at 370 nm for the ferrioxalate solution:

The absorbance of the above ferrioxalate solution at 370 nm was measured to be 3.35. The fraction of light absorbed (f) by this solution was calculated using eq 3, where A is the measured absorbance at 370 nm.

$$f = 1 - 10^{-A}$$
 (S3)

 $f = 1 - 10^{-3.35} = 0.99955$



Figure S17. Absorption spectra of three irradiation experiments and non-irradiation experiment

4.11.2 Determination of the reaction quantum yield at 370 nm

A mixture of ethylbenzene (0.3 mmol) and acetone (1.5 mL) were added to a reaction tube. The reaction mixture was open to the air and stirred at room temperature under the irradiation of an LED lamp (Kessil PR160L-370 nm Gen 2) for 10800s. After irradiation, the yield of the product **3a** was determined by ¹H NMR based on a trifluoromethoxybenzene standard and the final yield was 6.0% (1.80×10^{-5} mol).

Quantum Yield (Φ) = moles of product formed/ (flux × f × t) = 1.80 ×10⁻⁵/2.13 × 10⁻⁹× 0.999 × 10800) = 0.78

4.12 On/off experiments of 3a

Four parallel reactions were performed ethylbenzene (0.3 mmol) according to the General Procedure A. The yield of **3a** was recorded at the given times. The white area indicates the light irradiation, while the grey area indicates time in the dark.



Figure S18. On/off experiments of 3a.

5. Characterization Data for the Products

acetophenone (3a)⁶



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a colorless liquid (28 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.95 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 2.62 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.06, 137.18, 133.06, 128.55, 128.28, 26.55.

1-(4-methoxyphenyl)ethan-1-one (3b)⁷



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a white solid (34 mg, 77%). ¹H NMR (400 MHz,

CDCl₃) δ 7.96 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.58 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.77, 163.48, 130.59, 130.37, 113.68, 55.47, 26.35.

1-(p-tolyl)ethan-1-one (3c)⁷



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a colorless liquid (29 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.60 (s, 3H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.83, 143.86, 134.73, 129.24, 128.44, 26.53, 21.63.

1-(4-bromophenyl)ethan-1-one (3d)⁷



The product was purified by column chromatography on silica gel (eluent: 40:1 petroleum ether: ethyl acetate) as a white solid (52 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 2.60 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.01, 135.83, 131.89, 129.84, 128.30, 26.56.

4-acetylbenzonitrile (3e)⁷



The product was purified by column chromatography on silica gel (eluent: 40:1 petroleum ether: ethyl acetate) as a yellow solid (29 mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 2.67 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.53, 139.92, 132.53, 128.70, 117.92, 116.44, 26.78.

1-(4-nitrophenyl)ethan-1-one (3f)⁷



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (9 mg, 18%). ¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 2H), 2.70 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.30, 150.37, 141.38, 129.31, 123.86, 26.99 (s).

1-(thiophen-2-yl)ethan-1-one (3g)⁸



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a colorless oil (31 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.65 (m, 1H), 7.63 – 7.58 (m, 1H), 7.13 – 7.07 (m, 1H), 2.56 – 2.52 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 190.61, 144.54, 133.71, 132.46, 128.10, 26.84.

1-(pyridin-3-yl)ethan-1-one (3h)⁷



The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a yellow oil (20 mg, 57%). ¹H NMR (400 MHz, CDCl₃) δ 9.18 – 9.08 (m, 1H), 8.79 – 8.67 (m, 1H), 8.25 – 8.15 (m, 1H), 7.43 – 7.33 (m, 1H), 2.62 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.72, 153.47, 149.87, 135.49, 132.25, 123.65, 26.72.

1-(naphthalen-2-yl)ethan-1-one (3i)⁷



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a s white solid (36 mg, 71%).¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.65 – 7.55 (m, 2H), 2.75 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 198.11, 135.59, 134.49, 132.52, 130.21, 129.56, 128.49, 128.43, 127.80, 126.79, 123.90, 26.72.

1-([1,1'-biphenyl]-4-yl)ethan-1-one (3j) ⁷



The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a pale-yellow oil (32 mg, 54%). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 1H), 2.67 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.78, 145.79, 139.88, 135.86, 128.97, 128.93, 128.25, 127.28, 127.24, 26.69.

(4-acetylphenyl)boronic acid (3k) 9



The product was purified by column chromatography on silica gel (eluent: 4:1 petroleum ether: ethyl acetate) as a yellow solid (30 mg, 62%).¹H NMR (400 MHz, DMSO) δ 8.25 (s, 2H), 7.91 (s, 4H), 2.59 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 198.71, 138.29, 134.70, 127.41, 27.28.

Benzophenone (3l) ⁷



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a pale-yellow oil (50 mg, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.81 (m, 4H), 7.64 – 7.58 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 196.70, 137.64, 132.39, 130.04, 128.27.

1-phenylbutan-1-one (3m)⁷



The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a colorless oil (28 mg, 63%).¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 2.97 (t, *J* = 7.3 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.42, 137.13, 132.85, 128.54, 128.04, 40.53, 17.79, 13.90.

4-oxo-4-phenylbutanenitrile (3n)¹⁰



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a colorless liquid (29mg, 60%).¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 6.8 Hz, 2H), 7.63 (d, *J* = 6.5 Hz, 1H), 7.53 (d, *J* = 6.7 Hz, 2H), 3.41 (s, 2H), 2.80 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 195.35, 135.59, 133.92, 128.89, 128.03, 119.26, 34.28, 11.82.

1,3-diphenylpropan-1-one (3o)⁷



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a white solid (55 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.96 (m, 2H), 7.61 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 7.37 – 7.28 (m, 4H), 7.25 (t, *J* = 7.0 Hz, 1H), 3.34 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.18, 141.32, 136.96, 133.03, 128.61, 128.54, 128.44, 128.06, 126.15, 40.43, 30.19.

4-bromo-1-phenylbutan-1-one (3p)¹¹



The product was purified by column chromatography on silica gel (eluent: 40:1 petroleum ether: ethyl acetate) as a yellow liquid (58 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.97 (m, 2H), 7.59 (dt, *J* = 8.5, 1.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.57 (t, *J* = 6.3 Hz, 2H), 3.21 (t, *J* = 6.9 Hz, 2H), 2.34 (p, *J* = 6.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.78, 136.75, 133.24, 128.66, 128.02, 36.58, 33.64, 26.89.

1-phenylhexan-1-one (3q)¹²



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a pale-yellow oil (30mg, 58%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.95 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 1.83 – 1.69 (m, 2H), 1.43 – 1.34 (m, 4H), 0.96 – 0.91 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.60, 137.12, 132.84, 128.54, 128.05, 38.60, 31.57, 24.09, 22.54, 13.97.

1-phenylheptan-1-one (3r)¹²



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a pale-yellow oil (31 mg, 54%). ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.96 (m, 2H), 7.61 – 7.55 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 1.76 (m, 2H), 1.45 – 1.29 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.64, 137.10, 132.86, 128.55, 128.06, 38.66, 31.69, 29.07, 24.36, 22.56, 14.07.

3,4-dihydronaphthalen-1(2H)-one (3s) 7



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a pale-yellow oil (39 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 6.0 Hz, 1H), 3.00 (t, *J* = 6.1 Hz, 2H), 2.69 (t, *J* = 6.4 Hz, 2H), 2.19 – 2.10 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.34, 144.47, 133.37, 132.65, 128.75, 127.19, 126.63, 39.18, 29.72, 23.30.

isochroman-1-one (3t)⁷



The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a white solid (34 mg, 76%).¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 4.57 – 4.52 (m, 2H), 3.08 (t, *J* = 6.0 Hz, 2H). ¹³C NMR

(101 MHz, CDCl₃) δ 165.06, 139.59, 133.65, 130.30, 127.63, 127.26, 125.31, 67.31, 27.81.

3,4-dihydroisoquinolin-1(2H)-one (3u) ¹³



The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a yellow oil (36 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.35 (td, *J* = 7.2, 1.9 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 3.81 – 3.74 (m, 2H), 2.75 (t, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 160.28, 136.31, 131.03, 128.50, 127.39, 127.18, 127.06, 47.36, 25.02.

2,3-dihydro-1*H*-inden-1-one (3v)⁷



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a light yellow oil (32 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 3.11 (t, 2H), 2.68 – 2.61 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 206.91, 155.11, 137.04, 134.54, 127.22, 126.68, 123.61, 36.18, 25.77.

anthracen-9(10H)-one (3w)¹⁴



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a yellow solid (40 mg, 69%). ¹H NMR (400 MHz,

CDCl₃) δ 8.43 – 8.37 (m, 2H), 7.66 – 7.60 (m, 2H), 7.51 (d, *J* = 7.5 Hz, 4H), 4.40 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 184.28, 140.45, 132.74, 132.07, 128.46, 127.62, 127.03, 32.39.

anthracene-9,10-dione (3x)¹⁰



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a yellow solid (39 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 8.38 – 8.30 (m, 4H), 7.87 – 7.79 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 183.14, 134.10, 133.55, 127.23.

3,3-difluoro-4-(4-oxochroman-3-yl)-1-(3-(trifluoromethyl)phenyl)pyrrolidin-2one (3y) ⁷



The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a white solid (52 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 8.37 (d, *J* = 7.9 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 177.26, 156.19, 134.84, 126.75, 123.93, 121.86, 118.00.

9H-fluoren-9-one (3z)¹⁵



The product was purified by column chromatography on silica gel (eluent:50:1

petroleum ether: ethyl acetate) as a yellow solid (44 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 7.3 Hz, 2H), 7.56 – 7.48 (m, 4H), 7.31 (td, *J* = 7.3, 1.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 193.84, 144.44, 134.64, 134.19, 129.06, 124.30, 120.28.

acenaphthylen-1(2H)-one (3aa)⁷



The product was purified by column chromatography on silica gel (eluent: 40:1 petroleum ether: ethyl acetate) as a white solid (25 mg, 49%). ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.67 – 7.59 (m, 1H), 7.50 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 202.84, 142.95, 135.03, 134.73, 131.44, 130.98, 128.36, 127.98, 123.94, 121.42, 121.01, 42.00.

1-(4"-ethyl-5'-(4-ethylphenyl)-[1,1':3',1"-terphenyl]-4-yl)ethan-1-one (3ab)



The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a white solid (69 mg, 57%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.81 (m, 5H), 7.65 (d, *J* = 7.5 Hz, 4H), 7.35 (d, *J* = 7.4 Hz, 4 H), 2.75 (q, *J* = 14.3 Hz, 4H), 2.69 (s, 3H), 1.33 (t, *J* = 10.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 197.81, 145.89, 143.92, 142.51, 138.29, 128.98, 128.44, 127.45, 127.27, 125.83, 124.81, 28.58, 26.73, 15.63. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₀H₂₉O 405.2218; Found 405.2215.

1-(4-(1H-benzo[d]imidazol-1-yl)phenyl)ethan-1-one (3ac) ¹⁶



The product was purified by column chromatography on silica gel (eluent: 5:1 petroleum ether: ethyl acetate) as a white solid (30 mg, 43%). ¹H NMR (400 MHz, CDCl₃) δ 8.39 – 8.13 (m, 3H), 7.94 (s, 1H), 7.69 (d, *J* = 6.7 Hz, 3H), 7.41 (s, 2H), 2.71 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.63, 140.17, 136.30, 130.43, 124.41, 123.52, 120.75, 110.69, 99.99, 26.73.

2-(2-oxo-2-phenylethyl)isoindoline-1,3-dione (3ad) 10



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (23 mg, 29%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.92 (d, *J* = 2.8 Hz, 2H), 7.78 (s, 2H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 5.16 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 190.97, 167.92, 134.41, 134.15, 134.07, 132.24, 128.92, 128.16, 123.58, 44.22.

4-acetylphenyl (1r,3r,5r,7r)-adamantane-2-carboxylate (3ae)



The product was purified by column chromatography on silica gel (eluent: 25:1

petroleum ether: ethyl acetate) as a white solid (63 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 2.62 (s, 3H), 2.10 (d, *J* = 14.2 Hz, 9H), 1.80 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 196.96, 175.66, 154.98, 134.50, 129.89, 121.80, 41.17, 38.71, 36.40, 27.86, 26.64. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₂₃O₃ 299.1645; Found 299.1644.

1-tosyl-2,3-dihydroquinolin-4(1H)-one (3af)¹⁷



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (74 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.31 – 7.28 (m, 1H), 7.28 – 7.23 (m, 2H), 4.25 (t, *J* = 6.4 Hz, 2H), 2.44 – 2.38 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 192.73, 144.59, 142.37, 136.83, 134.73, 130.13, 127.76, 126.88, 125.71, 125.66, 124.61, 46.24, 36.53, 21.61.

benzaldehyde (3ag)¹



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a colorless liquid (19 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ 10.05 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.42, 136.40, 134.48, 129.76, 129.01. **2-methylbenzaldehyde (3ah)** ¹⁸

СНО
The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a yellow oil (21 mg, 60%). ¹H NMR (400 MHz, Chloroform-*d*) δ 10.30 (s, 1H), 7.82 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 2.70 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 192.88, 140.66, 134.16, 133.68, 132.07, 131.79, 126.35, 19.61.

3-fluorobenzaldehyde (3ai)¹



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a colorless liquid (13 mg, 36%). ¹H NMR (400 MHz, CDCl₃) δ 10.03 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.37 (td, *J* = 8.3, 2.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 190.90 (C-F, ⁴*J*_{C-F}, *J* = 2.3 Hz), 163.10 (C-F, ¹*J*_{C-F}, *J* = 249.4 Hz), 138.40 (C-F, ³*J*_{C-F}, *J* = 6.2 Hz), 130.79 (C-F, ³*J*_{C-F}, *J* = 7.6 Hz), 126.06 (C-F, ⁴*J*_{C-F}, *J* = 3.0 Hz), 121.60 (C-F, ²*J*_{C-F}, *J* = 21.8 Hz), 115.36 (C-F, ²*J*_{C-F}, *J* = 21.8 Hz).

2-chlorobenzaldehyde (3aj)¹



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a colorless liquid (26 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 10.51 (s, 1H), 7.95 (m, 1H), 7.57 – 7.53 (m, 1H), 7.50 – 7.46 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 189.86, 137.97, 135.14, 132.46, 130.62, 129.38, 127.30.

4-bromobenzaldehyde (3ak)¹



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a white solid (39 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 191.11, 135.06, 132.45, 130.98, 129.81.

3,5-dimethylbenzaldehyde (3al)¹⁹



The product was purified by column chromatography on silica gel (eluent: 100:1 petroleum ether: ethyl acetate) as a colorless oil (22 mg, 56%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.51 (s, 2H), 7.29 (s, 1H), 2.42 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 192.86, 138.78, 136.59, 136.24, 127.59, 21.09.

5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (4a) ²⁰



The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a colorless oil (17 mg, 51%). ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.52 (m, 2H), 7.48 – 7.39 (m, 3H), 6.44 (s, 1H), 2.79 (t, *J* = 5.6 Hz, 2H), 2.50 (t, *J* = 6.5 Hz, 2H), 2.21 – 2.13 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.98, 159.85, 138.80, 130.00, 128.77, 126.09, 125.45, 37.29, 28.13, 22.83.

(1R,6S)-4,7,7-trimethylbicyclo[4.1.0]hept-3-en-2-one (4b)



The product was purified by column chromatography on silica gel (eluent: 20:1

petroleum ether: ethyl acetate) as a colorless oil (20 mg, 66%). ¹H NMR (400 MHz, Chloroform-*d*) δ 5.84 (s, 1H), 2.70 – 2.57 (m, 1H), 2.33 (d, *J* = 20.8 Hz, 1H), 1.88 (s, 3H), 1.57 (d, *J* = 7.8 Hz, 1H), 1.46 (t, *J* = 7.8 Hz, 1H), 1.20 (s, 3H), 1.05 (s, 3H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 196.65, 158.93, 126.41, 32.85, 28.42, 27.86, 25.85, 23.66, 22.54, 14.37. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₀H₁₅O 151.1124; Found 151.1119.

(1R,5R)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one (4c)²⁰



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a colorless liquid (21 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 5.77 – 5.72 (m, 1H), 2.86 – 2.77 (m, 1H), 2.67 (td, *J* = 6.0, 1.7 Hz, 1H), 2.44 (t, *J* = 5.8 Hz, 1H), 2.10 (d, *J* = 9.1 Hz, 1H), 2.04 (s, 3H), 1.52 (s, 3H), 1.03 (s, 3H). ¹³C NMR (101 MHz, CH₂Cl₂) δ 204.05, 170.19, 121.19, 57.60, 54.06, 49.71, 40.86, 26.59, 23.58, 22.05.

(4S,4aR,6S)-4,4a-dimethyl-6-(prop-1-en-2-yl)-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (4d)²⁰



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a colorless liquid (30 mg, 69%). ¹H NMR (400 MHz, Chloroform-*d*) δ 5.79 (s, 1H), 4.75 (d, *J* = 10.3 Hz, 2H), 2.59 – 2.49 (m, 1H), 2.42 – 2.25 (m, 4H), 2.07 – 1.91 (m, 3H), 1.76 (s, 3H), 1.42 – 1.31 (m, 1H), 1.19 – 1.11 (m, 4H), 0.99 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 199.69, 170.56, 149.12, 124.70, 109.26, 43.93, 42.09, 40.47, 40.33, 39.33, 33.04, 31.63, 20.84, 16.86,

14.93.

2-oxo-2-phenylethyl (1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1carboxylate (3am)



The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a white solid (38 mg, 41%). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 5.52 (q, *J* = 40.0, 16.2 Hz, 2H), 2.61 – 2.51 (m, 1H), 2.19 – 2.10 (m, 1H), 2.04 – 1.95 (m, 1H), 1.80 – 1.71 (m, 1H), 1.19 (s, 3H), 1.18 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 190.83, 178.12, 166.99, 134.16, 133.84, 133.73, 130.19, 129.00, 128.50, 127.76, 91.15, 66.71, 54.98, 54.66, 30.84, 28.96, 16.60, 16.57, 9.79. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₈H₂₀NaO₅ 339.1209; Found 339.1208.

(1R,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(4-methoxyphenyl)-4oxobutanoate (3an)²¹



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a colorless oil (74 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.96 – 4.88 (m, 1H), 3.89 (s, 3H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.79 (t, *J* = 6.7 Hz, 2H), 2.39 – 2.30 (m, 1H), 1.96 – 1.88 (m, 1H), 1.77 – 1.72 (m, 1H), 1.70 – 1.61 (m, 1H), 1.29 – 1.21 (m, 2H), 1.01 (dd, *J* = 13.7, 3.4 Hz, 1H), 0.91 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.70, 173.28, 163.52, 130.29, 129.77, 113.73, 80.13, 55.48, 48.78, 47.80, 44.87, 36.65, 33.08, 28.74, 27.99, 27.10, 19.71, 18.85, 13.50.

4-(acetoxymethyl)-6-(4-acetylphenoxy)cyclohexane-1,2,3-triyl triacetate (3ao)



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a white solid (114 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 5.36 – 5.29 (m, 2H), 5.24 – 5.15 (m, 2H), 4.34 – 4.28 (m, 1H), 4.23 – 4.15 (m, 1H), 3.99 – 3.86 (m, 1H), 2.59 (s, 3H), 2.08 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 196.67, 170.52, 170.21, 169.39, 169.26, 160.24, 132.43, 130.49, 116.25, 98.17, 72.57, 72.26, 71.03, 68.14, 61.89, 26.49, 20.71, 20.62. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₂H₂₆NaO₁₁ 489.1373; Found 489.1400.

4-acetylphenyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (3ap)¹⁵



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a yellow solid (69 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H), 1.86 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 196.69, 194.17, 172.02, 159.37, 153.98, 138.56, 136.22, 135.16, 132.18, 131.20, 130.86, 130.05, 128.62, 121.43, 117.32, 79.43, 26.64, 25.43.

N-(4-acetylphenyl)-4-(N,N-dipropylsulfamoyl)benzamide (3aq)



The product was purified by column chromatography on silica gel (eluent: 4:1 petroleum ether: ethyl acetate) as a white solid (86 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 3.11 (t, *J* = 7.4 Hz, 4H), 2.63 (s, 3H), 1.61 – 1.50 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 197.08, 164.98, 142.90, 142.27, 138.47, 133.32, 129.75, 128.14, 127.30, 119.52, 49.99, 26.54, 21.93, 11.17. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₁H₂₇N₂O₄S 403.1691; Found 403.1689.

7-acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (3ar)²²



The product was purified by column chromatography on silica gel (eluent: 40:1 petroleum ether: ethyl acetate) as a white solid (45 mg, 58%). ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 1.6 Hz, 1H), 7.35 (d, *J* = 1.6 Hz, 1H), 2.65 (s, 3H), 2.62 (s, 2H), 1.45 (s, 6H), 1.38 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 204.69, 204.05, 164.59, 159.41, 139.21, 129.35, 123.25, 121.76, 53.25, 38.70, 35.77, 31.13, 30.94, 30.03.

4,6,6,7,8,8-hexamethyl-4,6,7,8-tetrahydrocyclopenta[g]isochromen-1(3H)-one (3as)



The product was purified by column chromatography on silica gel (eluent: 30:1 petroleum ether: ethyl acetate) as a white solid (40 mg, 49%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.07 (s, 1H), 4.56 – 4.44 (m, 1H), 4.30 – 4.17 (m, 1H), 3.16 (s,

1H), 1.96 - 1.82 (m, 1H), 1.42 - 1.29 (m, 9H), 1.14 - 1.00 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 165.85, 158.35, 151.15, 143.46, 125.06, 122.96, 119.81, 72.50, 54.14, 45.24, 44.61, 32.03, 29.06, 28.78, 25.78, 25.69, 16.96, 8.46. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₂₅O₂ 273.1854; Found 273.1848.

7-isopropyl-1,4a-dimethyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1carboxylic acid (3at) ⁹



The product was purified by column chromatography on silica gel (eluent: 15:1 petroleum ether: ethyl acetate) as a colorless oil (77 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 3.00 – 2.88 (m, 1H), 2.79 – 2.69 (m, 2H), 2.51 (d, *J* = 14.5 Hz, 1H), 2.39 (d, *J* = 12.4 Hz, 1H), 1.88 – 1.79 (m, 4H), 1.71 – 1.64 (m, 1H), 1.37 (s, 3H), 1.29 – 1.25 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 198.90, 183.02, 153.00, 146.97, 132.73, 130.61, 125.13, 123.51, 46.38, 43.56, 37.76, 37.15 (d, *J* = 18.9 Hz), 36.50, 33.61, 23.84, 23.76, 23.68, 18.13, 16.16.

(5-bromo-2-methylphenyl)(5-(4-fluorophenyl)thiophen-2-yl)methanone (3au)



The product was purified by column chromatography on silica gel (eluent: 50:1 petroleum ether: ethyl acetate) as a white solid (92 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.65 (m, 2H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.29 (d, *J* = 1.3 Hz, 1H), 7.22 – 7.12 (m, 3H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 188.42, 163.37 (C-F, ¹*J*_{C-F}, *J* = 250.3 Hz), 153.36, 142.72, 140.05, 136.85, 135.40, 133.18, 132.76, 130.51, 129.48 (C-F, ⁴*J*_{C-F}, = 3.4 Hz), 128.25 (C-F, ³*J*_{C-F} = 8.3 Hz), 124.14, 118.83, 116.32 (C-F, ²*J*_{C-F} = 22.0 Hz), 19.23. HRMS (ESI) m/z:

[M+H]⁺ Calcd for C₁₈H₁₃BrFOS 374.9854; Found 374.9851.

3-methoxy-11-methyl-5,6,7,8,8a,9-hexahydro-10H-9,4b-(epiminoethano)phenant hrene-10-one (3av)



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (38 mg, 45%). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.82 (s, 1H), 3.90 (s, 3H), 3.02 (s, 1H), 2.65 (d, *J* = 8.1 Hz, 1H), 2.40 (d, *J* = 13.8 Hz, 4H), 2.09 (t, *J* = 12.9 Hz, 2H), 1.93 (t, *J* = 12.8 Hz, 1H), 1.67 (d, *J* = 12.3 Hz, 1H), 1.61 – 1.48 (m, 3H), 1.47 – 1.35 (m, 2H), 1.27 (t, *J* = 12.8 Hz, 1H), 1.20 – 1.07 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 194.11, 164.91, 147.86, 128.81, 128.53, 111.76, 111.52, 68.58, 55.42, 47.69, 47.31, 43.23, 41.29, 38.17, 36.48, 26.12, 25.97, 21.95. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₁₈H₂₄NO₂ 286.1807; Found 286.1802.

5-(2-formyl-5-methylphenoxy)-2,2-dimethylpentanoic acid (3aw) 9



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a light yellow oil (46 mg, 59%). ¹H NMR (400 MHz, CDCl₃) δ 10.45 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 4.08 (t, *J* = 5.9 Hz, 2H), 2.41 (s, 3H), 1.92 – 1.81 (m, 2H), 1.82 – 1.71 (m, 2H), 1.28 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 189.60, 183.54, 161.46, 147.47, 128.29, 122.62, 121.66, 112.96, 68.43, 41.91, 36.77, 25.05, 24.92, 22.37.

3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6Hcyclopenta[a]phenanthren-6-one (3ax)²³



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (35 mg, 41%). ¹H NMR (400 MHz, DMSO) δ 9.58 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.00 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.54 (s, 1H), 3.54 (t, *J* = 8.1 Hz, 1H), 2.44 – 2.18 (m, 3H), 1.90 – 1.77 (m, 2H), 1.62 – 1.14 (m, 8H), 0.66 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 197.64, 156.12, 138.36, 133.44, 127.21, 121.69, 112.24, 80.30, 49.64, 43.95, 43.06, 42.61, 36.60, 30.23, 25.66, 22.88, 11.50.

3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6Hcyclopenta[a]phenanthren-6-one (3ay)



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (57mg, 61%). ¹H NMR (400 MHz, DMSO) δ 9.62 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.27 (s, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 5.40 (s, 1H), 2.43 – 2.26 (m, 3H), 2.11 (s, 1H), 1.91 – 1.60 (m, 7H), 1.47 – 1.22 (m, 3H), 0.75 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 197.62, 156.12, 138.26, 133.40, 127.31, 121.69, 112.18, 89.20, 78.43, 75.78, 49.10, 46.89, 43.90, 42.31, 40.69, 39.11, 32.66, 25.68, 22.56, 12.97. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₃O₃ 311.1647; Found 311.1642.

2,5,7,8-tetramethyl-4-oxo-2-(4,8,12-trimethyltridecyl)chroman-6-yl nicotinate (3az) ⁹



The product was purified by column chromatography on silica gel (eluent: 40:1 petroleum ether: ethyl acetate) as a brown solid (49 mg, 30%). ¹H NMR (400 MHz, CDCl₃) δ 9.47 (s, 1H), 8.91 (s, 1H), 8.51 (dt, J = 8.0, 1.8 Hz, 1H), 7.51 (dd, J = 7.8, 4.9 Hz, 1H), 2.79 (t, J = 14.8 Hz, 1H), 2.64 (t, J = 16.1 Hz, 1H), 2.46 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H), 1.83 – 1.67 (m, 2H), 1.58 – 1.49 (m, 2H), 1.42 – 1.12 (m, 20H), 0.88 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 194.37, 163.62, 156.63, 154.06, 141.48, 137.64, 136.73, 128.95, 125.21, 124.57, 123.59, 116.96, 80.21, 49.05, 39.37, 37.44, 37.39, 37.29, 37.23, 37.19, 37.15, 37.11, 32.79, 32.64, 27.96, 24.79 (d, J = 1.0 Hz), 24.42, 22.69, 22.60, 21.05, 19.73, 19.67, 19.61, 19.58, 19.54, 19.52, 14.02 (d, J = 11.2 Hz), 12.12.



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (58 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 6.1 Hz, 2H), 7.48 – 7.31 (m, 5H), 4.37 (d, *J* = 14.4 Hz, 1H), 3.89 (d, *J* = 14.6 Hz, 1H), 2.15 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 191.74, 169.83, 142.44, 133.95, 130.72, 130.08, 129.11, 128.80, 128.57, 127.72, 49.08, 23.19.

oxcarbazepine (3bb)²¹



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (41 mg, 55%). ¹H NMR (600 MHz, CDCl₃) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.33 (m, 3H), 5.02 (s, 2H), 4.47 (d, *J* = 14.2 Hz, 1H), 3.87 (d, *J* = 14.2 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 191.79, 155.71, 143.09, 141.35, 134.03, 133.98, 130.68, 130.24, 129.91, 129.35, 129.04, 128.70, 127.80, 127.36, 49.0.

ethyl 2-(4-(1-oxoisoindolin-2-yl)phenyl)butanoate (3bc) 24



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a yellow solid (46 mg, 48%). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 6.5 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 4.86 (s, 2H), 4.25 – 4.05 (m, 2H), 3.47 (t, *J* = 7.7 Hz, 1H), 2.19 – 2.05 (m, 1H), 1.87 – 1.78 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.03, 167.48, 140.09, 138.47, 135.33, 133.18, 132.09, 128.71, 128.40, 124.15, 122.64, 119.55, 60.70, 52.97, 50.74, 26.77, 14.20, 12.18.

4-([1,1'-biphenyl]-4-yl)-4-oxobutanoic acid (3bd)²¹



The product was purified by column chromatography on silica gel (eluent: 20:1

petroleum ether: ethyl acetate) as a white solid (39 mg, 52%). ¹H NMR (400 MHz, DMSO) δ 12.17 (s, 1H), 8.07 (d, J = 7.8 Hz, 2H), 7.84 (d, J = 7.7 Hz, 2H), 7.76 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 6.7 Hz, 1H), 3.31 3.29 (t, J = 5.4 Hz, 2H), 2.61 (t, J = 5.4 Hz, 2H). ¹³C NMR (101 MHz, DMSO) δ 198.50, 174.30, 145.00, 139.37, 135.71, 129.57, 129.05, 128.86, 127.45, 127.37, 33.60, 28.36.

2,6,10,10-tetramethyl-1-oxaspiro[4.5]dec-6-en-8-one (4e) ²⁰



The product was purified by column chromatography on silica gel (eluent: 40:1 petroleum ether: ethyl acetate) as a colorless oil (30 mg, 73%). ¹H NMR (400 MHz, CDCl₃) δ 5.75 (d, J = 15.1 Hz, 1H), 4.30 – 4.14 (m, 1H), 2.43 – 2.19 (m, 3H), 2.16 – 2.03 (m, 1H), 1.99 (d, J = 7.2 Hz, 3H), 1.86 – 1.75 (m, 1H), 1.65 – 1.47 (m, 1H), 1.32 (d, J = 5.9 Hz, 3H), 1.06 (d, J = 20.0 Hz, 3H), 1.01 (d, J = 12.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.71, 198.34, 168.27, 125.27, 124.87, 88.52, 77.95, 77.70, 50.23, 49.91, 41.62, 40.78, 35.01, 34.30, 32.69, 24.50, 24.40, 23.71, 23.00, 21.31, 20.44, 18.95.

3-hydroxy-10,13-dimethyl-1,3,4,8,9,10,11,12,13,14,15,16-dodecahydro-7Hcyclopenta[a]phenanthrene-7,17(2H)-dione (4f) ²⁰



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (39 mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ 5.76 (s, 1H), 3.78 – 3.59 (m, 1H), 2.90 – 2.73 (m, 1H), 2.60 – 2.37 (m, 4H), 2.21 – 2.08 (m, 1H), 2.01 – 1.55 (m, 10H), 1.26 (d, *J* = 14.4 Hz, 4H), 0.91 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 220.40, 201.08, 166.20, 125.93, 70.30, 50.11, 47.88, 45.76, 44.35, 41.88, 38.42, 36.32, 35.65, 31.12, 30.73, 24.18, 20.60, 17.45, 13.76.

3-hydroxy-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-1,2,3,4,8,9,10,11,12,13, 14,15,16,17-tetradecahydro-7H-cyclopenta[a]phenanthren-7-one (4g) ²⁵



The product was purified by column chromatography on silica gel (eluent: 20:1 petroleum ether: ethyl acetate) as a white solid (32 mg, 40%). ¹H NMR (400 MHz, CDCl₃) δ 5.70 (s, 1H), 3.74 – 3.62 (m, 1H), 2.52 (d, *J* = 16.6 Hz, 1H), 2.41 (t, *J* = 12.0 Hz, 2H), 2.25 (t, *J* = 11.2 Hz, 1H), 2.08 – 1.88 (m, 5H), 1.68 – 1.46 (m, 5H), 1.36 – 1.03 (m, 15H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H), 0.69 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 202.30, 165.16, 126.09, 70.50, 54.83, 49.97 (d, *J* = 2.8 Hz), 45.42, 43.11, 41.83, 39.48, 38.73, 38.29, 36.37, 36.19, 35.71, 31.20, 28.54, 28.00, 26.32, 23.84, 22.80, 22.55, 21.23, 18.88, 17.32, 11.98.

17-acetyl-3-hydroxy-10,13-dimethyl-1,2,3,4,8,9,10,11,12,13,14,15,16,17tetradecahydro-7H-cyclopenta[a]phenanthren-7-one (4h) ²⁵



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (32 mg, 49%). ¹H NMR (400 MHz, CDCl₃) δ 5.71 (s, 1H), 3.69 (s, 1H), 2.55 – 2.49 (m, 2H), 2.40 (t, *J* = 12.4 Hz, 1H), 2.28 ((t, *J* = 12.4 Hz, 1H), 2.14 (s, 3H), 2.08 – 1.94 (m, 4H), 1.79 – 1.37 (m, 10H), 1.21 (s, 3H), 0.67 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 209.84, 201.59, 165.71, 125.83, 70.36, 62.30, 50.01, 49.78, 45.23, 44.41, 41.86, 38.36, 37.68, 36.38, 31.62, 31.10, 26.47, 23.61, 21.14, 17.33, 13.27.

-octadecahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-1(3*H*)one (4i) ²⁵



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (32 mg, 37%). ¹H NMR (400 MHz, CDCl₃) δ 5.72 (s, 1H), 4.54 – 4.45 (m, 1H), 3.74 – 3.64 (m, 1H), 3.49 (d, *J* = 9.0 Hz, 1H), 3.41 (t, *J* = 10.7 Hz, 1H), 2.94 – 2.84 (m, 1H), 2.54 (d, *J* = 13.2 Hz, 1H), 2.42 (t, *J* = 12.3 Hz, 2H), 1.97 (d, *J* = 11.3 Hz, 2H), 1.91 – 1.86 (m, 1H), 1.77 – 1.42 (m, 15H), 1.24 (s, 3H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.81 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 201.74, 165.38, 125.92, 109.23, 80.95, 70.46, 66.81, 61.08, 49.79, 49.49, 44.88, 41.87, 41.58, 40.96, 38.72, 38.42, 36.34, 33.72, 31.43, 31.15, 30.32, 28.80, 20.96, 17.34, 17.14, 16.45, 14.66.

methyl-2,2,6a,6b,9,9,12a-heptamethyl-10,13-dioxo-1,3,4,5,6,6a,6b,7,8,8a,9,10, 11,12,12a,12b,13,14b-octadecahydropicene-4a(2H)-carboxylate (4j) ²⁵



The product was purified by column chromatography on silica gel (eluent: 10:1 petroleum ether: ethyl acetate) as a white solid (69 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 5.65 (s, 1H), 3.65 (s, 3H), 3.27 – 3.19 (m, 1H), 3.02 (d, *J* = 12.9 Hz, 1H), 2.85 (d, *J* = 13.5 Hz, 1H), 2.33 (s, 1H), 2.06 (t, *J* = 13.6 Hz, 1H), 1.78 – 1.49 (m, 11H), 1.38 (s, 3H), 1.29 – 1.21 (m, 4H), 1.12 (s, 3H), 1.01 (s, 3H), 0.94 (d, *J* = 7.9 Hz, 9H), 0.81 (s, 3H), 0.70 (d, *J* = 11.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 200.38, 177.52, 168.69, 127.91, 78.77, 61.79, 55.01, 51.92, 46.22, 45.04, 44.26, 43.48, 41.58, 39.14,

37.28, 33.71, 32.89, 31.61, 30.69, 28.12, 27.76, 27.32, 23.52 (d, *J* = 15.0 Hz), 22.96, 18.94, 17.41, 16.20, 15.58.

6. References

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7. ¹H, ¹³C and ¹⁹F NMR spectra of products



¹³C NMR Spectrum of Compound 3a



¹³C NMR Spectrum of Compound 3b





¹H NMR Spectrum of Compound 3c



¹³C NMR Spectrum of Compound 3c



¹³C NMR Spectrum of Compound 3d





¹³C NMR Spectrum of Compound 3f





¹³C NMR Spectrum of Compound 3g



¹³C NMR Spectrum of Compound 3h



¹³C NMR Spectrum of Compound 3i



¹H NMR Spectrum of Compound 3j



S60



S61

7.538 7.518



¹³C NMR Spectrum of Compound 31





¹³C NMR Spectrum of Compound 3m



¹³C NMR Spectrum of Compound 3n



¹H NMR (CDCl₃, 400MHz)



11 11 11 11 11 11 11 11 11 11 11 11 11	.73 .73 .69	33
000000000	NNNNN	-
SALL		1



¹H NMR (CDCl₃, 400MHz)



¹³C NMR Spectrum of Compound 3p



¹H NMR Spectrum of Compound 3q





¹³C NMR Spectrum of Compound 3r

60 132 132 132 14 14 14 14 14 14 14 14 14 14 14 14 14	36201 282 397 397 385 397 397 397 397 397 397 397 397 397 397
000044440000	0001001
0000000000000000	MANNANANAN



¹H NMR (CDCl₃, 400MHz)



¹³C NMR Spectrum of Compound 3s

8.11 8.09 7.55 7.55 7.55 7.55 7.55 7.55 7.55 7.5	4.55 4.55	3.09 3.08 3.06



¹H NMR (CDCl₃, 400MHz)



¹³C NMR Spectrum of Compound 3t


¹H NMR (CDCl₃, 400MHz)





32 446 32 35 446 32 35 446	24 65 65 65 65 65 65 65 65 65 65 65 65 65
	www.dddddd-



¹H NMR (CDCl₃, 400MHz)





¹³C NMR Spectrum of Compound 3w

6.35 68.35 7.83 7.83 7.83 7.83 7.83 7.83 7.83



¹H NMR (CDCl₃, 400MHz)



¹³C NMR Spectrum of Compound 3x



¹H NMR (CDCl₃, 400MHz)



¹³C NMR Spectrum of Compound 3y



¹H NMR (CDCl₃, 400MHz)





S77



¹³C NMR Spectrum of Compound 3ab



¹³C NMR Spectrum of Compound 3ac



S80







¹³C NMR Spectrum of Compound 3af

-10.05 77.92 77.56 77.56 77.56 77.56







¹H NMR Spectrum of Compound 3ag





¹³C NMR Spectrum of Compound 3ag



¹³C NMR Spectrum of Compound 3ah

-10.03 -10.02 -10.02 -7.55 -7.







¹³C NMR Spectrum of Compound 3ai



¹³C NMR Spectrum of Compound 3aj





¹H NMR (CDCl₃, 400MHz)





¹³C NMR Spectrum of Compound 3al







¹³C NMR Spectrum of Compound 4b



¹³C NMR Spectrum of Compound 4c



¹³C NMR Spectrum of Compound 4d



¹³C NMR Spectrum of Compound 3am



¹³C NMR Spectrum of Compound 3an



¹³C NMR Spectrum of Compound 3ao



¹³C NMR Spectrum of Compound 3ap



¹³C NMR Spectrum of Compound 3aq



¹³C NMR Spectrum of Compound 3ar



¹H NMR Spectrum of Compound 3as



¹H NMR Spectrum of Compound 3at





¹H NMR Spectrum of Compound 3au



¹H NMR Spectrum of Compound 3av



¹³C NMR Spectrum of Compound 3av





¹³C NMR Spectrum of Compound 3aw





¹³C NMR Spectrum of Compound 3ax


¹³C NMR Spectrum of Compound 3ay



¹³C NMR Spectrum of Compound 3az



¹³C NMR Spectrum of Compound 3ba





¹³C NMR Spectrum of Compound 3bb



¹H NMR (CDCl₃, 400MHz)



¹³C NMR Spectrum of Compound 3bc



¹³C NMR Spectrum of Compound 3bd





¹³C NMR Spectrum of Compound 4e



¹³C NMR Spectrum of Compound 4f



¹³C NMR Spectrum of Compound 4g



S115



¹³C NMR Spectrum of Compound 4i



¹H NMR Spectrum of Compound 4j



¹³C NMR Spectrum of Compound 4j