SUPPORTING INFORMATION

Stereoselective Access to Furan-fused [5.5.0] Bicyclic Heterocycles enabled by Gold-Catalyzed Asymmetric [8+4] Cycloaddition

Xunhua Wang^[1], Jianhua Wang^{*[2]}, and Xiaoxun Li ^{*[1,3]}

1. Department of Medicinal Chemistry, Key Laboratory of Chemical Biology (Ministry of Education), NMPA Key Laboratory for Technology Research and Evaluation of Drug Products, School of Pharmaceutical Sciences, Cheeloo College of Medicine, Shandong University, Jinan, Shandong, 250012, China

2. Translational Pharmaceutical Laboratory, Jining First People's Hospital, Shandong First Medical University, Jining, 272000, China

Suzhou Research Institute of Shandong University, NO.388 Ruoshui Road, SIP, Suzhou, Jiangsu 215123, China

*Correspondence to: J. Wang: jianhua.wang_8710@163.com; X. Li: xli@sdu.edu.cn.

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1.General information

Unless otherwise noted, all the reactions for the preparation of the substrates were performed in oven-dried glassware under nitrogen atmosphere with freshly distilled solvents. The catalytic reactions were performed under nitrogen atmosphere. The solvents were purified by distillation from calcium hydride unless otherwise noted. All other commercial reagents were used without further purification unless otherwise indicated. ¹H NMR and ¹³C NMR spectra were recorded on Bruker 400 MHz spectrometer (ADVNCE III) using chloroform-d (CDCl₃) and dimethyl sulphoxide-d6 (DMSO- d6) as the internal standard. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.10) or tetramethylsilane (TMS δ 0.00) was used as a reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. The enantiomeric excesses (e.e.) was determined by HPLC analysis on LC-20AD/T LPGE KIT using Daicel CHIRALPAK® column. Xray diffraction analyses were carried out on a microcrystalline powder using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer using Cu radiation ($\lambda = 1.54184$ Å). If not specially mentioned, flash column chromatography was performed using 200-300 silica gel purchased from Yantai Chemicals (China). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization) as ionization method. Optical rotations were recorded on an AUTOPOL II digital polarimeter at 589 nm and are recorded as $[\alpha]_D^T$ (concentration in grams/100 mL solvent). The racemic 1-(1-alkynyl) cyclopropyl ketones ^[1-3], substituted tropones^[4] were prepared according to the reported procedures. The chiral gold catalyst was prepared according to the reported procedures.

2. Reaction optimizations

General procedure for the reaction optimization



To a dried tube was added $Ln(AuCl)_2$ (3.0 mol%) and catalyst (12.0 mol%) in the glove box, and the solvent (0.5 mL) was added. The mixture was stirred at room temperature for 10 min. Then the precipitate was removed and the remaining solution was transferred into a solution of cyclopropyl ketone **1a** (0.1 mmol, 1.0 equiv.) and tropone **2a** (x mmol) with 4 Å molecular sieves 150 mg in solvent (0.5 mL). The reaction was then stirred at the corresponding temperature. After the reaction was complete as monitored by TLC and HPLC analysis, it was filtered through a short pad of silica gel to remove catalyst rapidly. Then the solvent was removed under reduced pressure, and the residue was purified by a silica gel column using ethyl acetate/ petroleum ether (1/60-1/10) as the eluent to give the aim product **3a** and **asy-1a**.



Table 1. Investigation of chiral ligands

^a Unless otherwise indicated, all reactions were performed with **rac-1a** (0.1 mmol) and **2a** (0.08 mmol) in the presence of Ln(AuCl)₂ (3.0 mol%), AgPF₆ (12.0 mol%) in DCM (1.0 mL) at 0 °C under nitrogen atmosphere. ^b Isolated yield of product **3a**. ^c Determined by HPLC analysis. ^d Selectivity (s) values were calculated through the equation $s = \ln[(1 - C)(1 - ee_{1a})]/\ln[(1 - C)(1 + ee_{1a})]$, where C is the conversion; $C = ee_{1a}/(ee_{1a} + ee_{3a})$.

After optimization, L8 was selected for the following reaction optimization.

Table 2. Investigation of catalyst



Entry	catalyst	yield (3a) ^b	ee (3a) ^c	yield $(1a)^b$	ee (1a) ^c	time	S
1	AgPF ₆	39%	85%	38%	51%	24 h	20
2	AgOTf	36%	81%	41%	62%	20 h	18
3	AgNTf ₂	41%	71%	40%	95%	12 h	21
4	AgClO ₄	26%	78%	49%	65%	20 h	16
5	NaBAr ^F	40%	81%	38%	96%	12 h	37

^a Unless otherwise indicated, all reactions were performed with **rac-1a** (0.1 mmol) and **2a** (0.08 mmol) in the presence of **L8**(AuCl)₂ (3.0 mol%), catalyst (12.0 mol%) in DCM (1.0 mL) 0 °C under nitrogen atmosphere. ^b Isolated yield of product **3a**. ^c Determined by HPLC analysis. ^d Selectivity (s) values were calculated through the equation $s = \ln[(1 - C)(1 - ee_{1a})]/\ln[(1 - C)(1 + ee_{1a})]$, where C is the conversion; $C = ee_{1a}/(ee_{1a} + ee_{3a})$.

NaBAr^F = Sodium tetrakis (3,5-bis(trifluoro methyl)phenyl)borate

After optimization, NaBAr^F was selected for the following reaction optimization.

Ph ^w	0Me + n -1a	2a	L8(AuCl) ₂ (3.0 <u>NaBAr^F (12 r</u> solvent, ten 4Å MS	nol%) nol%) ıp.	Ph M O F 3a	e D + Ph	Ph Ph Ph	Me
Entry	temp.	solvent	yield (3a) ^b	ee (3a) ^c	yield (1a) ^b	ee (1a) ^c	time	S
1	0 °C	DCM	40%	81%	38%	96%	12 h	37
2	0 °C	DCE	31%	77%	35%	90%	12 h	23
3	0 °C	CHCl ₃	29%	80%	52%	75%	12 h	20
4	0 °C	PhF	21%	80%	53%	65%	12 h	18
5	0 °C	PhCl	38%	76%	36%	87%	12 h	20
6	0 °C	PhCF ₃	48%	65%	31%	99%	12 h	23
7	-10 °C	DCM	41%	83%	43%	94%	24 h	38
8	-20 °C	DCM	40%	89%	42%	89%	24 h	51
9	-30 °C	DCM	19%	91%	65%	38%	48 h	31

Table 3. Investigation of solvents and temperature

^a Unless otherwise indicated, all reactions were performed with **rac-1a** (0.1 mmol) and **2a** (0.08 mmol) in the presence of **L8**(AuCl)₂ (3.0 mol%), NaBAr^F (12.0 mol%) in solvent (1.0 mL) under nitrogen atmosphere. ^b Isolated yield of product **3a**. ^c Determined by HPLC analysis. ^d Selectivity (s) values were calculated through the equation $s = ln[(1 - C)(1 - ee_{1a})]/ln[(1 - C)(1 + ee_{1a})]$, where C is the conversion; C = $ee_{1a}/(ee_{1a} + ee_{3a})$.

After optimization, -20 °C was selected as the optimal reaction temperature.

3. Representative procedure and data for the synthesis of compound 3 or compound 4



To a dried flask was added L8AuCl (3.0 mol%) and NaBAr^F (12 mol%) in the glove box, and the solvent (1.0 mL) was added. Then the mixture was stirred at room temperature for 10 min. Then the solution was transferred into a solution of cyclopropyl ketone **1** (0.2 mmol, 1.0 equiv.) and tropone **2** (0.16 mmol, 0.8 equiv.) with 4 Å molecular sieves 300 mg in solvent (1.0 mL) at -20 °C. The reaction was then stirred at -20 °C for 12-72 h. After the reaction was monitored by TLC and HPLC analysis. The reaction was filtered by silica gel to remove catalyst rapidly. Then the solvent was removed under reduced pressure, and the residue was purified by a silica gel column using ethyl acetate/ petroleum ether (1/60-1/10) as the eluent to give the aim product, either compound **3** or compound **4**.



(5R,11R)-3-methyl-1,5-diphenyl-4,5-dihydro-11aH-cyclohepta[b]furo[3,4-

d]oxepine (3a)

White solid, 29 mg, m.p. = 80-82 °C; 67 mg, 40% yield; 89% ee; $[\alpha]_D^{20.0}$ =-1.4 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.6 min, t (minor) =7.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 3H), 3.01 (dd, *J* = 15.2, 4.3 Hz, 1H), 3.15 (dd, *J* = 15.2, 9.5 Hz, 1H), 3.28 (d, *J* = 6.0 Hz, 1H), 5.11 (dd, *J* = 9.5, 4.3 Hz, 1H), 5.30 (dd, *J* = 9.1, 6.0 Hz, 1H), 5.74 (d, *J* = 6.3 Hz, 1H), 6.31 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.44 (dd, *J* = 10.9, 6.4 Hz, 1H), 6.61 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.29-7.37 (m, 7H), 7.41-7.47 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 30.2, 40.1, 82.6, 113.2, 117.8, 120.9,

124.1, 125.9, 126.3, 126.8, 127.0, 127.8, 128.1, 128.3, 128.4, 128.7, 131.5, 140.6, 144.7, 146.4, 147.5; HRMS (ESI) m/z calcd for C₂₆H₂₂O₂ [M+H]⁺: 367.1693, found: 367.1691.



1-((1S,2R)-2-phenyl-1-(phenylethynyl)cyclopropyl)ethan-1-one (1a)

Yellow oil, 22 mg, 42% yield; 89% ee; $[\alpha]_D^{20.0}=72.1$ (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.2 min, t (minor) =5.7 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.77 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.12 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.51 (s, 3H), 2.96 (t, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.14 (d, *J* = 6.8 Hz, 3H), 7.18-7.23 (m, 3H), 7.24-7.30 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 26.5, 29.7, 33.4, 39.2, 84.5, 87.4, 123.0, 127.3, 128.0, 128.1, 128.2, 128.8, 131.4, 136.0, 204.9.



(5*R*,11*R*)-3-methyl-5-phenyl-1-(*p*-tolyl)-4,5-dihydro-11aH-cyclohepta[b]furo [3,4-d]oxepine (3b)

White solid, m.p. = 98-100 °C; 32 mg, 42% yield; 92% ee; $[\alpha]_D^{20.0}$ =-5.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.1 min, t (minor) =5.7 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.16 (s, 3H), 2.27 (s, 3H), 2.94 (dd, *J* = 15.2, 4.3 Hz, 1H), 3.07 (dd, *J* = 15.2, 9.4 Hz, 1H), 3.17 (d, *J* = 6.0 Hz, 1H), 5.05 (dd, *J* = 9.4, 4.2 Hz, 1H), 5.23 (dd, *J* = 9.1, 6.1 Hz, 1H), 5.67 (d, *J* = 6.3 Hz, 1H), 6.23 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.37 (dd, *J* = 10.9, 6.4 Hz, 1H), 6.53 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.23-7.28 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 21.3, 30.4, 40.2, 82.7, 113.0, 117.7, 120.2, 124.2, 125.8, 126.2, 126.8, 127.8, 128.1, 128.3, 128.6, 128.7, 129.1, 136.8, 140.7, 144.8, 146.1, 147.7; HRMS (ESI) m/z calcd for C₂₇H₂₄O₂ [M+H]⁺: 381.1849, found: 381.1845.



1-((*1S*,2*R*)-2-phenyl-1-(*p*-tolylethynyl)cyclopropyl)ethan-1-one (1b)

Yellow oil, 22 mg, 40% yield; 94% ee; $[\alpha]_D^{20.0}$ =58.9 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 99/1, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.9 min, t (minor) =5.4 min];¹H NMR (400 MHz, CDCl₃) δ 1.75 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.11 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.32 (s, 3H), 2.50 (s, 3H), 2.95 (t, *J* = 8.5 Hz, 1H), 6.93-6.95 (m, 4H), 7.17-7.22 (m, 3H), 7.22-7.29 (m, 2H);¹³C NMR (100 MHz, CDCl₃) δ 21.5, 26.5, 29.7, 33.4, 39.2, 84.6, 86.6, 120.0, 127.3, 128.0, 128.8, 129.0, 131.3, 136.0, 138.2, 205.1.



(5*R*,11*R*)-3-methyl-5-phenyl-1-(m-tolyl)-4,5-dihydro-11aH-cyclohepta[b]furo [3,4-d]oxepine (3c)

White solid, m.p. = 80-82 °C; 31 mg, 40% yield; 88% ee; $[\alpha]_D^{20.0}$ =-2.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.9 min, t (minor) =5.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.14 (s, 3H), 2.25 (s, 3H), 2.94 (dd, *J* = 15.1, 6.0 Hz, 1H), 3.06 (dd, *J* = 15.1, 9.4 Hz, 1H), 3.15 (d, *J* = 6.0 Hz, 1H), 5.04 (dd, *J* = 9.1, 3.7 Hz, 1H), 5.16-5.22 (m, 1H), 5.68 (d, *J* = 6.3 Hz, 1H), 6.23 (dd, *J* = 8.4, 6.0 Hz, 1H), 6.38 (dd, *J* = 10.8, 6.4 Hz, 1H), 6.53 (dd, *J* = 10.8, 5.4 Hz, 1H), 6.96 (d, *J* = 5.1 Hz, 1H), 7.09-7.16 (m, 2H), 7.18-7.24 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 21.6, 30.6, 40.2, 82.7, 112.8, 117.8, 120.7, 123.4, 124.1, 125.7, 126.7, 126.9, 127.6, 127.8, 128.1, 128.3, 128.4, 128.7, 131.3, 137.9, 140.8, 144.8, 146.3, 147.7; HRMS (ESI) m/z calcd for C₂₇H₂₄O₂ [M+H]⁺:381.1849, found: 381.1846.



1-((1S,2R)-2-phenyl-1-(m-tolylethynyl)cyclopropyl)ethan-1-one (1c)

Yellow oil, 24 mg, 43% yield; 97% ee; $[\alpha]_D^{20.0}=99.7$ (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.1 min, t (minor) =5.5 min];¹H NMR (400 MHz, CDCl₃) δ 1.83 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.19 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.26 (s, 3H), 2.58 (s, 3H), 3.03 (t, *J* = 8.5 Hz, 1H), 6.89-6.97 (m, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.26-7.36 (m, 3H), 7.31-7.37 (m, 2H);¹³C NMR (100 MHz, CDCl₃) δ 21.2, 26.5, 29.7, 33.4, 39.2, 84.6, 87.0, 122.8, 127.3, 128.0, 128.1, 128.4, 128.8, 128.9, 132.0, 136.0, 137.9, 205.0.



(5*R*,11*R*)-3-methyl-5-phenyl-1-(*o*-tolyl)-4,5-dihydro-11aH-cyclohepta[b]furo [3,4-d] oxepine (3d)

White solid, m.p. = 84-86 °C; 28 mg, 37% yield; 90% ee; $[\alpha]_D^{20.0}$ =-0.8 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/THF = 99/1, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.0 min, t (minor) =5.8 min];¹H NMR (400 MHz, CDCl₃) δ 1.93 (s, 3H), 2.23 (s, 3H), 2.86 (dd, *J* = 14.9, 6.6 Hz, 1H), 2.95 (d, *J* = 6.0 Hz, 1H), 3.09 (dd, *J* = 14.9, 5.2 Hz, 1H), 5.06-5.18 (m, 2H), 5.76 (d, *J* = 6.2 Hz, 1H), 6.00 (dd, *J* = 9.3, 5.4 Hz, 1H), 6.33 (dd, *J* = 10.9, 6.1 Hz, 1H), 6.45 (dd, *J* = 10.9, 5.4 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.14-7.18 (m, 3H), 7.18-7.25 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 11.2, 20.5, 29.8, 40.4, 83.2, 113.4, 115.8, 120.9, 123.7, 125.2, 125.4, 126.6, 127.9, 128.0, 128.1, 128.3, 128.4, 130.3, 130.6, 131.3, 137.9, 140.8, 145.5, 146.5, 147.5; HRMS (ESI) m/z calcd for C₂₇H₂₄O₂ [M+H]⁺: 381.1849, found: 381.1849.



1-((1S,2R)-2-phenyl-1-(o-tolylethynyl)cyclopropyl)ethan-1-one (1d)

Yellow oil, 21.3 mg, 39% yield; 95% ee; $[\alpha]_D^{20.0}$ =73.8 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 99/1, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.4 min, t (minor) =7.7 min];¹H NMR (400 MHz, CDCl₃) δ 1.86 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.09 (s, 3H), 2.19 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.61 (s, 3H), 3.07 (t, *J* = 8.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 7.04-7.16 (m, 3H), 7.24-7.35 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 20.5, 26.5, 29.8, 33.5, 39.1, 83.4, 91.1, 122.8, 125.5, 127.3, 128.0, 128.1, 128.9, 129.3, 131.9, 136.0, 140.0, 205.0.



(*5R*,*11aR*)-1-(4-ethylphenyl)-3-methyl-5-phenyl-4,5-dihydro-11aH-cyclohepta[b] furo[3,4-d]oxepine (3e)

White solid, m.p. = 100-102 °C; 28 mg, 36% yield; 91% ee; $[\alpha]_D^{20.0}$ =-0.9 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.4 min, t (minor) =5.7 min];¹H NMR (400 MHz, CDCl₃) δ 1.25 (t, *J* = 7.5 Hz, 3H), 2.25 (s, 3H), 2.65 (q, *J* = 7.5 Hz, 2H), 3.02 (dd, *J* = 15.1, 4.2 Hz, 1H), 3.16 (dd, *J* = 15.1, 9.6 Hz, 1H), 3.28 (d, *J* = 6.1 Hz, 1H), 5.13 (dd, *J* = 9.5, 4.2 Hz, 1H), 5.33 (dd, *J* = 9.1, 6.0 Hz, 1H), 5.75 (d, *J* = 6.4 Hz, 1H), 6.33 (dd, *J* = 9.1, 5.6 Hz, 1H), 6.46 (dd, *J* = 10.9, 6.3 Hz, 1H), 6.62 (dd, *J* = 10.8, 5.4 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H) 7.29-7.45 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 15.5, 28.7, 30.3, 40.1, 82.6, 113.0, 117.7, 120.2, 124.2, 125.8, 126.2, 126.8, 127.7, 127.9, 128.1, 128.3, 128.7, 128.9, 140.7, 143.1, 144.8, 146.0, 147.7; HRMS (ESI) m/z calcd for C₂₈H₂₆O₂ [M+H]⁺: 395.2006, found: 395.2003.



1-((1S,2R)-1-((4-ethylphenyl)ethynyl)-2-phenylcyclopropyl)ethan-1-one (1e)

Yellow oil, 24 mg, 42% yield; 93% ee; $[\alpha]_D^{20.0}$ =63.9 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.7 min, t (minor) =5.3 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.20 (t, *J* = 7.6 Hz, 3H), 1.85 (dd, *J* = 7.9, 4.2 Hz, 1H), 2.20 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.60 (s, 3H), 2.61 (q, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 8.5 Hz, 1H), 7.06-7.08 (m, 4H), 7.26-7.38 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 15.4, 26.5, 28.8, 29.7, 33.4, 39.2, 84.6, 86.6, 120.2, 127.2, 127.8, 128.0, 128.7, 131.4, 136.0, 144.5, 205.1.



(5*R*,11*R*)-3-methyl-5-phenyl-1-(4-propylphenyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d] oxepine (3f)

White solid, m.p. = 84-86 °C; 33 mg, 40% yield; 85% ee; $[\alpha]_D^{20.0}$ =-0.5 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.3 min, t (minor) =5.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.60-1.67 (m, 2H), 2.23 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.99 (dd, *J* = 15.2, 4.2 Hz, 1H), 3.14 (dd, *J* = 15.2, 9.5 Hz, 1H), 3.26 (d, *J* = 6.1 Hz, 1H), 5.11 (dd, *J* = 9.5, 4.2 Hz, 1H), 5.30 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.73 (d, *J* = 6.3 Hz, 1H), 6.30 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.44 (dd, *J* = 10.9, 6.4 Hz, 1H), 6.60 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.30-7.38 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 13.9, 24.5, 30.3, 37.9, 40.1, 82.6, 113.0, 117.7, 120.2, 124.2, 125.8, 126.1, 126.8, 127.7, 128.1, 128.3, 128.5, 128.7, 128.9, 140.7, 141.6, 144.8, 146.0, 147.7; HRMS (ESI) m/z calcd for C₂₉H₂₈O₂ [M+H]⁺: 409.2162, found: 409.2162.



1-((15,25)-2-phenyl-1-((4-propylphenyl)ethynyl)cyclopropyl)ethan-1-one (1f)

Yellow oil, 23 mg, 38% yield; 88% ee; $[\alpha]_D^{20.0}=87.1$ (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.6 min, t (minor) =5.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 0.82 (t, *J* = 7.3 Hz, 3H), 1.50 (p, *J* = 7.5 Hz, 2H), 1.75 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.11 (dd, *J* = 9.2, 4.2 Hz, 1H), 2.44 (d, *J* = 7.8 Hz, 2H), 2.50 (s, 3H), 2.95 (t, *J* = 8.5 Hz, 1H), 6.90-6.99 (m, 4H), 7.14-7.28 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 13.8, 24.4, 26.5, 29.7, 33.4, 38.0, 39.2, 84.6, 86.6, 120.2, 127.3, 128.0, 128.4, 128.8, 131.3, 136.0, 143.0, 205.1.



(*5R*,*11R*)-5-(3-bromophenyl)-3-methyl-1-(naphthalen-1-yl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3g)

White solid, m.p. = 110-112 °C; 40 mg, 40% yield; 82% ee; $[\alpha]_D^{20.0}$ =-4.4 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.0 min, t (minor) =5.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.07 (s, 3H), 2.92 (dd, *J* = 15.0, 6.1 Hz, 1H), 3.09 (d, *J* = 6.0 Hz, 1H), 3.28 (dd, *J* = 15.1, 5.1 Hz, 1H), 5.10 (dd, *J* = 9.2, 6.1 Hz, 1H), 5.25 (t, *J* = 5.6 Hz, 1H), 5.87 (d, *J* = 6.1 Hz, 1H), 5.97 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.41 (dd, *J* = 11.0, 6.1 Hz, 1H), 6.50 (dd, *J* = 10.9, 5.4 Hz, 1H), 7.19-7.27 (m, 2H), 7.42-7.46 (m, 3H), 7.46-7.48 (m, 1H), 7.48-7.52 (m, 2H), 7.90-7.84 (m, 2H), 7.98-8.09 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 11.4, 29.9, 40.5, 82.3, 113.4, 115.7, 121.9, 122.3, 123.6, 125.0, 125.1, 125.2, 126.1, 126.4, 126.5, 127.7, 128.2, 128.6, 128.7, 129.0, 129.1, 129.7, 129.9, 131.0, 132.4, 133.8, 143.1, 144.9, 146.9, 147.4; HRMS (ESI) m/z calcd for C₃₀H₂₃BrO₂ [M+H]⁺: 495.0954, found: 495.0955.



1-((*1S*,2*R*)-2-(3-bromophenyl)-1-(naphthalen-1-ylethynyl)cyclopropyl)ethan-1one (1g)

Yellow oil, 29 mg, 37% yield; 93% ee; $[\alpha]_D^{20.0}$ =42.4 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.6 min, t (minor) =11.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.85 (dd, J = 8.0, 4.4 Hz, 1H), 2.16 (dd, J = 9.1, 4.4 Hz, 1H), 2.61 (s, 3H), 3.04 (d, J = 8.4 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 8.1 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 7.32-7.41 (m, 4H), 7.43-7.53 (m, 2H), 7.70 (t, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 26.4, 29.8, 33.5, 38.1, 83.0, 91.5, 120.4, 122.4, 125.2, 125.8, 126.4, 126.9, 127.9, 128.2, 128.7, 129.9, 130.5, 130.6, 132.0, 133.1, 133.2, 138.6, 204.5.



(5*R*,11*R*)-3-methyl-5-phenyl-1-(thiophen-3-yl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3h)

White solid, m.p. = 104-106 °C; 31 mg, 42% yield; 80% ee; $[\alpha]_D^{20.0}$ =-1.9 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.8 min, t (minor) =7.6 min];¹H NMR (400 MHz, CDCl₃) δ 2.17 (s, 3H), 2.91 (dd, *J* = 15.4, 3.2 Hz, 1H), 2.98 (d, *J* = 6.4 Hz, 1H), 3.09 S13 (dd, J = 15.5, 9.8 Hz, 1H), 5.07 (dd, J = 9.8, 3.1 Hz, 1H), 5.19 (dd, J = 8.9, 6.5 Hz, 1H), 5.75 (d, J = 6.3 Hz, 1H), 6.27 (dd, J = 9.0, 5.5 Hz, 1H), 6.45 (dd, J = 10.9, 6.3 Hz, 1H), 6.57 (dd, J = 10.9, 5.5 Hz, 1H), 7.05-7.09 (m, 1H), 7.14-7.18 (m, 1H), 7.17-7.22 (m, 1H), 7.23-7.26 (m, 1H), 7.26-7.32 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 32.3, 40.6, 83.4, 111.6, 117.8, 119.8, 120.0, 124.1, 125.4, 125.5, 125.9, 126.5, 127.2, 128.1, 128.4, 129.0, 132.2, 141.1, 144.8, 145.0, 145.6; HRMS (ESI) m/z calcd for C₂₄H₂₀O₂S [M+H]⁺: 373.1257, found: 373.1260.



1-((1S,2R)-2-phenyl-1-(thiophen-3-ylethynyl)cyclopropyl)ethan-1-one (1h)

Yellow oil, 22 mg, 41% yield; 86% ee; $[\alpha]_D^{20.0}=25.8$ (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 99/1, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.7 min, t (minor) =8.6 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.83 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.19 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.56 (s, 3H), 3.02 (t, *J* = 8.5 Hz, 1H), 6.81 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.13 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.17 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.24-7.31 (m, 3H), 7.31-7.39 (m, 2H);¹³C NMR (100 MHz, CDCl₃) δ 26.5, 29.7, 33.4, 39.2, 79.5, 86.9, 122.0, 125.2, 127.3, 128.0, 128.3, 128.8, 129.7, 136.0, 204.9.

(5*R*,11*R*)-5-(4-fluorophenyl)-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3i)

White solid, m.p. = 86-88 °C; 30 mg, 39% yield; 85% ee; $[\alpha]_D^{20.0}$ =-1.9 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.3 min, t (minor) =5.3 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, 3H), 3.00 (dd, *J* = 15.1, 4.6 Hz, 1H), 3.09 (dd, *J* = 15.2, 9.2 Hz, 1H), 3.29 (d, *J* = 6.0 Hz, 1H), 5.10 (dd, *J* = 9.2, 4.6 Hz, 1H), 5.30 (dd, *J* = 9.2, 5.9 Hz, 1H), 5.71 (d, *J* = 6.4 Hz, 1H), 6.30 (dd, *J* = 9.3, 5.5 Hz, 1H), 6.44 (dd, *J* = 10.9, 6.4 Hz, 1H), 6.61 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.01 (t, *J* = 8.7 Hz, 2H), 7.20-7.25 (m, 1H), 7.26-7.36 (m, 4H), 7.44 (d, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 29.9, 40.0, 81.7, 113.5, 115.1 (d, J = 21.3 Hz), 117.5, 120.7, 124.1, 126.0, 126.3, 127.1, 128.0, 128.4, 128.5, 128.6 (d, J = 8.0 Hz), 131.4, 136.4 (d, J = 3.2 Hz), 144.4, 146.5, 147.5, 162.6 (d, J = 246.2 Hz); HRMS (ESI) m/z calcd for C₂₆H₂₁FO₂ [M+H]⁺: 384.1526, found: 384.1521.



1-((1S,2R)-2-(4-fluorophenyl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1i)

Yellow oil, 21 mg, 37% yield; 95% ee; $[\alpha]_D^{20.0}=57.4$ (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.7 min, t (minor) =7.7 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.78 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.18 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.58 (s, 3H), 3.01 (t, *J* = 8.5 Hz, 1H), 7.03 (t, *J* = 8.7 Hz, 2H), 7.14 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.21-7.27 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 26.7, 29.7, 33.2, 38.3, 84.6, 87.2, 114.9 (d, *J* = 21.5 Hz), 122.9, 128.2, 128.3, 130.3 (d, *J* = 8.1 Hz), 131.4, 131.8 (d, *J* = 3.1 Hz), 162.2 (d, *J* = 245.7 Hz), 204.8.



(*5R*,*11aR*)-5-(4-chlorophenyl)-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3j)

White solid, m.p. = 110-112 °C; 30 mg, 37% yield; 90% ee; $[\alpha]_D^{20.0}$ =-3.1(0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 98/2, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.8 min, t (minor) =5.8 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.15 (s, 3H), 2.93 (dd, *J* = 15.2, 4.6 Hz, 1H), 3.01 (dd, *J* = 15.2, 9.0 Hz, 1H), 3.20 (d, *J* = 5.9 Hz, 1H), 5.01 (dd, *J* = 9.2, 4.7 Hz, 1H), 5.22 (dd, *J* = 9.1, 6.2 Hz, 1H), 5.65 (d, *J* = 6.4 Hz, 1H), 6.23 (dd, *J* = 9.1, 5.7 Hz, 1H), 6.37 (dd, *J* = 11.0, 6.4 Hz, 1H), S15 6.54 (dd, J = 11.0, 5.5 Hz, 1H), 7.12-7.22 (m, 4H), 7.22-7.30 (m, 3H), 7.36 (d, J = 7.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 29.9, 40.0, 81.7, 113.4, 117.4, 120.7, 124.0, 126.0, 126.3, 127.1, 128.1, 128.2, 128.4, 128.5, 131.4, 133.9, 139.0, 144.3, 146.5, 147.5; HRMS (ESI) m/z calcd for $C_{26}H_{21}ClO_2$ [M+H]⁺: 401.1303, found: 401.1300.



1-((1S,2R)-2-(4-chlorophenyl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1j)

Yellow oil, 22 mg, 39% yield; 82% ee; $[\alpha]_{D}^{20.0}$ =61.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm \times 25 cm), *n*-hexane/2-propanol = 98/2, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.9 min, t (minor) =5.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.72 (dd, J = 7.9, 4.3 Hz, 1H), 2.12 (dd, J = 9.1, 4.3 Hz, 1H), 2.52 (s, 3H), 2.93 (t, J = 8.5 Hz, 1H), 7.09 $(dd, J = 7.4, 2.2 Hz, 2H), 7.13-7.17 (m, 2H), 7.18-7.22 (m, 3H), 7.23-7.27 (m, 2H); {}^{13}C$ NMR (100 MHz, CDCl₃) δ 26.7, 29.7, 33.3, 38.2, 84.8, 87.0, 122.8, 128.2, 128.3, 128.4, 130.0, 131.4, 133.1, 134.6, 204.7.



(5R,11R)-5-(4-bromophenyl)-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3k)

White solid, m.p. = 122-124 °C; 34 mg, 38% yield; 90% ee; $[\alpha]_{D}^{20.0}$ = -4.8 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm \times 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, $\lambda = 254$ nm, t (major) =6.2 min, t (minor) =9.4 min]; ¹H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.93 (dd, J = 15.2, 4.8 Hz, 1H), 3.01 (dd, J = 15.2, 8.9 Hz, 1H), 3.20 (d, J = 6.0 Hz, 1H), 5.00 (dd, J = 8.9, 4.7 Hz, 1H), 5.22 (dd, J = 9.1, 6.0 Hz, 1H),5.66 (d, *J* = 6.3 Hz, 1H), 6.23 (dd, *J* = 9.2, 5.6 Hz, 1H), 6.37 (dd, *J* = 10.9, 6.3 Hz, 1H), 6.54 (dd, J = 10.9, 5.5 Hz, 1H), 7.12-7.18 (m, 3H), 7.26 (t, J = 7.7 Hz, 2H), 7.34-7.43 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 29.9, 40.0, 81.7, 113.4, 117.4, 120.6, 122.1, 124.0, 126.0, 126.3, 127.1, 128.1, 128.4, 128.5, 128.6, 131.3, 131.4, 139.5, 144.3, 146.5, 147.5; HRMS (ESI) m/z calcd for C₂₆H₂₁BrO₂ [M+H]⁺: 445.0798, found: 445.0796.



1-((1S,2R)-2-(4-bromophenyl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1k)

Yellow oil, 25 mg, 37% yield; 85% ee; $[\alpha]_D^{20.0}=107.8$ (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.0 min, t (minor) =5.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.78 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.18 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.58 (s, 3H), 2.98 (t, *J* = 8.5 Hz, 1H), 7.12-7.20 (m, 4H), 7.23-7.28 (m, 3H), 7.46 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 29.7, 33.2, 38.2, 84.9, 86.9, 121.2, 122.8, 128.3, 128.4, 130.4, 131.1, 131.4, 135.2, 204.7; HRMS (ESI) m/z calcd. for C₁₉H₁₅BrO [M+H]⁺: 375.0946, found: 375.0947.



(5*R*,11*R*)-3-methyl-1-phenyl-5-(*p*-tolyl)-4,5-dihydro-11aH-cyclohepta[b]furo[3,4d]oxepine (3l)

White solid, m.p. = 87-89 °C; 27 mg, 35% yield; 86% ee; $[\alpha]_D^{20.0}$ =-2.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.7 min, t (minor) =9.7 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 3H), 2.34 (s, 3H), 2.96 (dd, *J* = 15.2, 4.2 Hz, 1H), 3.16 (dd, *J* = 15.2, 10.0 Hz, 1H), 3.29 (d, *J* = 6.0 Hz, 1H), 5.07 (dd, *J* = 10.0, 4.2 Hz, 1H), 5.30 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.71 (d, *J* = 6.4 Hz, 1H), 6.31 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.43 (dd, *J* = 5.7 min) 10.9, 6.4 Hz, 1H), 6.59 (dd, J = 10.9, 5.5 Hz, 1H), 7.14 (d, J = 7.9 Hz, 2H), 7.21-7.26 (m, 3H), 7.33 (t, J = 7.6 Hz, 2H), 7.43 (dd, J = 7.5, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 30.0, 40.0, 82.4, 113.2, 118.0, 121.0, 124.1, 126.0, 126.1, 126.8, 126.9, 127.7, 128.4, 128.7, 128.9, 131.4, 137.6, 137.9, 144.7, 146.4, 147.4; HRMS (ESI) m/z calcd for C₂₇H₂₄O₂ [M+H]⁺: 381.1849, found: 381.1850.



1-((1S,2R)-1-(phenylethynyl)-2-(p-tolyl)cyclopropyl)ethan-1-one (11)

Yellow oil, 20 mg, 36% yield; 94% ee; $[\alpha]_D^{20.0}$ =59.7 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.9 min, t (minor) =5.1 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.81 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.19 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.35 (s, 3H), 2.58 (s, 3H), 2.99 (t, *J* = 8.5 Hz, 1H), 7.12-7.19 (m, 5H), 7.21-7.31 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 26.7, 29.7, 33.4, 39.3, 84.4, 87.6, 123.2, 128.0, 128.2, 128.6, 128.7, 131.4, 132.9, 137.0, 205.0.



(5*S*,11*aR*)-5-(4-(*tert*-butyl)phenyl)-3-methyl-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3m)

White solid, m.p. = 80-82 °C; 31 mg, 36% yield; 86% ee; $[\alpha]_D^{20.0}$ =-2.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.9 min, t (minor) =6.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.35 (s, 9H), 2.28 (s, 3H), 2.36 (s, 3H), 3.00 (dd, *J* = 15.2, 4.0 Hz, 1H), 3.19 (dd, *J* = 15.2, 9.9 Hz, 1H), 3.27 (d, *J* = 6.1 Hz, 1H), 5.11 (dd, *J* = 9.9, 3.9 Hz, 1H), 5.33 (dd, J = 9.1, 6.1 Hz, 1H), 5.79 (d, J = 6.3 Hz, 1H), 6.34 (dd, J = 9.2, 5.5 Hz, 1H), 6.48 (dd, J = 10.9, 6.3 Hz, 1H), 6.63 (dd, J = 10.9, 5.4 Hz, 1H), 7.17 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.30-7.40 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 30.6, 31.4, 34.6, 40.2, 82.6, 112.8, 118.0, 120.3, 124.3, 125.2, 125.7, 126.1, 126.5, 127.5, 128.7, 128.8, 129.1, 136.7, 137.9, 145.0, 145.9, 147.7, 151.0; HRMS (ESI) m/z calcd for C₃₁H₃₂O₂ [M+H]⁺: 437.2475, found: 437.2480.



1-((1S,2R)-2-(4-(tert-butyl)phenyl)-1-(p-tolylethynyl)cyclopropyl)ethan-1-one (1m)

Yellow oil, 24 mg, 37% yield; 83% ee; $[\alpha]_D^{20.0}$ =67.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.5 min, t (minor) =4.3 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.26 (s, 9H), 1.76 (dd, *J* = 7.9, 4.2 Hz, 1H), 2.11 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.22 (s, 3H), 2.49 (s, 3H), 2.94 (t, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 7.11-7.18 (m, 2H), 7.26-7.33 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 26.5, 29.7, 31.5, 33.4, 34.6, 39.2, 84.3, 87.0, 120.0, 125.0, 128.5, 128.9, 131.3, 133.1, 138.1, 150.2, 205.2.



(5*S*,*11aR*)-5-([1,1'-biphenyl]-4-yl)-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3n)

White solid, m.p. = 74-76 °C; 33 mg, 37% yield; 87% ee; $[\alpha]_D^{20.0}$ =-5.5 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.2 min, t (minor) =7.1 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 3H), 3.03 (dd, *J* = 15.2, 4.3 Hz, 1H), 3.19 (dd, *J* = 15.2, 9.5 Hz, 1H), 3.30 (d, J = 6.0 Hz, 1H), 5.15 (dd, J = 9.6, 4.2 Hz, 1H), 5.32 (dd, J = 9.1, 6.0 Hz, 1H), 5.78 (d, J = 6.4 Hz, 1H), 6.32 (dd, J = 9.3, 5.6 Hz, 1H), 6.45 (dd, J = 10.9, 6.4 Hz, 1H), 6.61 (dd, J = 10.9, 5.5 Hz, 1H), 7.19-7.24 (m, 1H), 7.33 (t, J = 7.6 Hz, 3H), 7.38-7.47 (m, 6H), 7.55-7.60 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 30.1, 40.1, 82.3, 113.3, 117.8, 120.9, 124.1, 125.9, 126.2, 126.9, 127.0, 127.1, 127.3, 127.4, 127.8, 128.4, 128.7, 128.8, 131.4, 139.6, 140.8, 141.0, 144.6, 146.4, 147.4; HRMS (ESI) m/z calcd for C₃₂H₂₆O₂ [M+H]⁺: 443.2006, found: 443.2005.



1-((*IS*,*2R***)-2-([1,1'-biphenyl]-4-yl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1n)** Yellow oil, 27 mg, 39% yield; 92% ee; $[\alpha]_D^{20.0}$ =33.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =11.4 min, t (minor) =9.5 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.81 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.16 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.53 (s, 3H), 3.01 (t, *J* = 8.5 Hz, 1H), 7.03-7.09 (m, 2H), 7.10-7.18 (m, 3H), 7.25-7.32 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.48-7.55 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 26.7, 29.7, 33.5, 39.0, 84.6, 87.4, 123.0, 126.8, 127.1, 127.4, 128.1, 128.3, 128.9, 129.1, 131.4, 135.1, 140.2, 140.9, 204.9.



(*5R*,*11R*)-5-(3-fluorophenyl)-3-methyl-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (30)

White solid, m.p. = 90-92 °C; 32 mg, 40% yield; 87% ee; $[\alpha]_D^{20.0}$ =-1.5 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.0 min, t (minor) =9.7 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.16 (s, 3H), 2.34 (s, 3H), 3.07 (dd, *J* = 6.3, 4.4 Hz, 2H), 3.15 (d, *J* = 6.2 Hz, 1H), 5.30 (dd, *J* = 9.1, 6.3 Hz, 1H), 5.53 (dd, *J* = 7.6, 4.9 Hz, 1H), 5.82 (d, *J* = 6.3 Hz, 1H), 6.30 (dd, *J* = 9.1, 5.5 Hz, 1H), 6.49 (dd, *J* = 10.9, 6.2 Hz, 1H), 6.64 (dd, *J* = 10.8, 5.5 Hz, 1H), 7.02-7.11 (m, 2H), 7.14 (d, J = 7.9 Hz, 2H), 7.24-7.30 (m, 1H), 7.31-7.39 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 11.4, 21.3, 30.1, 40.4, 75.9 (d, J = 3.3 Hz), 112.5, 115.3 (d, J = 21.9 Hz), 117.4, 119.8, 123.9 (d, J = 3.6 Hz), 124.1, 125.4, 126.4, 127.7 (d, J = 3.8 Hz), 127.9, 128.1 (d, J = 13.0 Hz), 128.5, 128.7, 129.0, 129.4 (d, J = 8.3 Hz), 136.8, 144.6, 146.3, 147.8, 159.6 (d, J = 246.3 Hz); HRMS (ESI) m/z calcd for C₂₇H₂₃FO₂ [M+H]⁺: 399.1405, found: 399.1403.



1-((1S,2R)-2-(3-fluorophenyl)-1-(p-tolylethynyl)cyclopropyl)ethan-1-one (10)

Yellow oil, 22 mg, 38% yield; 96% ee; $[\alpha]_D^{20.0}=21.5$ (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.0 min, t (minor) =6.7 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.81 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.21 (dd, *J* = 9.0, 4.3 Hz, 1H), 2.29 (s, 3H), 2.59 (s, 3H), 3.05 (t, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.02-7.13 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.24-7.28 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 25.0, 29.5, 32.2, 32.8 (d, *J* = 4.3 Hz), 83.8, 86.3, 115.1 (d, *J* = 21.5 Hz), 119.8, 123.5 (d, *J* = 3.6 Hz), 123.9 (d, *J* = 14.2 Hz), 128.9 (d, *J* = 8.2 Hz), 129.0, 129.3 (d, *J* = 3.6 Hz), 131.3, 138.2, 162.7 (d, *J* = 247.7 Hz), 204.9.



(*5R*,*11R*)-5-(3-chlorophenyl)-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d] oxepine (3p) White solid, m.p. = 80-82 °C; 27 mg, 34% yield; 92% ee; $[\alpha]_D^{20.0}$ =-2.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.3 min, t (minor) =4.8 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.23 (s, 3H), 2.99-3.12 (m, 2H), 3.24 (d, *J* = 6.1 Hz, 1H), 5.09 (dd, *J* = 8.6, 4.8 Hz, 1H), 5.29 (dd, *J* = 9.1, 6.1 Hz, 1H), 5.78 (d, *J* = 6.3 Hz, 1H), 6.31 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.46 (dd, *J* = 10.9, 6.3 Hz, 1H), 6.63 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.20-7.29 (m, 4H), 7.31-7.36 (m, 3H), 7.42-7.46 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 30.2, 40.1, 81.8, 113.2, 117.3, 120.6, 124.0, 124.8, 125.9, 126.3, 127.0, 127.1, 128.1, 128.2, 128.4, 128.5, 129.6, 131.3, 134.2, 142.7, 144.3, 146.6, 147.6; HRMS (ESI) m/z calcd for C₂₆H₂₁ClO₂ [M+H]⁺: 401.1303, found: 401.1296.



1-((15,2R)-2-(3-chlorophenyl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1p)

Yellow oil, 21 mg, 36% yield; 96% ee; $[\alpha]_D^{20.0}$ =63.4 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.7 min, t (minor) =6.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.80 (dd, *J* = 7.9, 4.4 Hz, 1H), 2.18 (dd, *J* = 9.1, 4.4 Hz, 1H), 2.59 (s, 3H), 3.00 (t, *J* = 8.5 Hz, 1H), 7.14-7.21 (m, 3H), 7.23-7.29 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 29.7, 33.3, 38.2, 85.0, 86.8, 122.8, 127.2, 127.5, 128.3, 128.4, 128.7, 129.3, 131.4, 133.9, 138.2, 204.6.



(*5R*,*11R*)-5-(3-bromophenyl)-3-methyl-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d] oxepine (3q)

White solid, m.p. = 110-112 °C; 35 mg, 38% yield; 87% ee; $[\alpha]_D^{20.0}$ =-2.4 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.6 min, t (minor) =5.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.13 (s, 3H); 2.26 (s, 3H), 2.97 (dd, *J* = 6.7, 4.8 Hz, 2H), 3.13 (d, *J* = 6.1 Hz, 1H), 5.00 (dd, *J* = 8.2, 5.0 Hz, 1H), 5.21 (dd, *J* = 9.1, 6.1 Hz, 1H), 5.70 (d, *J* = 6.3 Hz, 1H), 6.22 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.38 (dd, *J* = 10.9, 6.3 Hz, 1H), 6.55 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.16-7.21 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.31-7.38 (m, 1H), 7.42 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 21.3, 30.4, 40.1, 81.8, 113.0, 117.2, 119.9, 122.4, 124.2, 125.3, 125.7, 126.3, 128.0, 128.4, 128.6, 129.1, 129.8, 129.9, 131.1, 136.9, 143.0, 144.4, 146.2, 147.8; HRMS (ESI) m/z calcd for C₂₇H₂₃BrO₂ [M+H]⁺: 459.0890, found: 459.0894.



1-((1S,2R)-2-(3-bromophenyl)-1-(p-tolylethynyl)cyclopropyl)ethan-1-one (1q)

Yellow oil, 26 mg, 37% yield; 97% ee; $[\alpha]_D^{20.0}$ =41.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.4 min, t (minor) =7.2 min];¹H NMR (400 MHz, CDCl₃) δ 1.78 (dd, *J* = 7.9, 4.4 Hz, 1H), 2.16 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.31 (s, 3H), 2.58 (s, 3H), 2.97 (t, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.17-7.24 (m, 2H), 7.36-7.43 (m, 1H), 7.44 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 26.6, 29.7, 33.3, 38.0, 85.2, 85.9, 119.7, 122.1, 127.7, 129.1, 129.5, 130.3, 131.4, 131.6, 138.4, 138.5, 204.8.



(5*R*,11*R*)-5-(2-chlorophenyl)-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3r)

White solid, m.p. = 98-100 °C; 29 mg, 36% yield; 86% ee; $[\alpha]_D^{20.0}$ =-1.9 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 99.5/0.5, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.0 min, t (minor) =6.3 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.03 (s, 3H), 2.91 (dd, *J* = 15.2, 7.3 Hz, 1H), 2.99 (d, *J* = 6.4 Hz, 1H), 3.06 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.22 (t, *J* = 7.7 Hz, 1H), 5.53 (dd, *J* = 7.3, 3.6 Hz, 1H), 5.83 (d, *J* = 6.2 Hz, 1H), 6.20-6.27 (m, 1H), 6.46 (dd, *J* = 10.7, 6.6 Hz, 1H), 6.60 (dd, *J* = 10.8, 5.7 Hz, 1H), 7.11-7.16 (m, 3H), 7.24 (d, *J* = 7.1 Hz, 2H), 7.26-7.24 (m, 2H), 7.36-7.39 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.3, 30.3, 40.7, 79.5, 111.8, 117.5, 120.3, 123.8, 125.1, 126.6, 126.7, 127.0, 127.5, 127.7, 128.3, 128.5, 128.9, 129.3, 131.4, 131.8, 138.6, 144.6, 146.8, 147.7; HRMS (ESI) m/z calcd for C₂₆H₂₁ClO₂ [M+H]⁺: 401.1213, found: 401.1217.



1-((1S,2R)-2-(2-chlorophenyl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1r)

Yellow oil, 25 mg, 42% yield; 82% ee; $[\alpha]_D^{20.0}$ =52.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.0 min, t (minor) =8.1 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.86 (dd, *J* = 8.0, 4.3 Hz, 1H), 2.26 (dd, *J* = 8.8, 4.3 Hz, 1H), 2.62 (s, 3H), 3.06 (t, *J* = 8.4 Hz, 1H), 6.94-7.04 (m, 2H), 7.17-7.23 (m, 4H), 7.24-7.27 (m, 2H), 7.41-7.46 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 25.2, 29.4, 32.1, 37.8, 83.2, 87.0, 122.9, 126.5, 128.0, 128.2, 128.7, 129.2, 129.4, 131.4, 134.7, 136.8, 204.9.



(*5R*,*11R*)-5-(2-bromophenyl)-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3s)

White solid, m.p. = 126-128 °C; 33 mg, 37% yield; 85% ee; $[\alpha]_D^{20.0}$ =-1.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.1 min, t (minor) =5.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.04 (s, 3H), 2.90 (dd, *J* = 15.3, 7.3 Hz, 1H), 2.98 (d, *J* = 6.5 Hz, 1H), 3.08 (dd, *J* = 15.2, 3.7 Hz, 1H), 5.23 (dd, *J* = 8.9, 6.5 Hz, 1H), 5.47 (dd, *J* = 7.3, 3.7 Hz, 1H), 5.84 (d, *J* = 6.2 Hz, 1H), 6.24 (dd, *J* = 9.1, 5.5 Hz, 1H), 6.48 (dd, *J* = 10.8, 6.2 Hz, 1H), 6.60 (dd, *J* = 10.8, 5.5 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.14-7.21 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 11.3, 30.5, 40.7, 81.8, 111.7, 117.5, 120.3, 122.0, 123.8, 125.1, 125.7, 126.6, 127.0, 127.3, 127.7, 128.3, 128.5, 129.2, 131.4, 132.6, 140.2, 144.6, 146.8, 147.7; HRMS (ESI) m/z calcd for C₂₆H₂₁BrO₂ [M+H]⁺: 445.0798, found: 445.0796.



1-((1S,2R)-2-(2-bromophenyl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1s)

Yellow oil, 25 mg, 37% yield; 93% ee; $[\alpha]_D^{20.0}$ =32.9 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.4 min, t (minor) =8.5 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.79 (dd, *J* = 8.0, 4.3 Hz, 1H), 2.18 (dd, *J* = 8.7, 4.3 Hz, 1H), 2.56 (s, 3H), 2.96 (t, *J* = 8.4 Hz, 1H), 6.85-6.96 (m, 2H), 7.06-7.16 (m, 5H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 25.7, 29.5, 32.3, 40.4, 83.3, 87.0, 122.9, 127.1, 127.5, 128.0, 128.2, 128.9, 129.6, 131.4, 132.4, 136.4, 205.0.



(*5R*,*11R*)-5-(3-bromo-4-methylphenyl)-3-methyl-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3t)

White solid, m.p. = 70-74 °C; 36 mg, 38% yield; 94% ee; $[\alpha]_D^{20.0}$ =-3.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.8 min, t (minor) =6.1 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 3H), 2.36 (s, 3H), 2.40 (s, 3H), 3.00 (dd, *J* = 15.2, 4.4 Hz, 1H), 3.11 (dd, *J* = 15.2, 9.3 Hz, 1H), 3.25 (d, *J* = 6.0 Hz, 1H), 5.06 (dd, *J* = 9.3, 4.3 Hz, 1H), 5.31 (dd, *J* = 9.1, 6.0 Hz, 1H), 5.77 (d, *J* = 6.3 Hz, 1H), 6.32 (dd, *J* = 9.2, 5.5 Hz, 1H), 6.47 (dd, *J* = 10.9, 6.3 Hz, 1H), 6.63 (dd, *J* = 10.8, 5.5 Hz, 1H), 7.14-7.23 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 22.7, 30.2, 40.0, 81.5, 113.1, 117.4, 120.0, 124.2, 124.7, 125.6, 125.8, 126.2, 127.9, 128.5, 128.6, 129.1, 130.6, 130.8, 136.8, 137.6, 140.1, 144.4, 146.1, 147.7; HRMS (ESI) m/z calcd for C₂₈H₂₅BrO₂ [M+H]⁺: 473.1111, found: 473.1106.



1-((*1S*,2*R*)-2-(3-bromo-4-methylphenyl)-1-(*p*-tolylethynyl)cyclopropyl)ethan-1one (1t)

Yellow oil, 27 mg, 37% yield; 91% ee; $[\alpha]_D^{20.0}=33.3$ (0.1, CH₂Cl₂); [Daicel Chiralpak IJ-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =8.6 min, t (minor) =7.6 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.67 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.08 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.23 (s, 3H), 2.30 (s, 3H), 2.50 (s, 3H), 2.85

(t, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 7.01-7.07 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 22.6, 26.7, 29.6, 33.3, 37.9, 85.1, 86.2, 119.8, 124.4, 127.8, 129.0, 130.2, 131.4, 132.2, 135.6, 136.7, 138.3, 204.8.



(*5R*,*11R*)-5-(4-bromo-2-methylphenyl)-3-methyl-1-(p-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3u)

White solid, m.p. = 78-80 °C; 33 mg, 35% yield; 83% ee; $[\alpha]_D^{20.0}$ =-3.2 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.0 min, t (minor) =5.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.19 (s, 3H), 2.33 (s, 3H), 2.37 (s, 3H), 2.93 (dd, *J* = 15.2, 3.9 Hz, 1H), 3.09 (dd, *J* = 15.2, 8.8 Hz, 1H), 3.15 (d, *J* = 6.2 Hz, 1H), 5.25-5.31 (m, 2H), 5.69 (d, *J* = 6.3 Hz, 1H), 6.30 (dd, *J* = 9.1, 5.5 Hz, 1H), 6.45 (dd, *J* = 10.9, 6.3 Hz, 1H), 6.61 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.10-7.19 (m, 3H), 7.26 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 19.2, 21.3, 29.4, 40.3, 78.6, 112.2, 117.6, 120.0, 121.7, 124.0, 125.6, 126.2, 127.5, 127.7, 128.5, 128.6, 128.8, 129.1, 133.1, 136.8, 137.5, 137.6, 144.5, 146.1, 147.8; HRMS (ESI) m/z calcd for C₂₈H₂₅BrO₂ [M+H]⁺:473.1111, found: 473.1009.



1-((*1S*,2*R*)-2-(4-bromo-2-methylphenyl)-1-(p-tolylethynyl)cyclopropyl)ethan-1one (1u) Yellow oil, 24 mg, 36% yield; 90% ee; $[\alpha]_D^{20.0}$ =56.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IJ-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 95/5, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =8.5 min, t (minor) =10.0 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.85 (dd, J = 8.0, 4.1 Hz, 1H), 2.16 (dd, J = 8.8, 4.1 Hz, 1H), 2.28 (s, 3H), 2.30 (s, 3H), 2.61 (s, 3H), 2.89 (t, J = 8.4 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.99-7.04 (m, 3H), 7.31 (dd, J = 8.2, 2.1 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 19.5, 21.5, 26.3, 29.4, 32.0, 37.1, 83.7, 86.0, 119.7, 121.2, 128.7, 129.0, 129.6, 131.3, 132.6, 134.3, 138.3, 141.1, 205.2.



(*5R*,*11aR*)-3-methyl-5-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (3v)

White solid, m.p. = 90-92 °C; 37 mg, 44% yield; 80% ee; $[\alpha]_D^{20.0}$ =-4.8 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.4 min, t (minor) =5.8 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.20 (s, 3H), 3.15 (dd, *J* = 15.1, 3.6 Hz, 1H), 3.28 (dd, *J* = 15.1, 5.1 Hz, 1H), 3.35 (dd, *J* = 15.1, 9.1 Hz, 1H), 5.33 (dd, *J* = 9.1, 6.2 Hz, 1H), 5.64 (d, *J* = 6.3 Hz, 1H), 5.94 (dd, *J* = 9.1, 3.5 Hz, 1H), 6.33 (dd, *J* = 9.1, 5.5 Hz, 1H), 6.42 (dd, *J* = 10.9, 6.3 Hz, 1H), 6.60 (dd, *J* = 10.8, 5.5 Hz, 1H), 7.20-7.25 (m, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.41-7.49 (m, 3H), 7.50-7.58 (m, 3H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H);¹³C NMR (100 MHz, CDCl₃) δ 11.5, 30.0, 40.5, 78.8, 112.1, 118.3, 121.0, 123.4, 123.5, 123.9, 125.2, 125.6, 126.2, 126.4, 127.0, 127.5, 128.4, 128.6, 128.7, 129.0, 130.8, 131.4, 133.8, 135.8, 141.5, 144.6, 146.5, 147.7; HRMS (ESI) m/z calcd for C₃₀H₂₄O₂ [M+H]⁺:417.1849, found: 417.1846.



1-((1S,2R)-2-(naphthalen-1-yl)-1-(phenylethynyl)cyclopropyl)ethan-1-one (1v)

Yellow oil, 22 mg, 35% yield; 98% ee; $[\alpha]_D^{20.0}=65.7 (0.1, CH_2Cl_2)$; [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.1 min, t (minor) =8.0 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.06 (dd, *J* = 7.9, 4.0 Hz, 1H), 2.30 (dd, *J* = 8.8, 4.0 Hz, 1H), 2.67 (s, 3H), 3.51 (t, *J* = 8.4 Hz, 1H), 6.62-6.76 (m, 2H), 6.99-7.07 (m, 2H), 7.10 (dd, *J* = 6.9, 2.0 Hz, 1H), 7.36 (d, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.48-7.55 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.86-7.92 (m, 1H), 7.94-8.00 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 26.5, 29.8, 32.7, 36.6, 83.4, 87.3, 122.8, 123.6, 125.1, 125.8, 125.9, 126.3, 127.8, 128.0, 128.2, 128.7, 131.3, 132.8, 133.4, 133.6, 205.5.



(*5R*,*11aS*)-1-(cyclohex-1-en-1-yl)-3-methyl-5-phenyl-4,5-dihydro-11aH-cyclohepta [b]furo[3,4-d]oxepine (3w)

Yellow solid, 25 mg, 34% yield; 35% ee; $[\alpha]_D^{20.0}$ =42.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =3.9 min, t (minor) =5.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.56-1.64 (m, 2H), 1.65-1.70 (m, 2H), 2.09-2.16 (m, 2H), 2.17 (s, 3H), 2.21-2.30 (m, 1H), 2.32-2.40 (m, 1H), 2.90 (dd, *J* = 15.1, 4.2 Hz, 1H), 3.09 (dd, *J* = 15.2, 10.0 Hz, 1H), 3.18 (d, *J* = 5.9 Hz, 1H), 5.04 (dd, *J* = 10.0, 4.2 Hz, 1H), 5.27 (dd, *J* = 9.2, 5.9 Hz, 1H), 5.69 (d, *J* = 6.4 Hz, 1H), 5.80 (dt, *J* = 4.0, 2.2 Hz, 1H), 6.21-6.29 (m, 1H), 6.40 (dd, *J* = 11.0, 6.3 Hz, 1H), 6.54 (dd, *J* = 10.9, 5.5 Hz, 1H), 7.28-7.34 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 11.4, 22.2, 22.7, 25.5, 26.4, 29.8, 39.9, 82.4, 113.2, 117.1, 119.1, 124.8, 125.4, 125.8, 126.9, 127.7, 128.1, 128.2, 128.5, 128.6, 140.7, 144.6, 145.1, 149.7; HRMS (ESI) m/z calcd for C₂₆H₂₆O₂ [M+H]⁺: 371.2006, found: 371.2009.



1-((*IS*,*2R***)-1-(cyclohex-1-en-1-ylethynyl)-2-phenylcyclopropyl)ethan-1-one (1w)** Yellow oil, 19.5 mg, 37% yield; $[\alpha]_D^{20.0} = -55.2$ (0.1, CH₂Cl₂); 53% ee; [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, $\lambda =$ 254 nm, t (major) =4.4 min, t (minor) =4.8 min];¹H NMR (400 MHz, CDCl₃) δ 1.45-1.57 (m, 4H), 1.71 (dd, *J* = 7.9, 4.2 Hz, 1H), 1.87 (tq, *J* = 4.9, 2.1 Hz, 2H), 2.00 (td, *J* = 5.8, 2.9 Hz, 2H), 2.11 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.51 (s, 3H), 2.94 (dd, *J* = 9.1, 8.0 Hz, 1H), 5.81 (tt, *J* = 4.0, 1.9 Hz, 1H), 7.20-7.27 (m, 3H), 7.28-7.34 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 22.3, 25.6, 26.5, 28.9, 29.5, 33.4, 39.0, 84.4, 86.4, 120.5, 127.1, 127.9, 128.7, 134.1, 136.1, 205.4.



(5R,11aS)-2-methoxy-3-methyl-1,5-diphenyl-2,4,5,11a-tetrahydrocyclohepta

[2,3]oxepino[4,5-c]pyrrole (3x)

Yellow solid, m.p. = 92-94 °C; 24.5 mg, 31% yield; 73% ee; $[\alpha]_D^{20.0}$ =-3.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 99/1, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.6 min, t (minor) =8.9 min];¹H NMR (400 MHz, CDCl₃) δ 2.18 (s, 3H), 3.02 (dd, *J* = 15.2, 4.4 Hz, 1H), 3.14-3.21 (m, 2H), 3.56 (s, 3H), 5.06 (dd, *J* = 9.7, 4.4 Hz, 1H), 5.30 (dd, *J* = 9.2, 5.9 Hz, 1H), 5.68 (d, *J* = 6.3 Hz, 1H), 6.13-6.20 (m, 1H), 6.35 (dd, *J* = 10.9, 6.4 Hz, 1H), 6.49 (dd, *J* = 10.9, 5.4 Hz, 1H), 7.22-7.28 (m, 2H), 7.30-7.35 (m, 6H), 7.39-7.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 8.4, 30.4, 40.5, 65.3, 82.7, 111.1, 112.8, 115.6, 120.9, 124.5, 125.0, 125.8, 126.7, 126.9, 127.7, 127.9, 128.1, 128.2, 128.4, 129.3, 130.7, 141.2, 145.6; HRMS (ESI) m/z calcd for C₂₇H₂₅NO₂ [M+H]⁺: 396.1958, found: 396.1955.

S30

(*E*)-1-((*1S*,2*R*)-2-phenyl-1-(phenylethynyl)cyclopropyl)ethan-1-one-O-methyl oxime (1x)

Yellow oil, 22 mg, 38% yield; 37% ee; $[\alpha]_D^{20.0}$ =-41.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 99.5/0.5, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.6 min, t (minor) =4.9 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.67 (dd, *J* = 7.4, 5.1 Hz, 1H), 2.13 (s, 3H), 2.16 (dd, *J* = 5.5, 3.3 Hz, 1H), 2.67 (dd, *J* = 8.9, 7.4 Hz, 1H), 3.87 (s, 3H), 7.03-7.11 (m, 2H), 7.14-7.22 (m, 3H), 7.22 -7.28 (m, 1H) 7.29-7.36 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 21.0, 26.6, 34.4, 61.7, 82.3, 88.7, 123.4, 126.7, 127.7, 127.9, 128.1, 128.6, 131.5, 137.3, 156.0.



(*5R*,*11R*)-7-chloro-3-methyl-5-phenyl-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4a)

White solid, m.p. = 86-88 °C; 28 mg, 34% yield; 88% ee; $[\alpha]_D^{20.0}$ =-1.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.8 min, t (minor) =5.3 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.02 (s, 3H), 2.28 (s, 3H), 2.96 (dd, *J* = 15.3, 7.0 Hz, 1H), 3.07 (dd, *J* = 15.2, 4.7 Hz, 1H), 3.23 (d, *J* = 6.5 Hz, 1H), 5.33-5.42 (m, 2H), 6.17-6.25 (m, 1H), 6.48 (d, *J* = 11.2 Hz, 1H), 6.56 (ddd, *J* = 11.3, 5.2, 1.3 Hz, 1H), 7.05-7.08 (m, 2H), 7.23-7.26 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 11.4, 21.3, 30.8, 39.9, 82.2, 116.8, 117.5, 118.9, 124.9, 126.5, 126.8, 127.2, 128.1, 128.2, 128.5, 128.8, 129.0, 129.6, 137.1, 139.9, 140.4, 146.6, 147.9; HRMS (ESI) m/z calcd for C₂₇H₂₃ClO₂ [M+H]⁺: 415.1435, found: 415.1434.



(*5R*,*11aR*)-5-(4-bromophenyl)-7-chloro-3-methyl-1-phenyl-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4b)

White solid, m.p. = 98-100 °C; 30 mg, 31% yield; 94% ee; $[\alpha]_D^{20.0}$ =-1.4 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.6 min, t (minor) =4.9 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.09 (s, 3H), 2.97 (dd, *J* = 15.3, 6.7 Hz, 1H), 3.14 (dd, *J* = 15.3, 4.8 Hz, 1H), 3.32 (d, *J* = 6.5 Hz, 1H), 5.37-5.48 (m, 2H), 6.29 (ddd, *J* = 9.1, 5.3, 1.3 Hz, 1H), 6.56 (d, *J* = 11.2 Hz, 1H), 6.66 (dd, *J* = 11.2, 5.3 Hz, 1H), 7.16-7.22 (m, 2H), 7.24-7.28 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.40-7.48 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 11.4, 30.7, 39.9, 81.3, 116.6, 117.9, 119.4, 122.1, 125.0, 126.9, 127.0, 127.4, 128.2, 128.3, 129.1, 129.5, 131.2, 131.4, 139.4, 139.5, 147.1, 147.9; HRMS (ESI) m/z calcd for C₂₆H₂₀BrClO₂ [M+H]⁺: 479.0408, found: 479.0409.



(5*R*,11*aR*)-5-(4-bromo-2-methylphenyl)-7-chloro-3-methyl-1-phenyl-4,5-dihydro-11aH-cyclohepta[b]furo[3,4-d]oxepine (4c)

White solid, m.p. = 96-98 °C; 35 mg, 35% yield; 90% ee; $[\alpha]_D^{20.0}$ =-1.5 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.1 min, t (minor) =4.9 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.01 (s, 3H), 2.27 (s, 3H), 2.33 (s, 3H), 2.89 (dd, *J* = 15.3, 6.8 Hz, 1H), 2.97 (dd, *J* = 15.2, 4.6 Hz, 1H), 3.20 (d, *J* = 6.5 Hz, 1H), 5.37 (dd, *J* = 9.0, 6.5 Hz, 1H), 5.50 (dd, J = 6.8, 4.6 Hz, 1H), 6.20 (ddd, J = 9.0, 5.3, 1.3 Hz, 1H), 6.46 (d, J = 11.2 Hz, 1H), 6.55 (dd, J = 11.2, 5.2 Hz, 1H), 7.03-7.10 (m, 3H), 7.19 (dd, J = 8.3, 2.2 Hz, 1H), 7.21-7.27 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 11.4, 19.2, 21.4, 29.3, 39.9, 78.0, 116.8, 117.4, 118.9, 121.8, 124.9, 126.8, 127.0, 127.4, 128.4, 128.8, 128.9, 129.1, 129.5, 133.0, 137.2, 137.3, 137.4, 139.6, 146.6, 148.1; HRMS (ESI) m/z calcd for C₂₈H₂₄BrClO₂ [M+H]⁺: 507.0561, found: 507.0566.



(5*R*,11*aR*)-7-(4-fluorobenzyl)-3-methyl-5-phenyl-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4d)

White solid, m.p. = 78-80 °C; 35 mg, 36% yield; 83% ee, $[\alpha]_D^{20.0}$ =-2.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.1 min, t (minor) =6.0 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.16 (s, 3H), 2.25 (s, 3H), 2.83-2.98 (m, 2H), 3.11-3.21 (m, 3H), 5.06 (dd, *J* = 9.8, 3.9 Hz, 1H), 5.41 (dd, *J* = 8.9, 6.4 Hz, 1H), 6.18-6.31 (m, 2H), 6.46 (dd, *J* = 11.1, 5.3 Hz, 1H), 6.64-6.82 (m, 4H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.18-7.25 (m, 7H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 31.0, 34.8, 40.2, 82.9, 114.8 (d, *J* = 21.0 Hz), 117.8, 120.5, 122.4, 125.2, 126.2, 126.6, 126.7, 127.6, 128.3, 128.4, 128.7, 129.1, 130.0 (d, *J* = 7.7 Hz), 132.6, 136.7, 136.8 (d, *J* = 2.2 Hz), 140.6, 140.8, 146.0, 147.9, 161.2 (d, *J* = 243.0 Hz); HRMS (ESI) m/z calcd for C₃₄H₂₉FO₂ [M+H]⁺: 489.2224, found: 489.2229.



(5*R*,11*aR*)-7-(4-bromobenzyl)-3-methyl-5-(*m*-tolyl)-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4e) White solid, m.p. = 86-88 °C; 41 mg, 37% yield; 90% ee, $[\alpha]_D^{20.0}$ =-3.3 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.6 min, t (minor) =4.8 min];¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, 3H), 2.30 (s, 3H), 2.33 (s, 3H), 2.93 (dd, *J* = 15.3, 3.8 Hz, 1H), 3.05 (d, *J* = 15.0 Hz, 1H), 3.17-3.27 (m, 3H), 5.08 (dd, *J* = 10.0, 3.7 Hz, 1H), 5.48 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.28-6.37 (m, 2H), 6.55 (dd, *J* = 11.1, 5.3 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 2H), 7.08-7.13 (m, 4H), 7.15-7.19 (m, 2H), 7.23-7.26 (m, 2H), 7.29-7.33 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 21.5, 31.4, 35.2, 40.3, 83.0, 117.9, 119.3, 120.4, 121.6, 123.6, 125.2, 126.1, 126.7, 127.4, 127.5, 128.3, 128.6, 129.0, 129.1, 130.4, 131.1, 132.7, 136.7, 138.0, 140.3, 140.5, 141.0, 146.0, 147.9; HRMS (ESI) m/z calcd for C₃₅H₃₁BrO₂ [M+H]⁺: 562.1608, found: 562.1610.



1-((*1S*,2*R*)-2-(*m*-tolyl)-1-(*p*-tolylethynyl)cyclopropyl)ethan-1-one (1y)

¹H NMR (400 MHz, CDCl₃) δ 1.82 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.18 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.31 (s, 3H), 2.35 (s, 3H), 2.58 (s, 3H), 2.98 (t, *J* = 8.5 Hz, 1H), 7.03-7.11 (m, 7H), 7.23 (t, *J* = 7.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 21.6, 26.6, 29.7, 33.4, 39.3, 84.6, 86.7, 120.0, 125.7, 127.9, 128.0, 129.0, 129.5, 131.3, 135.9, 137.5, 138.1, 205.2.



(5*R*,11*R*)-3-methyl-7-(4-methylbenzyl)-5-(*m*-tolyl)-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4f)
White solid, m.p. = 96-98 °C; 36 mg, 36% yield; 90% ee; $[\alpha]_D^{20.0}$ =-2.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =4.9 min, t (minor) =4.5 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 3H), 2.25 (s, 3H), 2.30 (s, 3H), 2.32 (s, 3H), 2.97 (dd, *J* = 15.3, 4.2 Hz, 2H), 3.16-3.23 (m, 1H), 3.24 (d, *J* = 6.4 Hz, 1H), 3.33 (d, *J* = 14.7 Hz, 1H), 5.12 (dd, *J* = 9.7, 4.0 Hz, 1H), 5.48 (dd, *J* = 8.9, 6.4 Hz, 1H), 6.30 (ddd, *J* = 8.8, 5.3, 1.3 Hz, 1H), 6.38 (d, *J* = 11.1 Hz, 1H), 6.53 (dd, *J* = 11.1, 5.3 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 7.07-7.15 (m, 5H), 7.15-7.20 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.1, 21.3, 21.5, 31.3, 35.1, 40.3, 82.9, 117.9, 120.6, 122.7, 123.7, 125.1, 126.2, 126.5, 127.3, 127.6, 128.2, 128.6, 128.7, 128.8, 128.9, 129.1, 132.8, 135.0, 136.7, 137.9, 138.1, 140.5, 140.6, 146.0, 147.8; HRMS (ESI) m/z calcd for C₃₆H₃₄O₂ [M+H]⁺: 499.2632, found: 499.2631.



Methyl-4-(((*5R*,*11R*)-3-methyl-5-(*m*-tolyl)-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepin-7-yl)methyl)benzoate (4g)

White solid, m.p. = 88-90 °C; 37 mg, 34% yield; 92% ee; $[\alpha]_D^{20.0}$ =-5.2 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =8.0 min, t (minor) =7.0 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.25 (s, 3H), 2.28 (s, 3H), 2.32 (s, 3H), 2.95 (dd, *J* = 15.4, 3.7 Hz, 1H), 3.16-3.28 (m, 3H), 3.35 (d, *J* = 15.2 Hz, 1H), 3.86 (s, 3H), 5.09 (dd, *J* = 9.9, 3.6 Hz, 1H), 5.48 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.29-6.40 (m, 2H), 6.55 (dd, *J* = 11.0, 5.3 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 7.06-7.12 (m, 4H), 7.13-7.17 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 21.5, 31.5, 35.9, 40.3, 52.0, 83.1, 117.9, 120.4, 121.3, 123.6, 125.1, 126.1, 126.7, 127.4, 127.5, 127.6, 128.3, 128.6, 128.7, 129.0, 129.1, 129.4, 132.6, 136.7, 138.0, 140.6, 141.2, 146.0, 147.0, 147.9, 167.3; HRMS (ESI) m/z calcd for C₃₇H₃₄O₄ [M+H]⁺: 543.2530, found: 543.2530.



(*5R*,*11R*)-3-methyl-5-(*m*-tolyl)-1-(*p*-tolyl)-7-(4-(trifluoromethyl)benzyl)-4,5dihydro-11aH-cyclohepta[b]furo[3,4-d]oxepine (4h)

White solid, m.p. = 100-102 °C; 41 mg, 37% yield; 90% ee; $[\alpha]_D^{20.0}$ =-2.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.8 min, t (minor) =4.6 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.28 (s, 3H), 2.29 (s, 3H), 2.34 (s, 3H), 2.95 (dd, *J* = 15.3, 3.7 Hz, 1H), 3.17-3.29 (m, 3H), 3.33 (d, *J* = 15.1 Hz, 1H), 5.10 (dd, *J* = 10.1, 3.7 Hz, 1H), 5.51 (dd, *J* = 8.9, 6.4 Hz, 1H), 6.33-6.42 (m, 2H), 6.58 (dd, *J* = 11.1, 5.3 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 7.06-7.13 (m, 3H), 7.13-7.18 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 21.5, 31.4, 35.7, 40.3, 83.1, 117.9, 120.4, 121.2, 123.1, 123.6, 124.9 (q, *J* = 3.7 Hz), 125.2, 126.0, 126.7, 124.9 (q, *J* = 209.5 Hz), 127.4, 127.6, 128.3, 128.6, 128.8, 129.0, 129.1, 132.7, 136.8, 138.0, 140.5, 141.3, 145.5, 146.0, 147.9; HRMS (ESI) m/z calcd for C₃₆H₃₁F₃O₂ [M+H]⁺: 553.2349, found: 553.2347.



(5R,11R)-3-methyl-7-(4-nitrobenzyl)-5-(*m*-tolyl)-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4i) White solid, m.p. = 98-100 °C; 34 mg, 32% yield; 95% ee; $[\alpha]_D^{20.0}$ =-4.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =10.9 min, t (minor) =7.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.28 (s, 3H), 2.29 (s, 3H), 2.34 (s, 3H), 2.94 (dd, *J* = 15.4, 3.5 Hz, 1H), 3.20-3.29 (m, 2H), 3.32 (s, 2H), 5.09 (dd, *J* = 10.2, 3.5 Hz, 1H), 5.51 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.31-6.43 (m, 2H), 6.60 (dd, *J* = 11.0, 5.4 Hz, 1H), 6.94-7.00 (m, 2H), 7.07-7.20 (m, 6H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.7, 21.3, 21.5, 31.5, 36.1, 40.3, 83.2, 117.9, 120.2, 120.4, 123.3, 123.5, 125.2, 126.0, 126.9, 127.4, 127.8, 128.4, 128.5, 129.0, 129.1, 129.2, 132.4, 136.8, 138.1, 140.5, 141.7, 146.0, 146.1, 148.0, 149.5; HRMS (ESI) m/z calcd for C₃₅H₃₁NO₄ [M+H]⁺: 530.2326, found: 530.2326.



(5*R*,11*aR*)-7-(3-chlorobenzyl)-3-methyl-5-(*m*-tolyl)-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4j)

White solid, m.p. = 82-84 °C; 39 mg, 38% yield; 90% ee; $[\alpha]_D^{20.0}$ =-1.4 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.6 min, t (minor) =4.8 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.27 (s, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 2.96 (dd, *J* = 15.4, 3.8 Hz, 1H), 3.07 (d, *J* = 15.0 Hz, 1H), 3.20-3.23 (m, 3H), 5.10 (dd, *J* = 10.1, 3.7 Hz, 1H), 5.50 (dd, *J* = 8.9, 6.4 Hz, 1H), 6.31-6.36 (m, 1H), 6.37 (d, *J* = 11.0 Hz, 1H), 6.57 (dd, *J* = 11.1, 5.3 Hz, 1H), 6.80 (td, *J* = 4.6, 1.6 Hz, 1H), 6.85-6.89 (m, 1H), 7.04-7.09 (m, 2H), 7.11-7.16 (m, 5H), 7.19-7.27 (m, 2H), 7.30-7.35 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 21.5, 31.4, 35.4, 40.3, 83.1, 117.9, 120.5, 121.4, 123.6, 125.2, 125.8, 126.1, 126.7, 126.8, 127.4, 127.5, 128.3, 128.6, 128.7, 129.0, 129.1, 129.3, 132.6, 133.8, 136.7, 138.0, 140.5, 141.1, 143.4, 146.0, 147.9; HRMS (ESI) m/z calcd for C₃₅H₃₁ClO₂ [M+H]⁺: 519.1865, found: 519.1861.



(*5R*,*11R*)-7-(2-fluorobenzyl)-3-methyl-5-(*m*-tolyl)-1-(*p*-tolyl)-4,5-dihydro-11aHcyclohepta[b]furo[3,4-d]oxepine (4k)

White solid, m.p. = 80-82 °C; 35 mg, 35% yield; 92% ee; $[\alpha]_D^{20.0}$ =-2.6 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.7 min, t (minor) =6.3 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.16 (s, 3H), 2.21 (s, 3H), 2.24 (s, 3H), 2.90 (dd, *J* = 15.3, 3.8 Hz, 1H), 3.05-3.16 (m, 3H), 3.28 (d, *J* = 15.3 Hz, 1H), 5.06 (dd, *J* = 9.6, 3.7 Hz, 1H), 5.41 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.21-6.25 (m, 1H), 6.32 (d, *J* = 11.1 Hz, 1H), 6.48 (dd, *J* = 11.1, 5.3 Hz, 1H), 6.70-6.77 (m, 1H), 6.78-6.85 (m, 2H), 6.95-7.01 (m, 2H), 7.02-7.10 (m, 5H), 7.23 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 21.5, 28.2 (d, *J* = 3.6 Hz), 31.5, 40.4, 82.9, 114.8 (d, *J* = 22.3 Hz), 117.9, 120.5, 120.8, 123.5, 123.8 (d, *J* = 3.6 Hz), 125.1, 126.2, 126.6, 127.2 (d, *J* = 7.9 Hz), 127.3, 127.4, 128.0 (d, *J* = 15.7 Hz), 128.2, 128.7, 128.8, 129.1, 130.8 (d, *J* = 4.8 Hz), 132.6, 136.7, 137.9, 140.6, 141.2, 146.0, 147.8, 160.9 (d, *J* = 244.6 Hz); HRMS (ESI) m/z calcd for C₃₅H₃₁FO₂ [M+H]⁺: 503.2381, found: 503.2377.



(*5R*,*11R*)-7-(4-bromo-3-chlorobenzyl)-3-methyl-5-(*m*-tolyl)-1-(*p*-tolyl)-4,5dihydro-11aH-cyclohepta[b]furo[3,4-d]oxepine (4l)

White solid, m.p. = 90-92 °C; 45 mg, 38% yield; 89% ee; $[\alpha]_D^{20.0}$ =-3.2 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =7.0 min, t (minor) =5.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.20 (s, 3H), 2.23 (s, 3H), 2.26 (s, 3H), 2.85 (dd, J = 15.4, 3.6 Hz, 1H), 2.99 -3.21(m, 4H), 5.00 (dd, J = 10.2, 3.6 Hz, 1H), 5.42 (dd, J = 8.9, 6.5 Hz, 1H), 6.22-6.33 (m, 2H), 6.55 (dd, J = 8.2, 2.1 Hz, 1H), 6.50 (dd, J = 11.1, 5.3 Hz, 1H), 6.84 (d, J = 2.1 Hz, 1H), 7.00-7.12 (m, 6H), 7.19-7.27 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 11.7, 21.3, 21.6, 31.4, 35.1, 40.3, 83.2, 117.9, 119.1, 120.3, 120.8, 123.6, 125.2, 126.0, 126.8, 127.4, 127.7, 128.3, 128.4, 128.6, 129.0, 129.1, 130.4, 132.5, 133.1, 133.7, 136.8, 138.1, 140.4, 141.4, 142.5, 146.0, 147.9; HRMS (ESI) m/z calcd for C₃₅H₃₀BrClO₂ [M+H]⁺: 597.1035, found: 597.1039.



(*5R*,*11R*)-3-methyl-7-(naphthalen-1-ylmethyl)-5-phenyl-1-(*p*-tolyl)-4,5-dihydro-11aH-cyclohepta[b]furo[3,4-d]oxepine (4m)

White solid, m.p. = 110-112 °C; 32 mg, 31% yield; 89% ee, $[\alpha]_D^{20.0}$ =-4.5 (0.1, CH₂Cl₂); [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.8 min, t (minor) =6.2 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 3H), 2.30 (s, 3H), 3.01 (dd, *J* = 15.2, 4.3 Hz, 1H), 3.19-3.37 (m, 3H), 3.84 (d, *J* = 15.7 Hz, 1H), 5.19 (dd, *J* = 9.7, 4.2 Hz, 1H), 5.50 (dd, *J* = 9.0, 6.2 Hz, 1H), 6.25-6.34 (m, 2H), 6.46 (dd, *J* = 11.1, 5.3 Hz, 1H), 7.01 (d, *J* = 6.8 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.20 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.26-7.34 (m, 5H), 7.35-7.42 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.80-7.86 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 30.5, 32.7, 40.2, 82.7, 117.8, 120.7, 122.3, 124.2, 125.3, 125.4, 132.5, 133.7, 136.7, 136.8, 140.2, 140.4, 146.1, 147.8; HRMS (ESI) m/z calcd for C₃₈H₃₂O₂ [M+H]⁺: 521.2475, found: 521.2476.

4. Large-scale reaction and synthetic transformations



To a dried flask was added L8AuCl (2.0 mol%) and NaBAr^F (8.0 mol%) in the glove box, and the DCM (25 mL) was added. Then the mixture was stirred at room temperature for 10 min. Then the solution was transferred into a solution of cyclopropyl ketone 1 (5.0 mmol, 1.0 equiv.) and tropone 2 (4.0 mmol, 0.8 equiv.) with 4 Å molecular sieves 8 g in DCM (25 mL) at -20 °C. The reaction was then stirred at -20 °C for 30 h. After the reaction was monitored by TLC and HPLC analysis. The reaction was filtered by silica gel to remove catalyst rapidly. Then the solvent was removed under reduced pressure, and the residue was purified by a silica gel column using ethyl acetate/ petroleum ether (1/80-1/30) as the eluent to give the target product 3b as white solid (0.76 g, 40% yield, 92% ee) and chiral 1b as yellow oil (0.56 g, 41% yield, 94% ee). [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.1 min, t (minor) =5.7 min]; [Daicel Chiralpak IB-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.0 min, t (minor) =5.7 min].

Synthetic transformations of products



The cycloadduct **3** (0.1 mmol) was added DCM (2.0 mL) and *p*-toluenesulfonic acid (0.2 mmol, 2.0 equiv.). The mixture was stirred at room temperature for 1 h. After the

reaction was monitored by TLC analysis, the reaction was filtered to afford the filtrate. The solvent was removed under reduced pressure. The residue was purified by a silica gel column with ethyl acetate/ petroleum ether (1/60-1/10) to give the desired product **5**.



(*R*)-1-(4-ethylphenyl)-3-methyl-5-phenyl-4,5-dihydro-8H-cyclohepta[b]furo[3,4d]oxepine (5a)

Yellow oil; 26 mg, 65% yield; 88% ee, $[\alpha]_D^{20.0}$ =-2.7 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.5 min, t (minor) =6.0 min];¹H NMR (400 MHz, CDCl₃) δ 1.26 (t, *J* = 7.6 Hz, 3H), 2.13 (s, 3H), 2.53 (dd, *J* = 13.1, 6.7 Hz, 1H), 2.66 (q, *J* = 7.7 Hz, 2H), 2.75 (dd, *J* = 13.1, 7.2 Hz, 1H), 2.89-2.98 (m, 2H), 5.32 (dd, *J* = 6.5, 4.0 Hz, 1H), 5.57 (dt, *J* = 8.3, 6.8 Hz, 1H), 6.22-6.31 (m, 2H), 6.40-6.45 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.30-7.33 (m, 1H), 7.32-7.39 (m, 4H), 7.43 (d, *J* = 8.2 Hz, 2H);¹³C NMR (100 MHz, CDCl₃) δ 11.4, 15.5, 28.8, 32.6, 34.9, 84.9, 111.7, 117.6, 119.7, 121.3, 126.2, 126.8, 127.3, 127.4, 127.5, 128.0, 128.5, 129.4, 132.2, 141.9, 143.1, 145.5, 145.7, 145.9; HRMS (ESI) m/z calcd for C₂₈H₂₆O₂ [M+H]⁺: 395.2006, found: 395.2001.



(R)-3-methyl-5-phenyl-1-(m-tolyl)-4,5-dihydro-8H-cyclohepta[b]furo[3,4-

d]oxepine (5b)

Yellow oil; 27 mg, 71% yield; 84% ee, $[\alpha]_D^{20.0}$ =-2.2 (0.1, CH₂Cl₂); [Daicel Chiralpak IC-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.3 min, t (minor) =4.1 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.13 (s, 3H), 2.35 (s, 3H), 2.53 (dd, *J* = 13.1, 6.8 Hz, 1H), 2.75 (dd, *J* = 13.1, 7.2 Hz, 1H), 2.90-3.01 (m, 2H), 5.33 (dd, *J* = 6.4, 4.0 Hz, 1H), 5.54-5.62 (m, 1H), 6.23-6.30 (m, 2H), 6.35-6.43

(m, 1H), 7.06 (d, J = 7.5 Hz, 1H), 7.20-7.28 (m, 1H), 7.27-7.34 (m, 3H), 7.32-7.37 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 11.4, 21.6, 32.6, 34.8, 84.9, 111.6, 117.8, 120.3, 121.5, 124.4, 126.2, 126.9, 127.4, 127.8, 127.9, 128.0, 128.1, 128.5, 131.7, 132.3, 137.5, 141.9, 145.7, 146.0, 146.1; HRMS (ESI) m/z calcd for C₂₇H₂₄O₂ [M+H]⁺:381.1849, found: 381.1846.



(R)-5-([1,1'-biphenyl]-4-yl)-3-methyl-1-phenyl-4,5-dihydro-8H-

cyclohepta[b]furo[3,4-d]oxepine (5c)

Yellow oil; 29 mg, 66% yield; 82% ee, $[\alpha]_D^{20.0}$ =-5.0 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =6.0 min, t (minor) =7.7 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.09 (s, 3H), 2.47 (dd, *J* = 13.1, 6.8 Hz, 1H), 2.70 (dd, *J* = 13.1, 7.2 Hz, 1H), 2.89-2.93 (m, 2H), 5.30 (dd, *J* = 6.2, 4.2 Hz, 1H), 5.48-5.55 (m, 1H), 6.16-6.26 (m, 2H), 6.29-6.39 (m, 1H), 7.14-7.22 (m, 2H), 7.26-7.29 (m, 2H), 7.34-7.40 (m, 4H), 7.43-7.47 (m, 2H), 7.50-7.54 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 32.5, 34.9, 84.7, 111.6, 117.8, 120.4, 121.4, 123.7, 126.6, 126.9, 127.0, 127.1, 127.2, 127.4, 127.5, 128.0, 128.9, 131.9, 132.1, 140.8, 140.9, 141.0, 145.7, 145.9, 146.0; HRMS (ESI) m/z calcd for C₃₂H₂₆O₂ [M+H]⁺: 443.2006, found: 443.2007.



(*R*)-5-(2-bromophenyl)-3-methyl-1-phenyl-4,5-dihydro-8Hcyclohepta[b]furo[3,4-d]oxepine (5d)

Yellow oil; 27 mg, 61% yield; 80% ee, $[\alpha]_D^{20.0}$ =-2.2 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.3 min, t (minor) =5.9 min]; ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.54 (dd, *J* = 13.2, 6.9 Hz, 1H), 2.70-2.77 (m, 2H), 2.94 (dd, *J* = 15.2, 3.7 Hz, 1H), 5.52-

5.59 (m, 1H), 5.60 (dd, J = 5.4, 3.6 Hz, 1H), 6.18-6.27 (m, 2H), 6.32 (d, J = 11.0 Hz, 1H), 7.07 (td, J = 7.6, 1.4 Hz, 1H), 7.14-7.24 (m, 3H), 7.25-7.28 (m, 1H), 7.40 (dd, J = 7.9, 1.7 Hz, 1H), 7.42-7.50 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 11.2, 31.4, 34.6, 83.2, 111.7, 117.5, 120.4, 121.3, 121.5, 127.0, 127.2, 127.3, 127.4, 127.5, 127.6, 128.0, 129.1, 131.8, 132.1, 132.7, 140.8, 145.6, 145.7, 146.2; HRMS (ESI) m/z calcd for C₂₆H₂₁BrO₂ [M+H]⁺: 445.0668, found: 445.0665.



To a stirred solution of **3b** (0.1 mmol) in methanol (2.0 mL), Pd/C (10%, 30 mg) was added and the reaction mixture was stirred at room temperature for 48 h under H₂ atmosphere. Subsequently, it was filtered to remove Pd/C and the solvent was evaporated in vacuo. The residue was purified by silica gel column with hexanes/ethyl acetate (30:1, v/v) to to afford **6** as white solid (32 mg, 82% yield).



(5R,6aR,11aR)-3-methyl-5-phenyl-1-(*p*-tolyl)-4,5,6a,8,9,10,11,11a-octahydro-7Hcyclohepta[b]furo[3,4-d]oxepine (6)

White solid, m.p. = 110-112 °C; 32 mg, 82% yield; 91% ee; $[\alpha]_D^{20.0}$ =-1.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =5.5 min, t (minor) =6.4 min]; ¹H NMR (400 MHz, CDCl₃) δ 1.27-1.40 (m, 1H), 1.51-1.60 (m, 2H), 1.62-1.75 (m, 2H), 1.75-1.90 (m, 3H), 1.97-2.07 (m, 1H), 2.24 (s, 3H), 2.38 (s, 3H), 2.36-2.41 (m, 1H), 2.75 (d, *J* = 15.2, 1H), 2.84-2.94 (m, 1H), 3.03 (dd, J = 11.3, 3.2 Hz, 1H), 3.99 (dd, J = 5.2, 2.7 Hz, 1H), 4.51 (d, J = 10.5 Hz, 1H), 7.21-7.25 (m, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.34-7.43 (m, 4H), 7.47 (d, J = 7.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.6, 21.3, 23.0, 26.9, 27.5, 30.2, 35.9, 37.0, 42.7, 83.4, 84.0, 119.3, 125.7, 126.1, 127.1, 127.6, 128.3, 129.1, 129.3, 136.5, 144.7, 145.0, 146.2; HRMS (ESI) m/z calcd for C₂₇H₃₀O₂ [M+H]⁺: 387.2322, found: 387.2320.



TBAF (0.4 mL, 1 mol/L in THF) was slowly added dropwise to a stirred solution of 4 Å MS (60 mg), chiral product (0.1 mmol) and the triflate (0.5 mmol) in dry THF (1.0 mL) at 0 °C under nitrogen. Then the mixture was stirred at room temperature for 2 h, the solution was quenched with saturated ammonium chloride and extracted with ethyl acetate. The combined organic phase was dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash chromatography on silica gel with PE/EA=1/30 to afford the aim product **7**. (75% yield)

(*7S*,*13R*,*14aS*)-8-methyl-7-phenyl-13-(*p*-tolyl)-8,13,14,14a-tetrahydro-7H-8,13epoxycyclohepta[b]naphtho[2,3-e]oxepine (7)



White solid, m.p. = 144-146 °C; 34 mg, 75% yield; 2:1 dr, 82% ee, 89% ee; $[\alpha]_D^{20.0}$ =-6.1 (0.1, CH₂Cl₂); [Daicel Chiralpak IA-3 (0.45 cm × 25 cm), *n*-hexane/2-propanol = 97/3, v = 1.0 mL•min⁻¹, λ = 254 nm, t (major) =8.5 min, 7.1 min, t (minor) =6.0 min, 15.4 min];¹H NMR (400 MHz, CDCl₃) δ 1.91 (s, 3H), 1.92 (s, 3H), 2.13-2.19 (m, 1H), 2.33 (s, 3H), 2.37-2.42 (m, 5H), 2.59-2.71 (m, 1H), 2.89-2.97 (m, 1H), 3.13-3.24 (m, 1H), 4.53 (dd, *J* = 8.8, 6.7 Hz, 1H), 4.73-4.85 (m, 2H), 5.20 (dd, *J* = 10.8, 2.0 Hz, 1H), 5.65 (dd, *J* = 8.9, 5.4 Hz, 1H), 5.78 (dd, *J* = 8.1, 6.1 Hz, 2H), 6.14 (dd, *J* = 8.9, 5.4 Hz, 1H), 6.36-6.45 (m, 2H), 6.48 (dd, *J* = 10.7, 5.4 Hz, 2H), 6.96-7.11 (m, 4H), 7.14-7.23 (m, 6H), 7.28-7.31 (m, 3H), 7.32-7.37 (m, 8H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 6.6 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.4, 21.2, 21.3, 36.9, 37.1, 42.7, 43.2, 83.5, 84.1, 88.5, 89.2, 92.6, 93.8, 109.4, 109.5, 117.4, 118.0, 118.2, 119.3, 120.6, 121.8, 123.2, 124.8, 125.0, 125.1, 125.2, 125.7, 125.8, 125.9, 127.0, 127.1, 127.3, 127.6, 127.8, 127.9, 128.0, 128.5, 128.6, 128.9, 129.0, 132.2, 132.8, 137.2, 137.8, 141.3, 141.4, 146.0, 146.4, 147.1, 147.8, 148.5, 148.9, 151.4, 152.1, 152.2, 153.0; HRMS (ESI) m/z calcd for C₃₃H₂₈O₂ [M+H]⁺: 457.2162, found: 457.2162.

5. X-ray crystallography data



Table 4 Crystal data and structure refinement for cu_240112c_0m.

Identification code	cu_240112c_0m
Empirical formula	$C_{26}H_{21}BrO_2$
Formula weight	445.34
Temperature/K	293.0
Crystal system	orthorhombic
Space group	P212121
a/Å	5.1768(16)

b/Å	10.008(3)
c/Å	40.889(11)
a/°	90
β/°	90
γ/°	90
Volume/Å ³	2118.4(11)
Z	4
$\rho_{calc}g/cm^3$	1.396
μ/mm^{-1}	2.787
F(000)	912.0
Crystal size/mm ³	$0.04 \times 0.01 \times 0.005$
Radiation	$CuK\alpha$ ($\lambda = 1.54178$)
2Θ range for data collection/°	4.322 to 133.188
Index ranges	$-5 \le h \le 6, -11 \le k \le 11, -47 \le l \le 48$
Reflections collected	22883
Independent reflections	3688 [$R_{int} = 0.0931$, $R_{sigma} = 0.0643$]
Data/restraints/parameters	3688/12/231
Goodness-of-fit on F ²	1.084
Final R indexes [I>=2 σ (I)]	$R_1=0.0968,wR_2=0.2688$
Final R indexes [all data]	$R_1 = 0.1395, wR_2 = 0.3017$
Largest diff. peak/hole / e Å $^{-3}$	0.92/-0.51
Flack parameter	0.095(17)

Table 5 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for cu_240112c_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	у	Z	U(eq)
Br1	-552(4)	-512(2)	2516.1(5)	94.6(9)

O2	5340(20)	2858(9)	3753(2)	77(3)
C2	6320(30)	4238(15)	4701(3)	84(5)
C4	7020(20)	3430(9)	4003(3)	70(4)
C5	9500(30)	2593(16)	4485(3)	86(5)
C7	8600(30)	3457(14)	4735(3)	79(4)
C10	7924(19)	7134(8)	3889(2)	74(4)
C18	6680(20)	5870(7)	3875(2)	63(3)
C13	5016(19)	5867(7)	3599(2)	71(4)
C21	5230(20)	7128(8)	3442(2)	81(5)
01	7030(18)	7911(6)	3621(2)	74(3)
C11	13080(20)	9473(10)	4177(3)	102(6)
C25	13400(20)	9071(11)	4499(3)	103(7)
C9	11910(20)	8039(13)	4625(2)	90(5)
C3	10090(20)	7408(11)	4429(2)	88(5)
C12	9766(18)	7809(9)	4106(2)	71(4)
C19	11260(20)	8842(10)	3980(2)	87(5)
C14	4990(30)	3521(11)	3438(2)	67(4)
C15	3510(20)	4757(8)	3467(4)	78(4)
C16	3715(17)	2476(9)	3209.5(19)	68(4)
C1	4568(16)	2307(10)	2890(2)	72(4)
C17	3290(20)	1425(11)	2682.6(16)	80(4)
C6	1167(19)	713(9)	2795(2)	73(4)
C8	315(16)	882(9)	3115(2)	71(4)
C24	1589(18)	1764(10)	3322.0(17)	72(4)
C20	5580(30)	4820(14)	4399(2)	76(4)
C22	7090(30)	4784(7)	4108(2)	61(3)
C23	4090(50)	7821(17)	3150(4)	106(6)
C26	8350(30)	2401(13)	4173(3)	78(4)

Table 6 Anisotropic Displacement Parameters (Å2×103) for cu_240112c_0m. TheAnisotropicdisplacementfactorexponenttakestheform:- $2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...].$

Atom	U11	U ₂₂	U33	U ₂₃	U13	U12
Br1	100.8(14)	90.8(13)	92.2(13)	-19.7(10)	-19.5(12)	2.1(9)
O2	88(7)	68(6)	75(6)	12(5)	-27(5)	-7(6)
C2	100(12)	84(10)	67(9)	20(8)	13(8)	-3(10)
C4	63(9)	77(9)	71(9)	6(7)	-1(7)	11(8)
C5	80(11)	95(11)	83(10)	9(9)	-4(9)	-19(10)
C7	85(11)	86(10)	68(9)	16(8)	-15(8)	-4(9)
C10	79(10)	69(9)	75(9)	4(8)	-7(8)	1(8)
C18	68(8)	57(8)	65(8)	1(6)	4(7)	5(7)
C13	75(10)	55(8)	83(9)	-3(7)	-15(7)	3(7)
C21	91(12)	71(9)	82(10)	19(8)	-13(9)	19(9)
01	92(7)	58(5)	71(6)	2(5)	2(5)	14(5)
C11	111(15)	75(11)	120(14)	-8(11)	20(12)	-50(12)
C25	77(11)	69(10)	160(20)	-37(12)	1(13)	-4(9)
C9	88(12)	102(12)	80(10)	-18(10)	-6(9)	11(11)
C3	82(13)	93(11)	88(11)	0(9)	-4(9)	-7(10)
C12	74(10)	63(8)	77(9)	7(7)	16(7)	9(7)
C19	100(13)	68(9)	94(11)	-3(9)	16(10)	-4(9)
C14	68(10)	67(8)	65(8)	1(6)	-11(6)	1(7)
C15	79(10)	70(9)	86(10)	10(8)	-18(8)	5(8)
C16	61(9)	79(9)	65(8)	-1(7)	1(7)	2(7)
C1	70(9)	81(9)	64(8)	4(7)	-1(7)	-8(8)
C17	85(11)	78(10)	78(9)	-2(8)	-13(9)	8(9)
C6	86(11)	68(9)	67(8)	-6(7)	-5(7)	12(8)
C8	73(9)	64(8)	76(9)	-6(7)	-7(7)	-2(7)

C24	79(10)	71(9)	65(8)	5(7)	-1(7)	-17(8)
C20	72(9)	78(9)	79(9)	-2(7)	13(8)	5(8)
C22	68(8)	55(8)	61(7)	10(6)	3(6)	-3(6)
C23	159(17)	81(11)	77(10)	-2(9)	-12(12)	50(13)
C26	78(10)	76(10)	80(10)	-12(8)	-11(8)	7(8)

Table 7 Bond Lengths for cu_240112c_0m.

Atom	Atom	n Length/Å	Atom	n Atom	₁ Length/Å
Br1	C6	1.896(6)	C21	C23	1.502(17)
O2	C4	1.460(3)	C11	C25	1.3900
O2	C14	1.460(3)	C11	C19	1.3900
C2	C7	1.419(3)	C25	C9	1.3900
C2	C20	1.420(3)	C9	C3	1.3900
C4	C22	1.422(3)	C3	C12	1.3900
C4	C26	1.419(3)	C12	C19	1.3900
C5	C7	1.419(3)	C14	C15	1.461(3)
C5	C26	1.420(3)	C14	C16	1.549(14)
C10	C18	1.4200	C16	C1	1.3900
C10	01	1.4200	C16	C24	1.3900
C10	C12	1.469(10)	C1	C17	1.3900
C18	C13	1.4200	C17	C6	1.3900
C18	C22	1.462(3)	C6	C8	1.3900
C13	C21	1.4200	C8	C24	1.3900
C13	C15	1.460(3)	C20	C22	1.421(3)
C21	O 1	1.4200			

Table 8 Bond Angles for cu_240112c_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	O2	C14	121.0(9)	C3	C12	C10	121.4(7)
C7	C2	C20	122.3(13)	C3	C12	C19	120.0
C22	C4	O2	126.8(10)	C19	C12	C10	118.6(7)
C26	C4	02	110.3(8)	C12	C19	C11	120.0
C26	C4	C22	122.2(9)	02	C14	C15	112.2(10)
C7	C5	C26	126.1(15)	02	C14	C16	106.2(8)
C5	C7	C2	122.7(15)	C15	C14	C16	113.3(9)
C18	C10	C12	136.8(7)	C13	C15	C14	113.1(10)
01	C10	C18	108.0	C1	C16	C14	120.9(7)
01	C10	C12	115.2(7)	C1	C16	C24	120.0
C10	C18	C22	124.8(8)	C24	C16	C14	119.0(7)
C13	C18	C10	108.0	C16	C1	C17	120.0
C13	C18	C22	127.2(8)	C6	C17	C1	120.0
C18	C13	C21	108.0	C17	C6	Br1	120.3(5)
C18	C13	C15	128.3(8)	C17	C6	C8	120.0
C21	C13	C15	123.5(8)	C8	C6	Br1	119.7(5)
C13	C21	C23	137.6(11)	C24	C8	C6	120.0
01	C21	C13	108.0	C8	C24	C16	120.0
01	C21	C23	114.4(11)	C2	C20	C22	124.7(11)
C10	01	C21	108.0	C4	C22	C18	120.5(9)
C25	C11	C19	120.0	C20	C22	C4	105.3(11)
C11	C25	C9	120.0	C20	C22	C18	116.6(9)
C3	C9	C25	120.0	C4	C26	C5	123.0(13)
C12	C3	C9	120.0				

Table 9 Torsion Angles for cu_240112c_0m.

A	B	С	D	Angle/°	Α	B	С	D	Angle/°
Br1	C6	C8	C24	179.1(7)	C25	C11	C19	C12	0.0
02	C4	C22	C18	-36(2)	C25	C9	C3	C12	0.0
02	C4	C22	C20	98.3(14)	C9	C3	C12	C10	177.9(9)
02	C4	C26	C5	-161.0(15)	C9	C3	C12	C19	0.0
02	C14	C15	C13	76.7(15)	C3	C12	C19	C11	0.0
02	C14	C16	C1	-135.9(9)	C12	C10	C18	C13	178.1(14)
02	C14	C16	C24	48.1(11)	C12	C10	C18	C22	-2.0(14)
C2	C20	C22	C4	70.0(18)	C12	C10	01	C21	-178.6(10)
C2	C20	C22	C18	-153.5(14)	C19	C11	C25	C9	0.0
C4	02	C14	C15	-70.1(14)	C14	02	C4	C22	46.6(19)
C4	02	C14	C16	165.6(10)	C14	02	C4	C26	-143.1(13)
C7	C2	C20	C22	-5(3)	C14	C16	C1	C17	-176.0(9)
C7	C5	C26	C4	33(3)	C14	C16	C24	C8	176.0(9)
C10	C18	C13	C21	0.0	C15	C13	C21	01	-174.5(12)
C10	C18	C13	C15	174.1(13)	C15	C13	C21	C23	6.0(18)
C10	C18	C22	C4	-145.3(11)	C15	C14	C16	C1	100.5(11)
C10	C18	C22	C20	85.2(14)	C15	C14	C16	C24	-75.6(11)
C10	C12	C19	C11	-177.9(9)	C16	C14	C15	C13	-163.0(10)
C18	C10	01	C21	0.0	C16	C1	C17	C6	0.0
C18	C10	C12	C3	-21.6(14)	C1	C16	C24	C8	0.0
C18	C10	C12	C19	156.3(9)	C1	C17	C6	Br1	-179.1(7)
C18	C13	C21	01	0.0	C1	C17	C6	C8	0.0
C18	C13	C21	C23	-179.5(18)	C17	C6	C8	C24	0.0
C18	C13	C15	C14	-46.7(18)	C6	C8	C24	C16	0.0
C13	C18	C22	C4	34.7(18)	C24	C16	C1	C17	0.0
C13	C18	C22	C20	-94.9(13)	C20	C2	C7	C5	-36(2)
C13	C21	01	C10	0.0	C22	C4	C26	C5	10(3)
C21	C13	C15	C14	126.6(10)	C22	C18	C13	C21	-179.9(12)

01	C10 C18	C13	0.0	C22 C18	C13	C15	-5.8(17)
01	C10 C18	C22	179.9(12)	C23 C21	01	C10	179.6(13)
01	C10 C12	C3	156.4(7)	C26 C4	C22	C18	154.6(14)
01	C10 C12	C19	-25.7(11)	C26 C4	C22	C20	-71.0(17)
C11	C25 C9	C3	0.0	C26 C5	C7	C2	1(3)

Table 10 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for cu_240112c_0m.

Atom	x	у	Z.	U(eq)
H2	5285.2	4373.41	4883.62	101
H5	10994.58	2106.51	4528.77	103
H7	9532.94	3514.94	4928.36	95
H11	14078.75	10163.42	4092.12	122
H25	14620.84	9493.15	4630.92	123
H9	12126.86	7769.87	4841.47	108
H3	9090.79	6716.85	4513.21	105
H19	11042.63	9110.38	3763.87	105
H14	6700.25	3740.1	3349.51	80
H15A	2858.61	5004.12	3252.69	94
H15B	2033.18	4600	3607.9	94
H1	5990.59	2784.14	2814.59	86
H17	3863.88	1312.23	2468.69	96
H8	-1108.02	404.92	3189.96	85
H24	1018.65	1876.83	3535.86	86
H20	3995.64	5254.86	4390.07	92
H22	8864.88	4914.66	4184.66	74
H23A	4280.98	8769.56	3174.41	159
H23B	2290.95	7601.04	3132.96	159

H23C	4972.03	7534.36	2955.46	159
H26	8463.15	1562.69	4076.21	94

Experimental

Single crystals of $C_{26}H_{21}BrO_2$ [cu_240112c_0m] were from DCM and hexane. A suitable crystal was selected and put on a diffractometer. The crystal was kept at 293.0 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

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- Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Crystal structure determination of [cu_240112c_0m]

Crystal Data for C₂₆H₂₁BrO₂ (*M* =445.34 g/mol): orthorhombic, space group P2₁2₁2₁ (no. 19), a = 5.1768(16) Å, b = 10.008(3) Å, c = 40.889(11) Å, V = 2118.4(11) Å³, Z = 4, T = 293.0 K, μ (CuK α) = 2.787 mm⁻¹, *Dcalc* = 1.396 g/cm³, 22883 reflections measured ($4.322^{\circ} \le 2\Theta \le 133.188^{\circ}$), 3688 unique ($R_{int} = 0.0931$, $R_{sigma} = 0.0643$) which were used in all calculations. The final R_1 was 0.0968 (I > 2 σ (I)) and wR_2 was 0.3017 (all data).

6. References

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3. Zhang, Y.; Zhang, J. Kinetic resolution of 1-(1-alkynyl)cyclopropyl ketones by gold(I)-catalyzed asymmetric [4+3]cycloaddition with nitrones: scope, mechanism and applications. *Chem. Commun.*, **2012**, *48*, 4710-4712.

4. Wang, Y.; Wu, Q. -Q.; Tian, S. -K. Access to 2-Alkyltropones via Organic Base-Catalyzed Tandem Deamination and Aldol Condensation of Tropinone-Derived Quaternary Ammonium Salts. *J. Org. Chem.* **2023**, 88, 16456-16466.

7. NMR spectra



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

7.227 7.1131 7.1131 6.958 6.9595 6.9557 6.9557 6.5377 6.5377 6.5377 6.5337 6.5337 6.5337 6.5316 6.5316 6.235 6.246 6.235 6.246 6.235 6.246 6.235 6.246 6.235 7.5568 5.5689 5.5268 5.5276













f1 (ppm)











210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

7 212 7 212 7 255 7





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)






















S79

























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S91







S94



fl (ppm)



S96








































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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

















8. Copies of HPLC spectra

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.546	5620860	482935	49.653
2	6.983	5699436	433519	50.347
		11320296	916453	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	5.603	12504098	1235300	94.500
2	7.215	727727	61883	5.500
		13231824	1297182	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.254	5591068	879092	50.037
2	5.707	5582704	823311	49.963
		11173772	1702403	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	5.223	13079845	1925536	94.635
2	5.677	741519	101879	5.365
		13821364	2027415	100.000



Peak#	Ret. Time	Area	Height	Area%
1	5.228	2055520	210033	49.482
2	5.861	2098532	192624	50.518
		4154052	402658	100.000



<Peak Table>

<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	5.108	8376088	873891	95.947
2	5.685	353803	31190	4.053
		8729891	905082	100.000





<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.007	3475061	558151	49.858
2	5.740	3494896	512551	50.142
		6969958	1070702	100.000



<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.860	12083746	1715256	96.943
2	5.427	381094	48427	3.057
		12464840	1763683	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.920	2597370	262079	49.140
2	5.456	2688240	218147	50.860
		5285610	480227	100.000

```
<Chromatogram>
```



Peak#	Ret. Time	Area	Height	Area%
1	4.901	7411552	714424	93.814
2	5.427	488723	38152	6.186
		7900276	752576	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.935	4996981	845986	49.887
2	5.330	5019603	811509	50.113
		10016584	1657494	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.058	25377505	3239751	98.481
2	5.457	391426	47039	1.519
		25768931	3286790	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.994	1270482	166244	49.321
2	6.397	1305452	170501	50.679
		2575934	336746	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	5.758	49030	6528	5.120
2	6.044	908520	128182	94.880
		957551	134710	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.604	2269904	193986	50.068
2	7.610	2263774	208146	49.932
		4533678	402132	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	6.350	10628025	938743	97.666
2	7.653	253995	24906	2.334
		10882019	963649	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.360	3396697	228599	50.533
2	5.492	3325074	258282	49.467
		6721771	486881	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.424	10878058	1319285	95.705
2	5.652	488126	46636	4.295
		11366184	1365921	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.989	13992583	1940578	50.103
2	5.870	13935130	1744909	49.897
		27927713	3685487	100.000



<Chromatogram>

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.703	8384148	1204282	96.560
2	5.348	298697	37359	3.440
		8682846	1241641	100.000



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Pea	k#	Ret. Time	Area	Height	Area%
	1	4.243	3696786	334853	50.891
	2	5.389	3567384	309468	49.109
			7264170	644321	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.269	10969755	1184280	92.636
2	5.427	872025	90432	7.364
		11841780	1274713	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.621	3997057	639988	49.866
2	5.185	4018500	607744	50.134
		8015557	1247732	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.617	7992679	1290926	94.027
2	5.181	507688	82385	5.973
		8500367	1373311	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.444	2234204	252067	49.624
2	6.139	2268020	235063	50.376
		4502225	487130	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.386	261674	18569	8.923
2	6.040	2671045	225103	91.077
		2932720	243672	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.728	1130506	121589	49.893
2	11.427	1135374	81798	50.107
		2265880	203387	100.000





Peak#	Ret. Time	Area	Height	Area%
1	7.598	6164321	652735	96.343
2	11.195	234001	17558	3.657
		6398322	670293	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.877	940250	90571	49.712
2	7.708	951131	72771	50.288
		1891382	163343	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	5.797	10770211	995826	90.102
2	7.625	1183138	99773	9.898
		11953349	1095599	100.000



<Peak Table>

F	°eak#	Ret. Time	Area	Height	Area%
	1	7.752	4711438	427883	50.327
	2	8.596	4650123	409630	49.673
			9361561	837513	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	7.663	12686546	915010	92.913
2	8.583	967732	64546	7.087
		13654279	979556	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.222	6604158	634537	49.999
2	5.343	6604420	535194	50.001
		13208579	1169731	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.258	5812723	385518	92.610
2	5.308	463869	39870	7.390
		6276592	425388	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.786	7339786	928354	49.640
2	7.760	7446328	854699	50.360
		14786115	1783053	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	6.747	2013899	239459	97.727
2	7.679	46839	5511	2.273
		2060738	244970	100.000





<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.764	2834889	176663	50.097
2	5.762	2823901	176840	49.903
		5658789	353503	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	4.790	7235510	555141	95.086
2	5.764	373944	27840	4.914
		7609453	582981	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.832	12693766	1493792	49.904
2	6.222	12742471	1536071	50.096
		25436237	3029862	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.363	590072	68984	9.041
2	5.868	5936848	761867	90.959
		6526920	830852	100.000


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.130	5222449	591998	50.578
2	9.107	5103118	297347	49.422
		10325567	889345	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	6.172	4394521	409611	94.899
2	9.438	236236	13911	5.101
		4630757	423521	100.000



Peak#	Ret. Time	Area	Height	Area%
1	6.056	2377005	247125	50.954
2	6.462	2288027	243098	49.046
		4665032	490223	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.410	349237	43536	7.616
2	5.979	4236167	584267	92.384
		4585403	627803	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.576	1627541	174855	50.625
2	9.782	1587344	103150	49.375
		3214885	278005	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.712	9719295	881759	93.003
2	9.739	731235	48360	6.997
		10450530	930119	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.849	5420871	881836	49.739
2	5.036	5477770	899067	50.261
		10898641	1780903	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.946	6423672	900512	97.134
2	5.088	189539	28458	2.866
		6613211	928970	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.793	2625812	253498	50.293
2	6.102	2595209	202471	49.707
		5221021	455969	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.850	5691035	532515	92.935
2	6.184	432628	30813	7.065
		6123663	563328	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.308	1157018	200762	50.063
2	4.527	1154117	193893	49.937
		2311136	394655	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.312	430394	72460	8.656
2	4.548	4542019	797877	91.344
		4972413	870337	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.162	8348663	825214	49.706
2	7.041	8447427	570113	50.294
		16796090	1395327	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	6.183	14204117	1355775	93.293
2	7.134	1021176	89279	6.707
		15225293	1445054	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.509	13504856	1203285	50.019
2	11.399	13494413	979477	49.981
		26999268	2182762	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	9.526	944724	80480	3.761
2	11.365	24174805	1713613	96.239
		25119528	1794092	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.289	943581	78973	49.645
2	10.194	957075	58859	50.355
		1900656	137832	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	6.054	11229945	843006	93.725
2	9.685	751857	45602	6.275
		11981802	888609	100.000



Peak#	Ret. Time	Area	Height	Area%
1	6.516	6170708	932143	49.858
2	6.810	6205933	921084	50.142
		12376641	1853227	100.000





Peak#	Ret. Time	Area	Height	Area%
1	6.659	213524	25499	2.064
2	6.980	10130513	1299106	97.936
		10344037	1324605	100.000





<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.344	5462244	704538	50.172
2	4.777	5424818	650437	49.828
		10887062	1354975	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%	<u>آ</u>
1	4.344	4213601	502968	95.938	[
2	4.770	178410	18390	4.062	1
		4392010	521358	100.000	



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.590	1341707	191408	48.924
2	6.901	1400738	185771	51.076
		2742445	377179	100.000





Peak#	Ret. Time	Area	Height	Area%
1	6.418	74833	10925	2.131
2	6.699	3436253	498232	97.869
		3511086	509157	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.604	3581824	471526	48.748
2	5.424	3765852	446169	51.252
		7347676	917695	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.590	11406748	1230981	93.712
2	5.426	765425	76673	6.288
		12172173	1307654	100.000



Peak#	Ret. Time	Area	Height	Area%
1	6.664	3601196	491617	49.621
2	7.007	3656201	467472	50.379
		7257397	959089	100.000





Peak#	Ret. Time	Area	Height	Area%
1	7.198	109280	15681	1.558
2	7.430	6903614	954829	98.442
		7012894	970510	100.000



<	Ρ	е	a	ΚI	a	b	le>

Peak#	Ret. Time	Area	Height	Area%
1	5.076	1524409	148029	49.967
2	5.415	1526438	100292	50.033
		3050848	248322	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	6.046	8549291	760004	92.821
2	6.329	661250	90789	7.179
		9210541	850793	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.900	28029676	3033169	49.570
2	7.895	28516250	2904272	50.430
		56545926	5937441	100.000





Peak#	Ret. Time	Area	Height	Area%
1	7.020	8738854	1085294	90.821
2	8.084	883197	99954	9.179
		9622050	1185248	100.000





<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.119	2583589	189045	48.955
2	5.553	2693860	172260	51.045
		5277450	361305	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	5.108	7586907	518294	92.412
2	5.438	622991	52252	7.588
		8209898	570546	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.414	3411384	443151	49.869
2	8.520	3429274	381422	50.131
		6840657	824573	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	7.415	6493249	822774	96.261
2	8.531	252193	28264	3.739
		6745442	851038	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.793	5054061	515663	49.187
2	6.064	5221160	463489	50.813
		10275221	979153	100.000

<Chromatogram>

mV



Peak#	Ret. Time	Area	Height	Area%
1	4.788	6217362	634459	97.242
2	6.071	176335	14131	2.758
		6393697	648590	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.804	6782815	321357	50.362
2	8.885	6685339	175620	49.638
		13468154	496977	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	7.604	850008	34444	4.300
2	8.551	18917006	480730	95.700
		19767014	515174	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.013	4795421	617041	49.973
2	5.232	4800508	586797	50.027
		9595929	1203838	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	4.972	10334277	1323005	91.749
2	5.193	929372	126452	8.251
		11263649	1449457	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.010	13074731	287851	49.988
2	10.576	13080785	215368	50.012
		26155515	503219	100.000





Peak#	Ret. Time	Area	Height	Area%
1	8.517	22518131	614221	95.242
2	10.023	1125019	24478	4.758
		23643150	638699	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.620	3708238	180656	49.796
2	7.431	3738561	231389	50.204
		7446799	412045	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.817	522206	61424	9.921
2	6.371	4741214	495177	90.079
		5263420	556602	100.000

<Chromatogram>



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.189	10084672	1166725	50.274
2	7.909	9974807	1063033	49.726
		20059479	2229758	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	7.141	4825749	553514	98.872
2	8.009	55058	4107	1.128
		4880807	557622	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	3.925	1679722	165463	50.101
2	5.455	1672960	140614	49.899
		3352682	306077	100.000

<Chromatogram>

mV



Peak#	Ret. Time	Area	Height	Area%
1	3.912	2264960	233238	67.521
2	5.162	1089511	117384	32.479
		3354471	350622	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.382	5939476	1029039	49.775
2	4.858	5993077	985437	50.225
		11932553	2014477	100.000



<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.369	2256226	300805	76.515
2	4.761	692522	97120	23.485
		2948748	397925	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.824	2671041	53204	49.228
2	9.254	2754865	45568	50.772
		5425906	98772	100.000



8.0

8.5

<Peak Table>

6.0

Peak#	Ret. Time	Area	Height	Area%
1	7.551	4795187	106744	86.384
2	8.954	755812	15497	13.616
		5550999	122241	100.000

7.0

6.5

7.5

9.0

9.5

10.0

10.5

11.0 min



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.866	17918018	2804583	49.450
2	5.191	18316856	2779849	50.550
		36234875	5584432	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.644	2130642	407799	68.348
2	4.908	986717	182263	31.652
		3117359	590062	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.335	5006545	420572	49.818
2	5.805	5043101	333278	50.182
		10049646	753850	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	5.322	970719	81787	5.949
2	5.780	15346844	1022212	94.051
		16317563	1103999	100.000





<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.007	3475061	558151	49.858
2	5.740	3494896	512551	50.142
		6969958	1070702	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	4.848	6661616	1026986	90.486
2	5.302	700444	101755	9.514
		7362060	1128741	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.454	7021508	776879	50.580
2	4.732	6860580	729825	49.420
		13882088	1506705	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.564	15214925	1586477	97.051
2	4.882	462370	45847	2.949
		15677294	1632324	100.000



Peak#	Ret. Time	Area	Height	Area%
1	6.056	2377005	247125	50.954
2	6.462	2288027	243098	49.046
		4665032	490223	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.977	326188	40486	6.074
2	6.374	5043623	602250	93.926
		5369811	642736	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.932	2121845	258030	49.845
2	5.152	2135063	246742	50.155
		4256908	504772	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.893	66599	6708	4.660
2	5.124	1362609	148245	95.340
		1429208	154953	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	9.010	13074731	287851	49.988
2	10.576	13080785	215368	50.012
		26155515	503219	100.000





Peak#	Ret. Time	Area	Height	Area%
1	8.561	19488391	508547	96.127
2	9.838	785099	18799	3.873
		20273490	527347	100.000





<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.164	5684031	624250	50.141
2	6.258	5651967	562652	49.859
		11335999	1186902	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.057	496042	46512	8.553
2	6.033	5303350	556501	91.447
		5799393	603013	100.000





<Peak Table>

P	eak#	Ret. Time	Area	Height	Area%
	1	5.007	3475061	558151	49.858
	2	5.740	3494896	512551	50.142
			6969958	1070702	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.860	12083746	1715256	96.943
2	5.427	381094	48427	3.057
		12464840	1763683	100.000


<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.773	5371683	520739	49.120
2	5.658	5564244	525546	50.880
		10935926	1046284	100.000

<Chromatogram>

m٧ 5.599 1250-1000-750-500-40 250-4.752 0-4.5 5.0 5.5 6.0 6.5 7.0 min 4.0

Peak#	Ret. Time	Area	Height	Area%
1	4.752	694840	63312	4.973
2	5.599	13276137	1316871	95.027
		13970977	1380183	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000

<Chromatogram>

mV



Peak#	Ret. Time	Area	Height	Area%
1	4.737	3488424	599666	93.595
2	5.142	238740	39094	6.405
		3727165	638760	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.533	3821090	375917	50.648
2	4.926	3723306	349918	49.352
		7544396	725835	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.536	1517214	148142	5.031
2	4.926	28637287	2804953	94.969
		30154501	2953096	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000



<Chromatogram>

<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.848	6661616	1026986	90.486
2	5.302	700444	101755	9.514
		7362060	1128741	100.000

S182



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.830	1526190	114426	49.687
2	7.830	1545423	107922	50.313
		3071613	222348	100.000





Peak#	Ret. Time	Area	Height	Area%
1	6.960	778989	63680	3.952
2	7.977	18930406	1406294	96.048
		19709395	1469974	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.776	5344563	905537	91.354
2	5.172	505830	76102	8.646
		5850393	981639	100.000



Peak#	Ret. Time	Area	Height	Area%
1	4.635	10036360	841826	50.675
2	5.855	9768993	810102	49.325
		19805353	1651928	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.622	808515	66142	4.758
2	5.812	16185716	1326549	95.242
		16994231	1392691	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000

<Chromatogram>

mV



Peak#	Ret. Time	Area	Height	Area%
1	4.677	8478584	1501854	97.373
2	5.028	228723	34882	2.627
		8707308	1536736	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	7.366	7998600	580157	49.332
2	11.170	8215331	449275	50.668
		16213932	1029432	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	7.361	382060	26184	2.251
2	10.919	16588560	886897	97.749
		16970620	913081	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000



m٧



Peak#	Ret. Time	Area	Height	Area%
1	4.776	8162941	1343918	92.221
2	5.178	688585	110721	7.779
		8851526	1454639	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.755	3837640	380328	50.138
2	5.516	3816576	369165	49.862
		7654216	749493	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.822	205301	24301	5.145
2	5.643	3785283	434929	94.855
		3990585	459230	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000

<Chromatogram>

mV



Peak#	Ret. Time	Area	Height	Area%
1	4.778	2681804	465063	92.283
2	5.176	224268	38096	7.717
		2906072	503159	100.000



Peak#	Ret. Time	Area	Height	Area%
1	6.323	2248715	131828	49.290
2	6.798	2313542	138155	50.710
		4562258	269984	100.000





Peak#	Ret. Time	Area	Height	Area%
1	6.331	424407	25882	4.169
2	6.749	9756231	597375	95.831
		10180638	623257	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000





Peak#	Ret. Time	Area	Height	Area%
1	4.769	11022498	1743172	91.247
2	5.167	1057399	152888	8.753
		12079897	1896061	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.263	4151806	363499	49.900
2	7.224	4168402	327244	50.100
		8320208	690743	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.229	568124	48421	5.474
2	6.953	9810810	795060	94.526
		10378933	843480	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	4.765	14476586	2315616	49.798
2	5.188	14594217	2205568	50.202
		29070803	4521184	100.000



<Chromatogram>

Peak#	Ret. Time	Area	Height	Area%
1	4.701	8616185	1392111	95.268
2	5.065	427991	61734	4.732
		9044177	1453845	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	6.235	5061596	477096	49.878
2	6.876	5086361	429699	50.122
		10147957	906796	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	6.175	1207652	101800	5.717
2	6.794	19916671	1779586	94.283
		21124322	1881385	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.007	3475061	558151	49.858
2	5.740	3494896	512551	50.142
		6969958	1070702	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	4.975	6007993	972690	91.604
2	5.684	550655	82285	8.396
		6558648	1054975	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.486	1708937	110722	49.812
2	6.074	1721832	95165	50.188
		3430769	205887	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	5.493	15400540	1606381	94.121
2	6.022	961945	95186	5.879
		16362485	1701567	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	3.845	560911	111590	49.985
2	4.346	561254	53300	50.015
		1122165	164889	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	3.848	9334545	1973981	91.959
2	4.386	816231	84538	8.041
		10150776	2058519	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.792	1653049	134091	50.000
2	7.203	1653072	114620	50.000
		3306121	248711	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.968	7302706	541864	90.911
2	7.705	730096	44319	9.089
		8032803	586183	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.478	154930	13616	49.156
2	6.039	160248	12747	50.844
		315177	26363	100.000

<Chromatogram>

mV



Peak#	Ret. Time	Area	Height	Area%
1	5.278	7542524	574813	89.906
2	5.871	846805	71735	10.094
		8389329	646548	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.509	927979	107446	49.545
2	6.358	945025	95512	50.455
		1873004	202958	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.508	2291169	253799	95.384
2	6.422	110878	9165	4.616
		2402047	262964	100.000



<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.757	1110242	109398	24.498
2	7.007	1172634	99184	25.875
3	8.290	1135739	86988	25.061
4	14.918	1113348	36406	24.567
		4531963	331976	100.000

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%
1	5.838	291288	20984	5.996
2	7.149	1455970	117880	29.968
3	8.482	3029972	202053	62.365
4	15.435	81204	2911	1.671
		4858433	343827	100.000



Peak#	Ret. Time	Area	Height	Area%
1	5.228	2055520	210033	49.482
2	5.861	2098532	192624	50.518
		4154052	402658	100.000





Peak#	Ret. Time	Area	Height	Area%
1	5.108	8376088	873891	95.947
2	5.685	353803	31190	4.053
		8729891	905082	100.000





<Peak Table>

Peak#	Ret. Time	Area	Height	Area%
1	5.007	3475061	558151	49.858
2	5.740	3494896	512551	50.142
		6969958	1070702	100.000

<Chromatogram>

mV



Peak#	Ret. Time	Area	Height	Area%
1	4.997	10414267	1777322	96.796
2	5.727	344759	52543	3.204
		10759026	1829865	100.000