Supporting Information

Effects of Haloniums on Gold-catalyzed Ring Expansion of 1-oxirany-1-alkynylcyclopropanes

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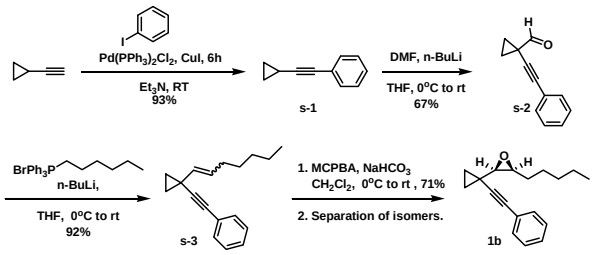
(I). Experimental procedures for synthesis of cyclopropyloxirane (1b).

(a) General Procedure

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula and septa apparatus. Toluene, benzene, tetrahydrofuran (THF) and Et_2O were dried with sodium, benzophenone and distilled before use. DMF, CH_2Cl_2 and TMEDA was dried over CaH_2 and distilled before use.

(b). Experimental procedures for synthesis of cyclopropyloxirane (1b)



(b-1). Synthesis of 1-(2-cyclopropylethynyl)benzene (s-1).

$Pd(PPh_3)_2Cl_2$ (210 mg, 2 mol%), CuI (114 mg, 4 mol%), and PhI (2.0 ml, 15.75 mmol) were dissolved in 30 ml of Et_3N. A solution of cyclopropylacetylene (1.0 g, 15 mmol) in 5 ml Et_3N was added dropwise into the mixture under N_2 and stirred at rt. When the reaction was complete as monitored by TLC, a brown precipitate appeared. Filtration, rotary evaporation, and flash chromatography on silica gel afforded **s-1 (**1.98 g, 13.95 mmol, 93 %) as a liquid.

(b-2). Synthesis of 1-(2-phenylethynyl)cyclopropanecarbaldehyde (s-2).

To a solution of **s-1** (1.4 g, 9.8 mmol) in anhydrous THF (20 ml) cooled to 0 ℃ was added *n*-BuLi (4.7 ml, 2.5 M in Hexane, 1.2 eq).The resulting mixture was stirred during a 1h period before the addition of DMF (0.83 ml, 1.2 eq). The reaction mixture was extracted with ethyl acetate, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residues were chromatographed through a silica gel column (hexane/ethyl acetate = 10/1) to afford compound **s-2** (1.16 g, 6.57 mmol, 67 %) as colorless oil.

(b-3). Synthesis of 1-(2-(1-(hept-1-enyl)cyclopropyl)ethynyl)benzene (s-3).

To a THF solution (20 mL) of hexyl(triphenyl)phosphonium bromide (3.35 g, 7.84 mmol) at 0 ℃ was added *n*-BuLi (2.5 mL, 2.5 M, 2.87 ml), and the mixture was stirred at 0 ℃ for 1.0 h. To this solution was added **s-2** (1.11 g, 6.53 mmol), and the mixture was stirred at rt for 1 h. The solution was quenched with water and concentrated in vacuo. The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column

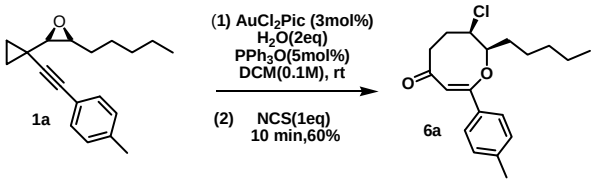
chromatographed (hexane) over a silica gel column to give the olefination product (major *cis*- isomer) **s-3** as a colorless oil (1.81 g, 7.21 mmol, 86 %).

(b-4). Synthesis of 2-pentyl-3-(1-(2-phenylethynyl)cyclopropyl)oxirane (1b).

To a CH_2Cl_2 solution (25 ml) of **s-3** (700 mg, 2.77 mmol) was added *m*-chloroperbenzoic acid (717 g, 4.15 mmol), and the mixtures were stirred for 1.5 h at 0 ℃. The resulting solution was quenched with an aqueous $NaHCO_3$ solution, extracted with diethyl ether, and dried over anhydrous $MgSO_4$ and concentrated in vacuo. The resulting mass was filtered through a small basic Al_2O_3 bed, then concentrated in vacuo, and eluted through a Et_3N-pretreated silica column (hexane/ethyl acetate = 25/1) to separate two isomers and afforded compound **1b** (major *cis*- isomer, 527 mg, 1.96 mmol, 71 %) as colorless oil.

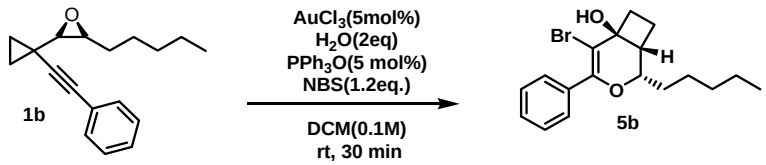
(II). **Experimental Procedures for Catalytic Operations.**

(a). Catalytic cyclization of cyclopropyloxirane (1a).



A solution of $PicAuCl_2$ (3 mol%) in dichloromethane (3.0 mL) was added compound **1a** (80 mg, 0.30 mmol), PPh_3O(4.17mg, 5 mol%) and H_2O (5.4×10^{-3} ml, 2 eq) dropwise at 25 ℃ and the solution was stirred for 1 min. Then NCS(39.3mg, 1 eq) was added and the solution kept stirring for another 10 min.The resulting solution was filtered through a celite bed, and eluted through a silica gel column (hexane/ethyl acetate = 20/1) to give compound **6a** (58 mg, 0.18 mmol, 60 %) as a colorless oil.

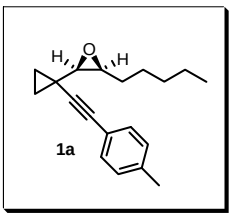
(b). Catalytic cyclization of 5-bromo-2-pentyl-4-phenyl-3-oxabicyclo-[4.2.0]oct-4-en-6-ol (5b).



A solution of $AuCl_3$ (5 mol%) in dichloromethane (3.0 mL) was added compound **1b** (80 mg, 0.30 mmol), PPh_3O(4.17mg, 5 mol%), NBS(63mg, 1.2eq) and H_2O (5.4×10^{-3} ml, 2 eq) dropwise at 25 ℃ and the solution was stirred for 30 min. The resulting solution was filtered through a celite bed, and eluted through a silica gel column (hexane/ethyl acetate = 10/1) to give compound **5b** (71 mg, 0.204 mmol, 68 %) as a colorless oil.

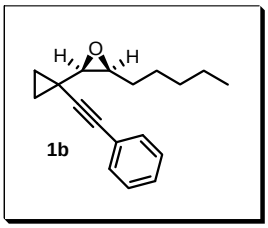
(III) Spectral Data for Compounds

Spectra data for 2-pentyl-3-(1-(2-*p*-tolylethynyl)cyclopropyl)oxirane (1a)



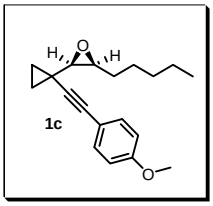
Colorless oil; IR (neat, cm^{-1}): 3078(m), 2210(w), 1961(s), 1598(m), 1251(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.24 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 3.25 (d, *J* = 4.0 Hz, 1 H), 2.98-2.93 (m, 1 H), 2.31 (s, 3 H), 1.78-1.70 (m, 2 H), 1.55-1.40 (m, 2 H), 1.38-1.29 (m, 4 H), 1.17-1.02 (m, 4 H), 0.96-0.84 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ137.7, 131.5 128.9, 120.3, 91.0, 78.0, 58.7, 57.1, 31.7, 27.2, 26.3, 22.6, 21.3, 14.0, 13.4, 13.2, 11.0; HRMS calcd for $C_{19}H_{24}O$: 268.1827, found: 268.1829.

Spectra data for 2-pentyl-3-(1-(phenylethynyl)cyclopropyl)oxirane (1b)



Colorless oil; IR (neat, cm^{-1}): 3312(m), 3070(s), 2947(m), 2150(m), 1454(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.36-7.34 (m, 2 H), 7.26-7.24 (m, 3 H), 3.26 (d, *J* = 4.0 Hz, 1 H), 2.96 (td, *J* = 6.0, 4.0 Hz, 1 H), 1.81-1.69 (m, 2 H), 1.57-1.51 (m, 1 H), 1.40-1.29 (m, 5 H), 1.63-1.04 (m, 2 H), 0.97-0.90 (m, 2 H), 0.87 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ131.6, 128.1, 127.7, 123.5, 91.8, 79.9, 58.6, 57.1, 31.7, 27.2, 26.3, 22.6, 13.9, 13.5, 13.3, 11.0; HRMS calcd for $C_{18}H_{22}O$: 254.1671, found: 254.1670.

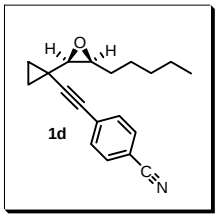
Spectra data for 2-(1-((4-methoxyphenyl)ethynyl)cyclopropyl)-3-pentyloxirane (1c)



Colorless oil; IR (neat, cm^{-1}): 3066(m), 2210(w), 1961(s), 1598(m), 1204(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.29 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 9.2 Hz, 2 H), 3.77 (s, 3 H), 3.25 (d, *J* = 4.0 Hz, 1 H), 2.95 (td, *J* = 6.4, 4.0 Hz, 1 H), 1.78-1.70 (m, 2 H), 1.56-1.50

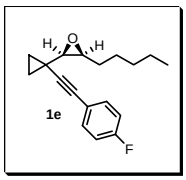
(m, 1 H), 1.38-1.31 (m, 5 H), 1.13-1.02 (m, 2 H), 0.92-0.95 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ159.0, 132.8 115.4, 113.6, 90.0, 77.6, 58.5, 56.9, 55.0, 31.6, 27.1, 26.2, 22.5, 13.8, 13.3, 13.0, 10.9; HRMS calcd for $C_{19}H_{24}O_2$: 284.1776, found: 284.1774.

Spectra data for 4-((1-(3-pentyloxiran-2-yl)cyclopropyl)ethynyl)benzonitrile (1d)



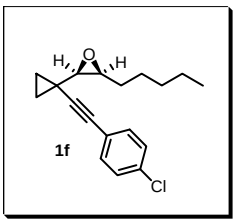
Colorless oil; IR (neat, cm^{-1}): 3078(m), 2210(w), 1961(s), 1598(m), 1251(s); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.55-7.53 (m, 2 H), 7.42-7.40 (m, 2 H), 3.24-3.23 (d, *J* = 4.0 Hz, 1 H), 2.98-2.94 (m, 1 H), 1.74-0.99 (m, 15 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ131.9, 131.7, 128.3, 118.3, 110.9, 96.9, 76.6, 58.4, 56.6, 31.1, 27.1, 26.2, 22.4, 13.8, 13.5, 11.0; HRMS calcd for $C_{19}H_{21}NO$: 279.1623, found: 279.1627

Spectra data for 2-(1-((4-fluorophenyl)ethynyl)cyclopropyl)-3-pentyloxirane (1e)



Colorless oil; IR (neat, cm^{-1}): 3148(m), 2210(w), 1961(s), 1598(m), 1495(s); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.32 (dd, *J* = 8.4, 5.2 Hz, 2 H), 6.94 (t, *J* = 8.4 Hz, 2 H), 3.23 (d, *J* = 4.0 Hz, 1 H), 2.95 (td, *J* = 6.2, 4.0 Hz, 1 H), 1.77-1.69 (m, 2 H), 1.56-1.51 (m, 1 H), 1.37-1.30 (m, 4H), 1.14-1.01 (m, 3H), 0.91-0.90 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ162.0 (d, *J* = 247.0 Hz), 133.3 (d, *J* = 9.0 Hz), 119.4 (d, *J* = 3.0 Hz), 115.3 (d, *J* = 22.0 Hz), 91.4, 76.8, 58.5, 56.9, 31.6, 27.1, 26.2, 22.5, 13.8, 13.4, 13.1, 10.9; HRMS calcd for $C_{18}H_{21}FO$: 272.1576, found: 272.1575.

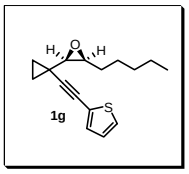
Spectra data fo 2-(1-((4-chlorophenyl)ethynyl)cyclopropyl)-3-pentyloxirane(1f)



Colorless oil; IR (neat, cm^{-1}): 3031(m), 2267(w), 1961(s), 1598(m), 1251(s); ^{1}H NMR

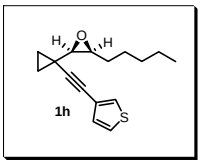
(400 MHz, $CDCl_3$): δ7.28-7.21 (m, 4 H), 3.23-3.22 (d, *J* = 4.0 Hz, 1 H), 2.95-2.94 (m, 1 H), 1.75-0.95 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ133.6, 132.7 128.4, 121.9, 92.9, 76.8, 58.5, 56.9, 31.6, 27.2, 26.3, 22.5, 13.9, 13.5, 13.3, 11.0; HRMS calcd for $C_{18}H_{21}ClO$: 288.1281, found:288.1287.

Spectra data for 2-pentyl-3-(1-(thiophen-2-ylethynyl)cyclopropyl)oxirane (1g)



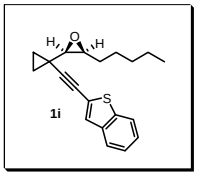
Colorless oil; IR (neat, cm^{-1}): 3078(m), , 1961(s), 1598(m);
^1H NMR (400 MHz, $CDCl_3$): δ7.17-7.09 (m, 2 H), 6.92-6.90 (m, 1 H), 3.24-3.23 (d, *J* = 4.0 Hz, 1 H), 2.95-2.94 (m, 1 H), 1.77-0.91 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ131.4, 126.7, 126.3, 123.5, 95.7, 71.1, 58.6, 56.8, 31.7, 27.2, 26.2, 22.5, 13.9, 13.6, 13.4,11.2; HRMS calcd for $C_{16}H_{20}OS$:260.1235, found: 260.1227

Spectra data for 2-pentyl-3-(1-(thiophen-3-ylethynyl)cyclopropyl)oxirane(1h)



Colorless oil; IR (neat, cm^{-1}): 3034(m), , 1961(s), 1598(m); ^1H NMR (400 MHz, $CDCl_3$): δ7.33-7.32 (m, 1 H), δ7.21-7.20 (m, 1 H),7.03-7.01 (m, 1 H), 3.24-3.23 (d, *J* = 4.0 Hz, 1 H), 2.97-2.93 (m, 1 H), 1.76-1.06 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ129.8, 128.0, 124.9, 122.3, 91.2, 72.9, 58.5, 56.9, 31.6, 27.1, 26.2, 22.5, 13.9, 13.4, 13.1,10.9; HRMS calcd for $C_{16}H_{20}OS$: 260.1235, found:260.1242.

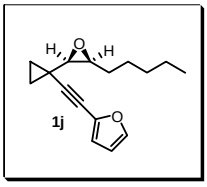
Spectra data for 2-(1-(benzo[b]thiophen-2-ylethynyl)cyclopropyl)-3-pentyloxirane(1i)



Colorless oil; IR (neat, cm^{-1}): 3028(m), 2210(w), 1958(s), 1598(m), 1251(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.72-7.66 (m, 2 H), δ7.33-7.23 (m, 3 H), 3.27-3.26 (m, 1 H), 2.98-2.96 (m, 1 H), 1.74-0.90 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ139.8,139.0,128.2,125.1,124.5 123.5, 123.4, 121.8, 97.9, 71.5, 58.6, 56.8, 31.7, 27.2, 26.3, 22.5, 13.9, 13.8, 13.6, 11.3; HRMS calcd for $C_{20}H_{22}OS$: 310.1391,

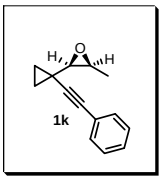
found:.310.1385.

Spectra data for 2-((1-(3-pentyloxiran-2-yl)cyclopropyl)ethynyl)furan (1j)



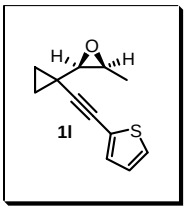
Colorless oil; IR (neat, cm^{-1}): 3078(m), 1961(s), 1598(m); ^1H NMR (400 MHz, $CDCl_3$): δ7.30 (m, 1 H), 6.46-6.45 (m, 1 H), 6.33-6.32 (m, 1 H), 3.20-3.19 (d, *J* = 4.0 Hz, 1 H), 2.91-2.87 (td, *J* = 8.0 Hz, 4.0 Hz, 1 H), 1.75-0.79 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ142.9, 137.1, 114.4, 110.5, 96.1, 79.3, 58.5, 56.5, 31.6, 27.1, 26.2, 13.8, 13.6, 13.4, 11.0; HRMS calcd for $C_{16}H_{20}O_2$: 244.1463, found:244.1478.

Spectra data for 2-methyl-3-(1-(phenylethynyl)cyclopropyl)oxirane (1k)



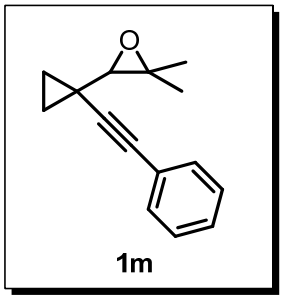
Colorless oil; IR (neat, cm^{-1}): 3080(m), 2953(m), 2099(m), 2144(m), 1495(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.37-7.35 (m, 2 H), 7.27-7.24 (m, 3 H), 3.24 (d, *J* = 4.0 Hz, 1 H), 3.09 (qd, *J* = 5.2, 4.0 Hz, 1 H), 1.45 (d, *J* = 5.2 Hz, 3 H), 1.17-1.05 (m, 2 H), 0.98-0.89 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ131.7, 128.2, 127.8, 123.5, 91.7, 78.0, 57.0, 45.1, 13.6, 13.2, 13.1, 11.0; HRMS calcd for $C_{14}H_{14}O$: 198.1045, found: 198.1043.

Spectra data for 2-methyl-3-(1-(thiophen-2-ylethynyl)cyclopropyl)oxirane (1l)



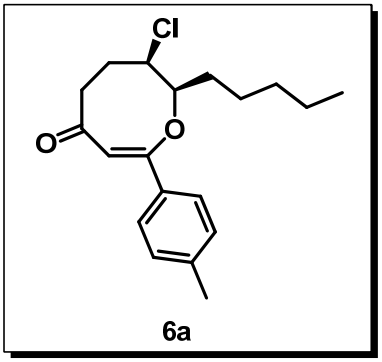
Colorless oil; IR (neat, cm^{-1}): 3078(m), 1961(s), 1598(m); ^1H NMR (400 MHz, $CDCl_3$): δ7.17-7.10 (m, 2 H), 6.92-6.90 (m, 1 H), 3.28-3.22 (m, 1 H), 3.11-3.05 (m, 1 H), 1.44-1.43 (d, *J* = 4.0 Hz, 3 H), 1.23-0.92 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ131.6, 126.7, 126.3, 123.5, 95.6, 70.9, 56.8, 54.2, 13.6, 13.3, 13.0, 11.1; HRMS calcd for $C_{12}H_{12}OS$: 204.0609, found:204.0615.

Spectra data for 2,2-dimethyl-3-(1-(phenylethynyl)cyclopropyl)oxirane (1m)



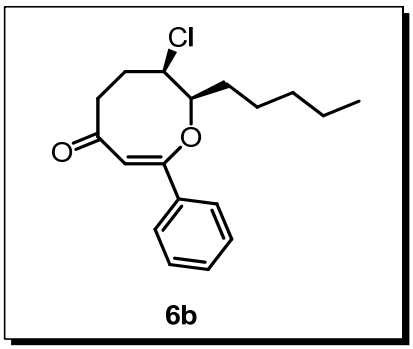
Colorless oil; IR (neat, cm^{-1}): 3081(m), 2911(m), 2093(m), 1239(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.37-7.35 (m, 2 H), 7.27-7.24 (m, 3 H), 3.08 (s, 1 H), 1.44 (s, 3 H), 1.33 (s, 3 H), 1.16-1.04 (m, 2 H), 0.98-0.84 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ131.5, 128.0, 127.6, 123.4, 91.8, 77.6, 63.4, 59.9, 24.8, 18.3, 13.5, 13.4, 11.7; HRMS calcd for $C_{15}H_{16}O$: 212.1201, found: 212.1203.

Spectra data for (Z)-3-chloro-2-pentyl-8-p-tolyl-4,5-dihydro-2H-oxocin-6(3H)-one (6a)



Colorless oil; IR (neat, cm^{-1}): 3149(m), 1667(m), 1495(s), 1225(m), 726(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.28-7.16 (m, 4 H), 5.60 (s, 1 H), 4.21 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.48 (td, *J* = 8.0, 4.0 Hz, 1 H), 2.99 (t, *J* = 4.0 Hz, 2 H), 2.42-2.37 (m, 1 H), 2.34 (s, 3 H), 2.17-2.07 (m, 1 H),1.60-0.80 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ210.0, 154.3, 139.2, 130.6, 129.3, 127.1, 101.6, 75.6, 63.8, 45.4, 31.9, 31.6, 24.6, 21.2, 13.9, 12.7; HRMS calcd for $C_{19}H_{25}ClO_2$: 320.1543, found:320.1546.

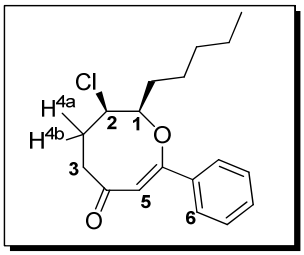
Spectra data for (Z)-3-chloro-2-pentyl-8-phenyl-4,5-dihydro-2H-oxocin-6(3H)-one (6b)



6b

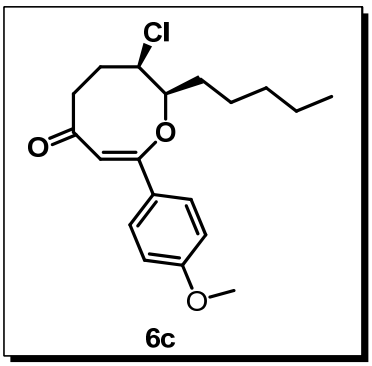
Colorless oil; IR (neat, cm^{-1}): 3132(m), 1941(w), 1901(s), 1673(m), 1495(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.40-7.29 (m, 5 H), 5.65 (s, 1 H), 4.21 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.49 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.01 (t, *J* = 4.0 Hz, 2 H), 2.46-2.07 (m, 2 H), 1.59-0.89 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ210.1, 154.2, 133.4, 129.1, 128.6, 127.1, 102.4, 75.7, 63.7, 45.3, 31.8, 31.6, 24.6, 22.3, 13.9, 12.6; HRMS calcd for $C_{18}H_{23}ClO_2$: 306.1387, found: 306.1385.

NOE-map of compound **6b**



irradiation	intensity increase
H^1 (δ 4.21)	H^2 (δ 3.49, 5.43 %), H^6 (δ 7.35, 6.98 %).
H^2 (δ 3.49)	H^1 (δ 4.21, 5.25 %), H^3 (δ 3.01, 1.31 %), H^{4b} (δ 2.26, 3.84 %).
H^3 (δ 3.01)	H^2 (δ 3.49, 1.46 %), H^{4a} (δ 2.41, 1.46 %), H^{4b} (δ 2.12, 1.53 %)
H^4 (δ 2.26)	H^2 (δ 3.49, 3.90 %), H^3 (δ 3.01, 34.63 %).
H^5 (δ 5.65)	H^6 (δ 7.35, 8.08 %).

Spectra data for (Z)-3-chloro-8-(4-methoxyphenyl)-2-pentyl-4,5-dihydro-2H-oxocin-6(3H)-one (6c)

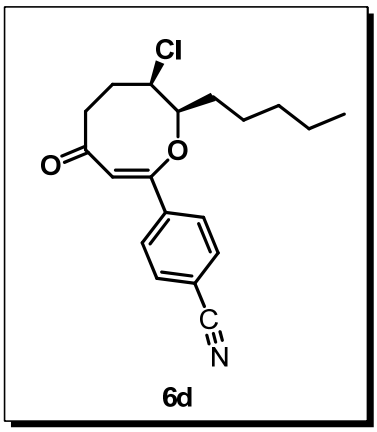


6c

Colorless oil; IR (neat, cm^{-1}): 3132(m), 1673(m), 1495(s), 1225(m), 724(s) ; ^1H NMR (400 MHz, $CDCl_3$): δ7.35-7.26 (m, 2 H), δ6.93-6.87 (m, 2 H), 5.55 (s, 1 H), 4.20 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.80 (s, 3H), 3.47 (td, *J* = 8.0, 4.0 Hz, 1 H),3.00 (t, *J* = 8.0 Hz, 2 H), 2.43-2.06 (m, 2 H), 1.56-0.80 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ210.2, 160.3, 154.0, 128.5, 114.0, 100.9, 75.5, 63.7,55.3, 45.3, 31.8, 31.6, 24.7, 22.4, 13.9, 12.6; HRMS calcd for $C_{19}H_{25}ClO_3$: 336.1492, found:336.1498.

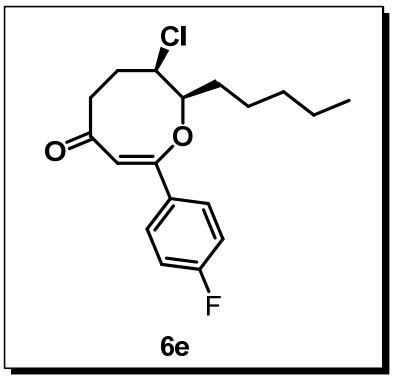
Spectra data for 4-((Z)-3-chloro-6-oxo-2-pentyl-3,4,5,6-tetrahydro-2H-oxocin-8-yl)benzonitrile (6d)



6d

Colorless oil; IR (neat, cm^{-1}): 3132(m), 2250(s), 1673(m), 1495(s), 1225(m), 724(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.68-7.65 (m, 2 H), δ7.49-7.47 (m, 2 H), 5.83 (s, 1 H), 4.17 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.50 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.01 (t, *J* = 8.0 Hz, 2 H), 2.45-2.41 (m, 1 H), 2.15-2.09 (m, 1 H), 1.54-0.80 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ209.0, 152.5, 138.0, 132.5, 127.3, 118.3, 112.7, 105.9, 76.2, 63.4, 45.3, 31.6, 31.5, 24.7, 22.3, 13.8, 12.2; HRMS calcd for $C_{19}H_{22}ClNO_2$: 331.1339, found:331.1345.

Spectra data for (Z)-3-chloro-8-(4-fluorophenyl)-2-pentyl-4,5-dihydro-2H -oxocin-6(3H)-one (6e)

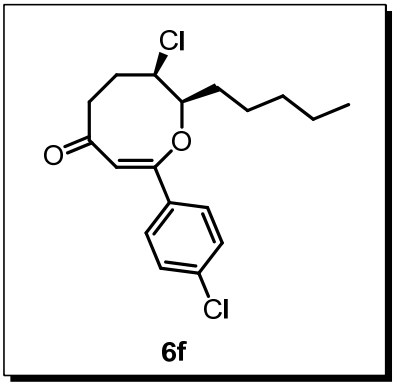


6e

Colorless oil; IR (neat, cm^{-1}): 3154(m), 1673(m), 1467(s), 1225(m), 724(s) ; ^1H NMR (400 MHz, $CDCl_3$): δ7.35-7.24 (m, 2 H), δ7.07-7.03 (m, 2 H), 5.60 (s, 1 H), 4.18 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.48 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.00 (t, *J* = 8.0 Hz, 2 H), 2.44-2.40 (m, 1 H), 2.14-2.09 (m, 1 H), 1.57-0.80 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ210.1, 153.3, 129.5, 129.0, 128.9, 115.8, 115.6, 102.3, 75.6, 63.6, 45.3, 31.7,

31.6, 24.6, 22.3, 13.8, 12.4; HRMS calcd for: $C_{18}H_{22}ClFO_2$: 324.1292, found:324.1297.

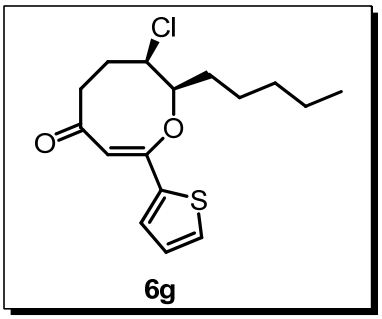
Spectra data for (Z)-3-chloro-8-(4-chlorophenyl)-2-pentyl-4,5-dihydro-2H-oxocin-6(3H)-one (6f)



6f

Colorless oil; IR (neat, cm^{-1}): 3157(m), 1673(m), 1495(s), 1228(m), 746(s) ; ^1H NMR (400 MHz, $CDCl_3$): δ7.29-7.17 (m, 4 H), 5.59 (s, 1 H), 4.12 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.42 (td, *J* = 8.0, 4.0 Hz, 1 H), 2.94 (t, *J* = 4.0 Hz, 2 H), 2.40-2.30 (m, 1 H), 2.10-2.00 (m, 1 H), 1.49-0.74 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ210.0, 153.2, 135.1, 131.9, 128.9, 128.3, 103.0, 75.8, 63.6, 45.4, 31.7, 31.6, 24.7, 22.4, 13.9, 12.4; HRMS calcd for $C_{18}H_{22}C_{l2}O_2$: 340.0997, found:340.0992.

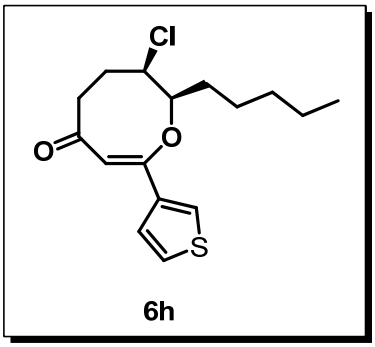
Spectra data for (Z)-3-chloro-2-pentyl-8-(thiophen-2-yl)-4,5-dihydro-2H-oxocin-6(3H)-one (6g)



6g

Colorless oil; IR (neat, cm^{-1}): 3147(m), 1673(m), 1495(s), 1225(m), 724(s) ; ^1H NMR (400 MHz, $CDCl_3$): δ7.28-7.27 (m, 1 H), δ7.14-7.13 (m, 1 H), δ7.02-7.00 (m, 1 H), 5.78 (s, 1 H), 4.45 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.53 (td, *J* = 8.0, 4.0 Hz, 1 H), 2.99 (t, *J* = 8.0 Hz, 2 H), 2.41-2.08 (m, 2 H), 1.63-1.23 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ209.6, 148.3, 135.9, 127.4, 126.8, 126.4, 102.4, 77.0, 63.8, 45.4, 32.0, 31.6, 24.7, 22.4,13.9, 12.8; HRMS calcd for $C_{16}H_{21}ClO_2S$: 312.0951, found:312.0957.

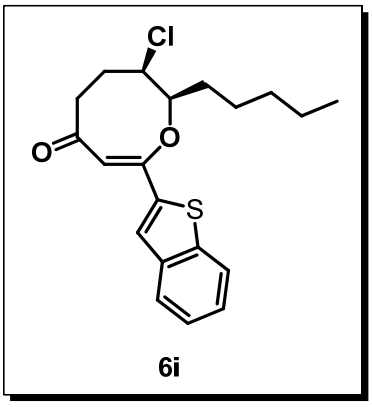
Spectra data for (Z)-3-chloro-2-pentyl-8-(thiophen-3-yl)-4,5-dihydro-2H-oxocin-6(3H)-one (6h)



6h

Colorless oil; IR (neat, cm^{-1}): 3143(m), 1673(m), 1498(s), 1225(m), 727(s) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.38-7.37 (m, 1 H), δ7.31-7.29 (m, 1 H), δ7.07-7.06 (m, 1 H), 5.70 (s, 1 H), 4.32 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.51 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.00 (t, *J* = 8.0 Hz, 2 H), 2.42-2.38 (m, 1 H), 2.17-2.06 (m, 1 H), 1.57-0.83 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ210.2, 149.8, 134.9, 126.3, 126.0, 123.9, 102.0, 76.0, 63.7, 45.3, 31.8, 31.6, 24.7, 22.4, 13.9, 12.4; HRMS calcd for $C_{16}H_{21}ClO_2S$: 312.0951, found:312.0957.

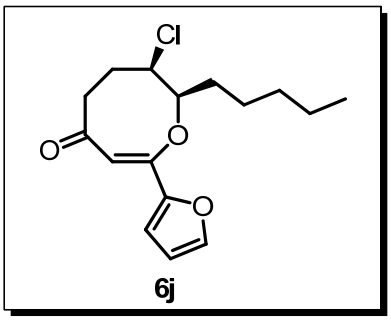
Spectra data for (Z)-8-(benzo[b]thiophen-2-yl)-3-chloro-2-pentyl-4,5-dihydro-2H-oxocin-6(3H)-one (6i)



6i

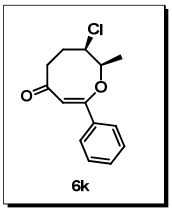
Colorless oil; IR (neat, cm^{-1}): 3146(m), 1673(m), 1495(s), 1225(m), 724(s) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.78-7.76 (m, 2 H), δ7.39 (m, 1 H), δ7.35-7.32 (m, 2 H),5.96 (s, 1 H), 4.56 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.58 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.02 (t, *J* = 4.0 Hz, 2 H), 2.43-2.12 (m, 2 H), 1.67-0.82 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ209.6, 148.6, 139.4, 136.1, 125.1, 124.7, 124.1, 123.3, 122.2, 104.6, 77.3, 63.7, 45.4, 32.0, 31.7, 24.7, 22.4, 13.9, 12.9; HRMS calcd for $C_{20}H_{23}ClO_2S$: 362.1107, found:362.1112.

Spectra data for (Z)-3-chloro-8-(furan-2-yl)-2-pentyl-4,5-dihydro-2H-oxocin-6(3H)-one (6j)



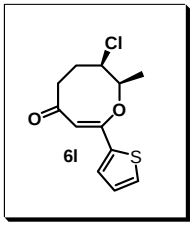
Colorless oil; IR (neat, cm^{-1}): 3132(m), 1673(m), 1495(s), 1225(m), 724(s) ; ^1H NMR (400 MHz, $CDCl_3$): δ7.36-7.36 (m, 1 H), δ6.54-6.53 (m, 1 H), δ6.40-6.39 (m, 1 H), 6.00 (s, 1 H), 4.46 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.54 (td, *J* = 8.0, 4.0 Hz, 1 H), 2.99 (t, *J* = 8.0 Hz, 2 H), 2.37-2.07 (m, 2 H), 1.55-0.84 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ209.9, 147.9, 145.2, 142.9, 111.2, 109.0, 103.5, 77.7, 63.7, 45.4, 31.9, 31.7,24.8, 22.4, 13.9, 12.6; HRMS calcd for $C_{16}H_{21}ClO_3$: 296.1179, found:296.1183.

Spectra data for (Z)-3-chloro-2-methyl-8-phenyl-4,5-dihydro-2H-oxocin-6(3H)-one (6k)



Colorless oil; IR (neat, cm^{-1}): 3132(m), 1673(m), 1495(s), 1225(m), 724(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.37-7.35 (m, 5 H), 5.76 (s, 1 H), 4.31 (qd, *J* = 12.0, 4.0 Hz, 1 H), 3.44 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.01 (t, *J* = 8.0 Hz, 2 H), 2.42-2.13 (m, 2 H), 1.17 (d, *J* = 4.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ209.1, 153.9, 133.5, 129.1, 128.7, 126.7, 103.2, 72.4, 65.8, 45.3, 17.7, 12.9; HRMS calcd for $C_{14}H_{15}ClO_2$: 250.0761, found: 250.0765.

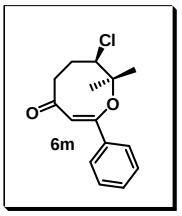
Spectra data for (Z)-3-chloro-2-methyl-8-(thiophen-2-yl)-4,5-dihydro-2H-oxocin-6(3H)-one (6l)



Colorless oil; IR (neat, cm^{-1}): 3156(m), 1673(m), 1495(s), 1225(m), 745(s); ^1H NMR (400 MHz, $CDCl_3$): δ7.28-6.99 (m, 3 H), 5.88 (s, 1 H), 4.54 (qd, *J* = 12.0, 4.0 Hz, 1 H), 3.46 (td, *J* = 8.0, 4.0 Hz, 1 H), 3.02 (t, *J* = 4.0 Hz, 2 H), 2.99-2.16 (m, 2 H), 1.28

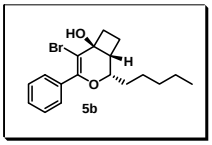
(d, *J* = 4.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ208.9, 148.0, 136.4, 127.5, 126.3, 103.1, 76.6, 65.8, 45.3, 29.6 18.0, 13.1; HRMS calcd for $C_{12}H_{13}ClO_2S$: 256.0325, found: 256.0327.

Spectra data for (Z)-3-chloro-2,2-dimethyl-8-phenyl-4,5-dihydro-2H-oxocin-6(3H)-one (6m)



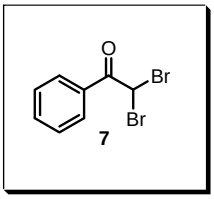
Colorless oil; IR (neat, cm^{-1}): 3132(m), 1673(m), 1495(s), 1225(m), 724(s); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.97-7.95 (m, 2 H), δ7.65-7.62 (m, 1 H), δ7.53-7.49 (m, 2 H), 5.90 (s, 1 H), 4.28 (t, *J* = 4.0 Hz, 1 H), 2.85 (td, *J* = 8.0, 4.0 Hz, 2 H), 2.34-2.15 (m, 2 H), 1.43 (s, 3 H);1.17 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ197.0, 143.5, 135.0, 129.0, 128.9, 114.8, 78.7, 65.0, 33.5, 29.1, 22.7; HRMS calcd for $C_{15}H_{17}ClO_2$: 264.0917, found:264.0923.

Spectral data for 5-bromo-2-pentyl-4-phenyl-3-oxabicyclo[4.2.0]oct-4-en-6-ol (5b)



Colorless oil; IR (neat, cm^{-1}): 3587(m), 3081(m), 1682(s), 1604(m), 1210(s), 558(s);:^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.38-7.34 (m, 3H), 3.90 (td, *J* = 8.0, 4.0 Hz, 1H), 2.83 (td, *J* = 8.0, 4.0 Hz, 1H), 2.69 (m, 1H), 2.24 - 1.42 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 135.6, 129.0, 128.9, 127.7, 105.4, 73.6, 71.3, 47.2, 35.5, 31.6, 24.9, 22.4, 13.9, 11.8; HRMS calcd for $C_{18}H_{23}BrO_2$: 350.0881, found:350.0875.

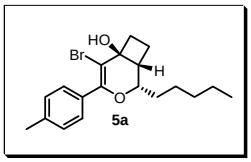
Spectra data for 2,2-dibromo-1-phenylethanone (7)



Colorless oil; IR (neat, cm^{-1}): 3081(m), 1710(s), 1604(m), 538(s);^{1}H NMR (400 MHz,

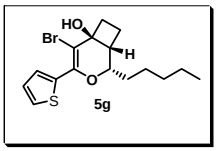
$CDCl_3$): δ8.07-8.05 (m, 2H), 7.64-7.47 (m, 3H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ185.9, 134.4, 130.8, 129.6, 128.9, 39.6, 29.6; HRMS calcd for $C_8H_6Br_2O$: 275.8785, found:275.8794.

Spectral data for 5-bromo-2-pentyl-4-p-tolyl-3-oxabicyclo [4.2.0]oct-4-en-6-ol(5a)



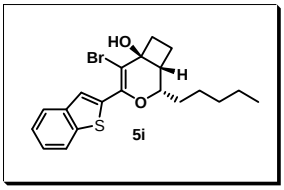
Colorless oil; IR (neat, cm^{-1}): 3533(m), 3081(m), 1682(s), 1604(m), 1210(s), 550(s);^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.88 (m, 1H), 2.84 ~ 2.79 (m, 1H), 2.35 (s, 3H), 2.21 ~ 2.08 (m, 2H), 1.77 ~ 1.70 (m, 1H), 1.63 ~ 1.39 (m, 5H), 1.34 ~ 1.22 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 138.9, 132.7, 129.0 (CH x 2), 128.5 (CH x 2), 105.1, 73.6, 71.4, 47.3, 35.5, 31.6 (CH_2 x 2), 25.0, 22.5, 21.4, 14.0, 11.9; HRMS calcd for $C_{19}H_{25}BrO_2$: 364.1038, found: 364.1045.

Spectral data for 5-bromo-2-pentyl-4-(thiophen-2-yl)-3-oxabicyclo [4.2.0]oct-4-en-6-ol (5g)



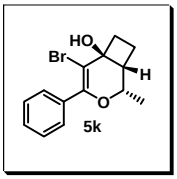
Colorless oil; IR (neat, cm^{-1}): 3587(m), 1682(s), 1210(s), 558(s);^1H NMR (400 MHz, $CDCl_3$): δ 7.77-7.76 (m, 1H), 7.38-7.36 (m, 1H), 7.06-7.04 (m, 1H), 3.88 (td, *J* = 8.0, 4.0 Hz, 1H), 2.81 (td, *J* = 12.0, 8.0 Hz, 1H), 2.62 (m, 1H), 2.19 - 2.08 (m, 2H) , 1.74 - 1.65 (m, 2H) ,1.56 – 1.32(m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 137.3, 129.0, 127.2,126.6, 105.3, 73.6, 71.6, 47.2, 35.6,31.5, 29.6, 25.0, 22.5, 14.0, 11.6 ; HRMS calcd for $C_{16}H_{21}BrO_2S$: 356.0446, found:356.0451.

Spectral data for 4-(benzo[b]thiophen-2-yl)-5-bromo-2-pentyl-3 -oxabicyclo [4.2.0]oct-4-en-6-ol (5i)



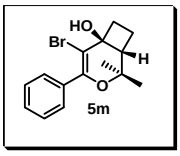
Colorless oil; IR (neat, cm^{-1}): 3606(m), 3081(m), 1682(s), 1604(m), 1210(s), 576(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.81 (m, 3H), 7.35-7.33 (m, 2H), 4.18 (td, *J* = 8.0, 4.0 Hz, 1H), 2.90 (td, *J* = 8.0, 4.0 Hz, 1H), 2.84 (m, 1H), 2.34 - 2.09(m, 4H) , 1.56 – 0.83(m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5,147.2, 140.0,138.6, 124.9, 124.3,124.3,124.1,122.0, 83.5, 79.3, 74.5, 46.7, 34.4,33.2, 29.6, 25.2, 22.5, 19.1, 14.0; HRMS calcd for $C_{20}H_{23}BrO_2S$: 406.0602, found:406.0615.

Spectral data for 5-bromo-2-methyl-4-phenyl-3-oxabicyclo [4.2.0]oct-4-en-6-ol (5k)



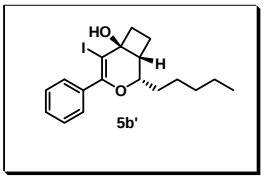
Colorless oil; IR (neat, cm^{-1}): 3587(m), 3081(m), 1682(s), 1604(m), 1210(s), 558(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.51 (m, 1H), 7.38-7.34 (m, 4H), 4.07 (qd, *J* = 8.0, 4.0 Hz, 1H), 2.77 (td, *J* = 8.0, 4.0 Hz, 1H), 2.58 (m, 1H), 2.22 – 2.02 (m, 4H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 135.6, 129.0, 128.9, 127.8, 105.4, 84.2, 69.7, 48.4, 35.2, 17.3, 11.5; HRMS calcd for $C_{14}H_{15}BrO_2$: 294.0255, found:294.0257.

Spectral data for 5-bromo-2,2-dimethyl-4-phenyl-3-oxabicyclo [4.2.0]oct-4-en-6-ol (5m)



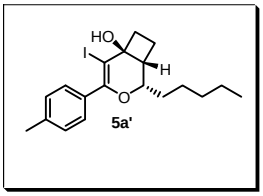
Colorless oil; IR (neat, cm^{-1}): 3587(m), 3081(m), 1682(s), 1604(m), 1210(s), 558(s); H NMR (400 MHz, $CDCl_3$): δ 7.50-7.47 (m, 2H), 7.36-7.34 (m, 3H),2.68 (t, *J* = 12.0, 1H), 2.54 (m, 1H), 2.19 – 2.00 (m, 4H), 1.33 (s, 3H) , 1.21(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 135.9, 128.9, 128.7, 127.7, 104.6, 74.7, 71.2, 51.9, 34.6, 24.9, 23.1,13.8; HRMS calcd for $C_{15}H_{17}BrO_2$: 308.0412, found:308.0415.

Spectral data for 5-iodo-2-pentyl-4-phenyl-3-oxabicyclo [4.2.0]oct-4-en-6-ol (5b')



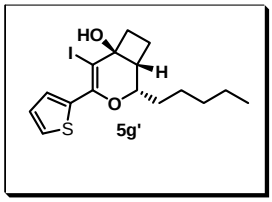
Colorless oil; IR (neat, cm^{-1}): 3598(m), 3081(m), 1682(s), 1604(m), 1210(s), 502(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.34 (m, 5H), 3.92 (td, *J* = 8.0, 4.0 Hz, 1H), 2.84 (td, *J* = 12.0, 8.0 Hz, 1H), 2.52 (m, 1H), 2.11 - 1.40 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 138.0, 129.3, 129.0, 127.8, 84.2, 73.9, 72.6, 46.1, 37.4, 31.7, 31.7,24.9, 22.5, 14.0, 12.1; HRMS calcd for $C_{18}H_{23}IO_2$: 398.0743, found:398.0751.

Spectral data for 5-iodo-2-pentyl-4-p-tolyl-3-oxabicyclo[4.2.0]oct-4-en-6-ol (5a')



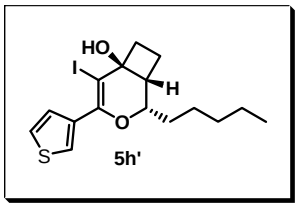
Colorless oil; IR (neat, cm^{-1}): 3587(m), 3081(m), 1682(s), 1632(m), 1210(s), 508(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.89 (m, 1H), 2.85 ~ 2.80 (m, 1H), 2.36 (s, 3H), 2.10 ~ 1.97 (m, 2H), 1.76 ~ 1.69 (m, 1H), 1.64 ~ 1.27 (m, 9H), 0.87 ~ 0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 138.9, 135.1, 129.2 (CH x 2), 128.4 (CH x 2), 83.9, 73.8, 72.6, 46.1, 37.4, 31.7, 31.6, 24.9, 22.5, 21.4, 14.0, 12.0; HRMS calcd for $C_{19}H_{25}IO_2$: 412.0899, found:412.0905.

Spectral data for 5-iodo-2-pentyl-4-(thiophen-2-yl)-3-oxabicyclo [4.2.0]oct-4-en-6-ol (5g')



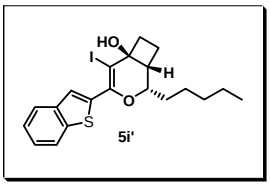
Colorless oil; IR (neat, cm^{-1}): 3587(m), 1682(s), 1210(s), 502(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.63 (m, 1H), 7.23-7.16 (m, 2H), 4.49 (td, *J* = 8.0, 4.0 Hz, 1H), 2.94 (td, *J* = 8.0, 4.0 Hz, 1H), 2.79 (m, 1H), 1.95 - 1.71 (m, 4H) , 1.33 – 0.82 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 136.7, 134.3, 132.3,127.5, 82.1, 74.6, 74.1, 45.5, 31.3,29.6, 26.8, 25.1, 24.9, 22.4, 13.9 ; HRMS calcd for $C_{16}H_{21}IO_2S$: 404.0307, found:404.0312.

Spectral data for 5-iodo-2-pentyl-4-(thiophen-3-yl)-3-oxabicyclo [4.2.0]oct-4-en-6-ol (5h')



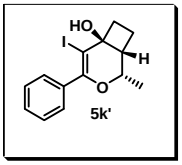
Colorless oil; IR (neat, cm^{-1}): 3587(m), 1682(s), 1210(s), 512(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.69 (m, 1H), 7.38-7.37 (m, 1H), 7.27-7.25 (m, 1H),3.89 (td, *J* = 8.0, 4.0 Hz, 1H), 2.83 (td, *J* = 8.0, 4.0 Hz, 1H), 2.47 (m, 1H), 2.06 - 1.97 (m, 4H) , 1.61 – 0.82 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 137.8, 128.3, 127.2,124.3, 84.1, 73.6, 72.7, 46.1, 37.4,31.7, 31.6, 25.0, 22.5, 14.0, 11.9; HRMS calcd for $C_{16}H_{21}IO_2S$: 404.0307, found:404.0312.

Spectral data for 4-(benzo[b]thiophen-2-yl)-5-iodo-2-pentyl-3-oxabicyclo[4.2.0]oct-4-en-6-ol (5i')



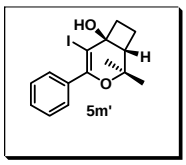
Colorless oil; IR (neat, cm^{-1}): 3587(m), 3081(m), 1682(s), 1604(m), 1210(s), 558(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.78 (m, 3H), 7.35-7.32 (m, 2H), 3.94 (td, *J* = 8.0, 4.0 Hz, 1H), 2.87 (td, *J* = 8.0, 4.0 Hz, 1H), 2.52 (m, 1H), 2.11 – 1.98(m, 2H) , 1.75 – 1.66(m, 2H),1.57 – 0.81(m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2,140.2, 138.9,138.8, 126.5, 125.1,124.3,124.2,122.0, 85.8, 74.0, 72.9, 46.1, 37.6,31.6, 31.6,25.0, 22.5, 14.0, 11.8; HRMS calcd for $C_{20}H_{23}IO_2S$: 454.0463, found:454.0467.

Spectral data for 5-iodo-2-methyl-4-phenyl-3-oxabicyclo[4.2.0]oct-4-en-6-ol (5k')



Colorless oil; IR (neat, cm^{-1}): 3587(m), 3081(m), 1682(s), 1604(m), 1210(s), 508(s);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.37-7.34 (m, 3H), 4.10 (qd, *J* = 8.0, 4.0 Hz, 1H), 2.78 (td, *J* = 8.0, 4.0 Hz, 1H), 2.53-2.52 (m, 1H), 2.08 – 1.74 (m, 4H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 138.0, 129.1, 128.9, 127.8, 84.2, 72.4, 69.9, 47.2, 37.1, 17.4, 11.7 ;HRMS calcd for $C_{14}H_{15}IO_2$: 342.0117, found:342.0124.

Spectral data for 5-iodo-2,2-dimethyl-4-phenyl-3-oxabicyclo [4.2.0]oct-4-en-6-ol (5m')



Colorless oil; IR (neat, cm^{-1}): 3587(m), 3081(m), 1682(s), 1604(m), 1210(s), 508(s); ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.34 (m, 5H), 2.69 (t, *J* = 8.0, 1H), 2.53 (m, 1H), 2.03 – 1.78 (m, 4H), 1.38 (s, 3H) , 1.21(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 138.3, 129.1, 128.7, 127.8, 83.4, 74.9, 72.4, 50.6, 36.5, 25.0, 23.2,14.0 ;HRMS calcd for $C_{15}H_{17}IO_2$: 356.0273, found:356.0277.