Supporting Information

Gold-Catalyzed Deoxygenated Cyclization of *cis*-2,4-Dien-1-als with Regioselective Addition of Two Nucleophiles. One-pot synthesis of Highly Functionalized Cyclopentane Framework.

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(1) Table S1. Catalyst screening with aldehyde **3 and allylSiMe₃.**

Cyclization of aldehyde **3** with allylsilane was unsuccessful when hard acids HOTf, Me₃SiOTf and BF₃·Et₂O were used. These catalysts preferably gave cyclopentenones **s1** and **s2**, given from the cycloisomerization of aldehyde **3** alone. Apparently, allylsilane was not a nucleophile as MeOH in this system, which can be trapped by the hypothetical allyl cation intermediate. PtCl₂ and PdCl₂ failed to give 1,4-addition product **14** even in hot benzene solution; the corresponding reaction led to cycloisomerization to give pyran **s3** preferably. The use of allylsilane nucleophile is only applicable to PPh₃AuSbF₆, which led to a much more clean 1,4-addition reaction when compared to AuCl, AuCl₃ and AgSbF₆ catalysts (entries 6-8); the yield of desired species **14** was up to 78%. The spectral data of compounds **s1-s3** have appeared in an early paper.^{4b}

Table S1.

entry	M (mol %)	condition	products
1	HOTf (3 mol%)	DCM (23 °C, 30 min)	s1/ s2 (65%, s1/s2=4.4)
2	Me ₃ SiOTf (5 mol%)	DCM (23 °C, 30 min)	s1/s2 (63%, s1/s2=2.5)
3	BF ₃ ·Et ₂ O (5 mol%)	DCM (23 °C, 30 min)	14 (16%), s1 (38%), 3 (11%)
4	PtCl ₂ (5 mol%)	benzene (80 °C, 60 min)	3 (45%), s3 (35%)
5	PdCl ₂ (CH ₃ CN) ₂ (5 mol%)	benzene (80 °C, 60 min)	3 (52%), s3 (27%)
6	AuCl (5 mol%)	DCM (23 °C, 12 h)	14 (3%), 3 (76%), s2 (5%)
7	AuCl ₃ (5 mol%)	DCM (23 °C, 12 h)	14 (36%), 3 (21%), s2 (27%)
8	AgSbF ₆ (5 mol%)	DCM (23 °C, 12 h)	14 (43%), 3 (11%), s2 (21%)
9	PPh ₃ AuCl/AgSbF ₆ (3 mol%)	DCM (23 °C, 25 min)	14 (78 %)

^a [substrate] = 0.56 M, DCM = dichloromethane, 3.0 equiv. allylSiMe₃ ^b Products were reported after separation from silica column.

(2) Table S2. Catalyst Screening with Aldehyde **3 with MeOH.**

Although we did not see cycloisomerization byproducts in the reaction of aldehyde **2** with MeOH; we noted that the initially formed 1,4-dimethoxycyclopentene **6** is unstable in the cases when hard acids HOTf, Me₃SiOTf and BF₃·Et₂O are used as catalysts (entries 1-3). PtCl₂ seems to be superior to PdCl₂ in this cyclization with a 51% yield of desired product **6** was obtained. The reaction with AuCl gave a messy reaction whereas AuCl₃ and AgSbF₆ showed a similar behavior to that observed for HOTf (entries 6-8). The AuPPh₃SbF₆ catalyst shows the best chemoselectivity and only gives desired cyclopentene **6** in 88% yield.

entry	catalyst (mol %)	condition	products
1	HOTf (3 mol%)	DCM (23 °C, 2 h)	6 (41%), s4 (25%), 3 (18%)
2	Me ₃ SiOTf (5 mol%)	DCM (23 °C, 30 min)	s4 (13%), s5 (72%)
3	BF ₃ ·Et ₂ O (5 mol%)	DCM (23 °C, 30 min)	6 (35%), s4 (32%)
4	PtCl ₂ (5 mol%)	benzene (80 °C, 60 min)	6 (51%), 3 (6%)
5	PdCl ₂ (CH ₃ CN) ₂ (5 mol%)	benzene (80 °C, 60 min)	6 (27%), 3 (6%)
6	AuCl (3 mol%)	DCM (23 °C, 5 h)	messy, 3 (24%)
7	AuCl ₃ (3 mol%)	DCM (23 °C, 30 min)	6 (25%), s4 (41%), 3 (4%)
8	AgSbF ₆ (5 mol%)	DCM (23 °C, 2 h)	6 (46 %), 3 (14%), s4 (19%)
9	PPh ₃ AuCl/AgSbF ₆ (3 mol%)	DCM (23 °C, 25 min)	6 (88 %, trans/cis= 4.6)

^a [substrate] = 0.56 M, DCM = dichloromethane. ^b Products were reported after separation from silica column.

(3) Table S3. Gold-catalyzed Cyclization of Aldehydes with Nucleophiles.

In addition to the data in Table 1, we also performed additional six compounds **32-37** obtained from the gold-catalyzed cyclization of aldehydes **1-3** with isopropanol, tosylamine, thiophenol, triethylsilane and 2-methylallylSiMe₃. These products were obtained in good yields; and these new examples demonstrate the reliability of this new cyclization. The spectral data of compounds **32-38** are provided in this Supporting Information.

aldehyde	Nu-E	temp (time) ^a	products ^b
(1) 2	ⁱ PrOH	25 °C (1 h)	32 (78%, B/A= 15.6)
(2) 1	TsHN-H	15 °C (30 min)	33 (82%, trans/cis=1.5)
(3) 3	TsHN-H	25 °C (20 min)	34 (82%, trans/cis=1.4)
(4) 1	PhS-H	25 °C (25 min)	35 (84%, trans/cis=1.5)
(5) 3	H-SiEt ₃	25 °C (40 min)	36 (74%)
(6) 3	2-CH ₃ allyl-SiMe ₃	15 °C (30 min)	37 (82%, trans/cis>20)

^a Nu-H (3.0 equiv.), [substrate] = 0.65 M, CH₂Cl₂, 3 mol% ClAuPPh₃/AgSbF₆

^b Products were purified from a silica column.

(4) Scheme S1. The Mechanism for Cyclization with Two Allylsilanes.

Scheme S1 illustrates a proposed mechanism for cyclization of *cis*-2,4-dien-1-al **2** with two molecules of allylsilane. The cationic gold activates the ene-carbonyl coupling of species **s-A** to yield allylic cationic intermediate **s-B**, which was allylation by allylsilane to give species **s-C**. The released TMS⁺ fragment is expected to be exchanged with OAuL to form siloxy species **s-D**. A subsequent ionization of this species by AuPPh₃⁺ yields the second allyl cation **s-E**, which was attacked by the allylsilane to form the diallylation product **13**. In this process, the released TMS⁺ fragment will react with TMSOAuL to give AuL⁺ and TMS₂O species.

(5) Synthesis of *cis*-2,4-Dien-1-als **27** and catalytic cyclization.

(a) General Procedures

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 and hexane were dried with sodium benzophenone and distilled before use. DMF, CH₂Cl₂ was dried over CaH₂ and distilled before use. Starting *cis*-dienals **1-3**, **s6** were readily prepared from cyclohexanone according to the procedure in literature.^{s1} Cycloisomerization products **s1-s3** have been reported in the same paper.

s1. Lo, C.-Y.; Lin, C.-C.; Cheng, H.-M.; Liu, R.-S. *Org. Lett.* **2006**, 8, 3153 (also see the text, reference 4b).

(b) Synthesis of (*E*)-2-(4-hydroxybut-1-enyl)cyclohex-1-enecarbaldehyde (**27**)

(b-1) Synthesis of (E)-2-(4-(tert-butyldimethylsilyloxy)but-1-enyl)cyclohex-1-enecarbaldehyde (s-9). Pd(OAc)₂ (119 mg, 0.53 mmol), PPh₃ (416 mg, 1.59 mmol) and K₂CO₃ (1.90 g, 13.75 mmol) were placed in a two necked flask under nitrogen atmosphere, and DME (20 mL) and H₂O (30 mL) were added *via* syringe. To this mixture was added 2-bromocyclohex-1-enecarbaldehyde **s-7** (2.00 g, 10.58 mmol) and (E)-4-(benzo[d][1,3,2]dioxaborol-2-yl)but-3-en-2-yl tert-butyl dimethylsilane **s-8** (3.86 g, 12.69 mmol), and reaction mixture was stirred at 90 °C for 24 h. The resulting mixture was partitioned between 50 mL diethyl ether/water (1:1, v/v), and the aqueous layer was washed with ether (20 mL x 2). The combined ether extracts were washed with a saturated NaCl solution, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residues were chromatographed through a silica gel column (hexane/ethyl acetate: 9/1) to afford compound **s-9** (2.46 g, 8.36 mmol, 79%) as colorless oil.

(b-2) Synthesis of (E)-2-(4-hydroxybut-1-enyl)cyclohex-1-enecarbaldehyde (27). To a THF solution (15 mL) of *tert*-butyldimethylsilyloxy-protected alcohol **s-9** (2.46 g, 8.36 mmol) was added 12.5 mL TBAF solution (1 M in THF, 12.53 mmol), and the mixture was stirred at room temperature for 2 h. The solution was concentrated under reduced pressure, and added with water (20 mL). The organic layer was extracted with ethyl acetate (20 mL x 3), washed with a saturated NaCl solution, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residues were passed through a short silica column (hexane/ethyl acetate: 6/4) to afford compound **27** (1.43 g, 7.93 mmol, 95%) as colorless oil.

(c) Experimental procedures for gold catalyzed cyclization. Synthesis of 2,3,4,5,6,7-hexahydro-1,3-dimethoxy-2,2-dimethyl-1H-indene (6). A CH₂Cl₂ (0.5 mL) solution of AuCl(PPh₃) (8.8 mg, 0.02 mmol) and AgSbF₆ (6.1 mg, 0.02 mmol) was stirred at 25 °C for 10 min, and cooled to 15 °C before addition of 2-(2-methyl-propenyl)-cyclohex-1-enecarbaldehyde (**3**) (100 mg, 0.60 mmol) and MeOH (58 mg, 1.80 mmol) in CH₂Cl₂ (0.6 mL). The mixture was stirred at 15 °C for 40 min. The solution was concentrated and eluted through a silica column (hexane/ether=20/1) to afford 2,3,4,5,6,7-hexahydro-1,3-dimethoxy-2,2-dimethyl-1H-indene (**6**) (106 mg, 84%).

Spectral data of compounds 1-38A,B and s4~5

Spectral data for 2-vinyl-cyclohex-1-enecarbaldehyde (1). IR(neat, cm⁻¹): 2950 (m), 2862

(m), 1690 (s), 1615(w), 1492 (m); ^1H NMR (400 MHz, CDCl_3): δ 10.30 (s, 1H), 7.28 (dd, J = 17.2, 10.8 Hz, 1H), 5.50 (d, J = 17.2 Hz, 1H), 5.39 (d, J = 10.8 Hz, 1H), 2.41~2.38 (m, 2H), 2.29~2.26 (m, 2H), 1.69~1.58 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 190.7, 151.9, 135.6, 131.7, 119.0, 26.9, 22.8, 21.7, 21.4; HRMS calcd for $\text{C}_9\text{H}_{12}\text{O}$: 136.0888, found 136.0876.

Spectral data for 2-((*E*)-hex-1-enyl)cyclohex-1-enecarbaldehyde (2). IR(neat, cm^{-1}): 2936 (m), 2862 (m), 1648 (s), 1430 (m); ^1H NMR (400 MHz, CDCl_3): δ 10.27 (s, 1H), 6.93 (d, J = 15.6 Hz, 1H), 6.05~5.98 (m, 1H), 2.40~2.38 (m, 2H), 2.27~2.23 (m, 2H), 2.21~2.17 (m, 2H), 1.64~1.57 (m, 4H), 1.42~1.29 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.0, 152.5, 137.0, 133.8, 125.1, 33.0, 31.1, 27.8, 22.7, 22.1, 21.9, 21.4, 13.7; HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: 192.1514, found 192.1517.

Spectral data for 2-(2-methyl-propenyl)cyclohex-1-enecarbaldehyde (3). IR(neat, cm^{-1}): 2930 (m), 2858 (m), 1666 (s), 1612 (s), 1450 (m); ^1H NMR (400 MHz, CDCl_3): δ 9.59 (s, 1H), 5.64 (s, 1H), 2.13~2.12 (m, 2H), 2.06~2.04 (m, 2H), 1.73 (s, 3H), 1.51~1.54 (m, 4H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.4, 156.4, 138.6, 134.6, 122.8, 31.7, 25.4, 21.8, 21.6, 21.4, 19.3; HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: 164.1201, found 164.1187.

Spectral data for 2,3,4,5,6,7-hexahydro-1,3-dimethoxy-1H-indene (4-*cis/trans*). IR(neat, cm^{-1}): 2928 (s), 2876 (m), 1664 (m); ^1H NMR (400 MHz, CDCl_3): (*cis*-isomer), δ 4.09 (brs, 2H), 3.28 (s, 6H), 2.48~2.44 (m, 1H), 2.16~2.12 (m, 2H), 1.96~1.92 (m, 2H), 1.62~1.57 (m, 5H); (*trans*-isomer), δ 4.35 (brs, 2H), 3.28 (s, 6H), 2.20~2.16 (m, 2H), 2.01~1.93 (m, 4H), 1.62~1.57 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): *cis*-isomer, δ 139.6, 84.4, 55.5, 35.0, 23.6, 22.6; *trans*-isomer, δ 141.3, 86.3, 56.6, 36.1, 23.7, 22.7; HRMS calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2$: 182.1307, found 182.1305.

Spectral data for 2-butyl-2,3,4,5,6,7-hexahydro-1,3-dimethoxy-1*H*-indene (5). Isomer A: IR(neat, cm^{-1}): 2928 (s), 2890 (m), 1660 (m); ^1H NMR (400 MHz, CDCl_3): δ 4.14 (d, $J = 6.4$ Hz, 1H), 3.93 (brs, 1H), 3.35 (s, 3H), 3.34 (s, 3H), 2.05~1.95 (m, 5H), 1.66~1.57 (m, 6H), 1.38~1.29 (m, 4H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 139.4, 139.3, 91.7, 86.6, 58.3, 57.0, 47.1, 30.7, 27.0, 24.0, 23.4, 23.0, 22.4, 22.4, 14.0; HRMS calcd for $\text{C}_{15}\text{H}_{26}\text{O}_2$: 238.1933, found 238.1938. Isomer B: IR(neat, cm^{-1}): 2929 (s), 2887 (m), 1660 (m); ^1H NMR (400 MHz, CDCl_3): δ 3.71 (brs, 2H), 3.29 (s, 6H), 2.17~2.13 (m, 2H), 1.95~1.92 (m, 3H), 1.66~1.60 (m, 4H), 1.46~1.34 (m, 6H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.9, 90.7, 55.1, 47.2, 33.9, 29.9, 23.6, 22.9, 22.4, 14.0; HRMS calcd for $\text{C}_{15}\text{H}_{26}\text{O}_2$: 238.1933, found 238.1938.

Spectral data for 2,3,4,5,6,7-hexahydro-1,3-dimethoxy-2,2-dimethyl-1*H*-indene (6-*cis/trans*). *cis*-isomer; IR(neat, cm^{-1}): 2918 (s), 2888 (m), 1670 (m); ^1H NMR (400 MHz, CDCl_3): δ 3.49 (s, 2H), 3.42 (s, 6H), 2.18~2.14 (m, 2H), 1.90~1.86 (m, 2H), 1.66~1.59 (m, 4H), 1.19 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 137.4, 93.9, 59.1, 46.6, 28.9, 23.5, 22.6, 16.5; HRMS calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2$: 210.1620, found 210.1608. *trans*-isomer; IR(neat, cm^{-1}): 2919 (s), 2888 (m), 1671 (m); ^1H NMR (400 MHz, CDCl_3): δ 3.69 (s, 2H), 3.42 (s, 6H), 2.12~2.07 (m, 2H), 1.94~1.90 (m, 2H), 1.66~1.57 (m, 4H), 1.07 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.3, 94.6, 59.4, 45.2, 23.7, 22.7, 22.5; HRMS calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2$: 210.1620, found 210.1608.

Spectral data for 2,3,4,5,6,7-hexahydro-1,3-diphenoxy-1*H*-indene (7-*cis/trans*). IR(neat, cm^{-1}): 3052 (m), 2918 (s), 1664 (m), 1612 (m), 1504 (m); ^1H NMR (400 MHz, CDCl_3): *cis*-isomer, δ 7.29~7.25 (m, 4H), 6.95~6.88 (m, 6H), 5.03~5.01 (m, 2H), 3.01~2.96 (m, 1H), 2.44~2.41 (m, 2H), 2.04~2.00 (m, 2H), 1.93~1.88 (m, 1H), 1.81~1.67 (m, 4H); *trans*-isomer, δ 7.29~7.25 (m, 4H), 6.95~6.88 (m, 6H), 5.28~5.26 (m, 2H), 2.40 (d, $J = 4.8$ Hz, 1H), 2.39 (d, $J = 4.8$ Hz, 1H), 2.39~2.31 (m, 2H), 2.07~2.04 (m, 2H), 1.81~1.67 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): *cis*-isomer, δ 158.4, 139.5, 129.5, 120.6, 115.4, 81.6, 38.5, 23.5, 22.3; *trans*-isomer, δ 158.4, 140.2, 129.5, 120.5, 115.3, 82.7, 38.5, 23.4, 22.3; HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$: 306.1620, found 306.1613.

Spectral data for 1,3-bis(allyloxy)-2-butyl-2,3,4,5,6,7-hexahydro-1H-indene (8B). IR(neat, cm^{-1}): 3102 (m), 2922 (s), 1670 (m), 1610 (m); ^1H NMR (400 MHz, CDCl_3): δ 5.94~5.85 (m, 2H), 5.24 (dd, $J = 17.2, 3.2$ Hz, 2H), 5.11 (dd, $J = 10.4, 1.2$ Hz, 2H), 3.95 (d, $J = 4.0$ Hz, 4H), 3.84 (brs, 2H), 2.19~2.15 (m, 2H), 1.98~1.87 (m, 3H), 1.66~1.57 (m, 4H), 1.48~1.30 (m, 6H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 139.2, 135.8, 116.3, 89.2, 68.8, 48.9, 33.8, 30.0, 23.9, 23.1, 22.7, 14.2; HRMS calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2$: 290.2246, found 290.2254.

Spectral data for 2-butyl-2,3,4,5,6,7-hexahydro- N^1,N^3 -ditosyl-1H-indene-1,3-diamine (9-B). IR(neat, cm^{-1}): 3220 (s), 2936 (s), 1663 (m), 1485 (m), 1330 (s); ^1H NMR (400 MHz, CDCl_3): δ 7.17 (d, $J = 8.0$ Hz, 4H), 7.26 (d, $J = 8.0$ Hz, 4H), 5.12 (d, $J = 8.8$ Hz, 2H), 3.55~3.54 (m, 2H), 2.41 (s, 6H), 1.92~1.88 (m, 2H), 1.65~1.61 (m, 3H), 1.59~1.57 (m, 4H), 0.99~0.91 (m, 4H), 0.74~0.72 (m, 2H), 0.68 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.0, 138.3, 137.5, 129, 127.0, 64.7, 52.8, 32.6, 28.5, 22.9, 22.6, 22.1, 21.4, 13.6; HRMS calcd for $\text{C}_{27}\text{H}_{36}\text{N}_2\text{O}_4\text{S}_2$: 516.2116, found 516.2119.

Spectral data for 2-butyl-2,3,4,5,6,7-hexahydro-1,3-bis(phenylthio)-1H-indene (10-A/B): (**10A**-isomer), IR(neat, cm^{-1}): 2946 (s), 2888 (m), 1620 (m), 1510 (m); ^1H NMR (400 MHz, CDCl_3): (**10A**-isomer), δ 7.35 (d, $J = 7.2$ Hz, 2H), 7.30 (d, $J = 7.2$ Hz, 2H), 7.24~7.15 (m, 6H), 3.90 (d, $J = 6.4$ Hz, 1H), 3.48 (d, $J = 6.4$ Hz, 1H), 2.36~2.22 (m, 3H), 1.96~1.77 (m, 3H), 1.69~1.59 (m, 5H), 1.24~1.11 (m, 4H), 0.78 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): (**10A**-isomer), δ 138.6, 137.9, 136.2, 135.5, 131.9(2xCH), 131.7(2xCH), 128.6(2xCH), 128.5(2xCH), 126.6, 126.5, 60.2, 59.7, 49.8, 30.4, 29.1, 24.7, 24.4, 22.7, 22.6, 22.5, 14.0; HRMS calcd for $\text{C}_{25}\text{H}_{30}\text{S}_2$: 394.1789, found 394.1786. (**10B**-isomer), IR(neat, cm^{-1}): 2940 (s), 2880 (m), 1624 (m), 1510 (m); ^1H NMR (400 MHz, CDCl_3): (**10B**-isomer), δ 7.44~7.35 (m, 4H), 7.30~7.18 (m, 6H), 3.62 (s, 2H), 2.45~2.38 (m, 1H), 2.38~2.25 (m, 2H), 1.97~1.82 (m, 2H), 1.71~1.60 (m, 4H), 1.48~1.38 (m, 2H), 1.27~1.10 (m, 4H), 0.78 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): (**10B**-isomer), δ 137.3(2xC), 136.3(2xC), 131.9(4xCH),

128.7(4xCH), 126.6(2xCH), 61.8(2xCH), 52.6, 34.8, 29.0, 24.6(3xCH₂), 22.5(2xCH₂), 13.9;
HRMS calcd for C₂₅H₃₀S₂: 394.1789, found 394.1788.

Spectral data for 2-butyl-2,3,4,5,6,7-hexahydro-1H-indene (11). IR(neat, cm⁻¹): 2927 (s), 2848 (m), 1670 (m); ¹H NMR (600 MHz, CDCl₃): δ 2.33~2.32 (m, 2H), 2.16~2.15 (m, 1H), 1.87~1.85 (m, 6H), 1.56~1.53 (m, 4H), 1.35~1.34 (m, 2H), 1.28~1.26 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 133.3, 42.8, 36.7, 36.5, 30.6, 25.8, 23.1, 22.8, 14.1; HRMS calcd for C₁₃H₂₂: 178.1721, found 178.1725.

Spectral data for 1,3-diallyl-2,3,4,5,6,7-hexahydro-1H-indene (12). IR(neat, cm⁻¹): 3080 (m), 2941 (s), 1670 (m), 1610 (m); ¹H NMR (600 MHz, CDCl₃): major *trans*-isomer, δ 5.77~5.72 (m, 2H), 5.01~4.93 (m, 4H), 2.52~2.51 (m, 2H), 2.24~2.22 (m, 2H), 1.97~1.93 (m, 2H), 1.91~1.73 (m, 6H), 1.61~1.46 (m, 4H), minor *cis*-isomer (selected peaks), δ 2.36~2.34 (m, 2H), 2.12~2.10 (m, 2H), the remaining peaks are overlapped with those of major isomer; ¹³C NMR (150 MHz, CDCl₃): *cis* and *trans* isomers, δ 137.7, 137.6, 137.2, 115.2, 115.1, 46.2, 45.9, 38.7, 38.1, 34.9, 34.4, 24.2, 23.1, 23.0; HRMS calcd for C₁₅H₂₂: 202.1722, found 202.1713.

Spectral data for 1,3-diallyl-2-butyl-2,3,4,5,6,7-hexahydro-1H-indene (13). IR(neat, cm⁻¹): 3095 (m), 2931 (s), 1674 (m), 1606 (m); ¹H NMR (600 MHz, CDCl₃): major isomer **13B**, δ 5.75~5.69 (m, 2H), 4.99~4.93 (m, 4H), 2.22~2.20 (m, 2H), 2.13~2.11 (m, 4H), 2.05~1.88 (m, 4H), 1.88~1.70 (m, 3H), 1.63~1.61 (m, 2H), 1.49~1.47 (m, 2H), 1.46~1.24 (m, 4H), 0.87 (t, *J* = 6.8Hz, 3H); minor **13A**-isomer (selected peaks), δ 2.52~2.49 (m, 2H), the remaining peaks are overlapped with those of major isomer; ¹³C NMR (150 MHz, CDCl₃): **13A/B** isomers, δ 138.7, 137.8, 137.7, 136.5, 136.1, 115.4, 115.3, 114.7, 53.5, 51.3, 47.6, 45.3, 38.6, 36.7, 36.0, 32.9, 30.9, 29.6, 28.2, 25.1, 24.4, 24.3, 23.1, 14.1; HRMS calcd for C₁₉H₃₀: 258.2348, found 258.2334.

Spectral data for 1,3-diallyl-2,3,4,5,6,7-hexahydro-2,2-dimethyl-1*H*-indene (14-*trans*). IR(neat, cm^{-1}): 3102 (m), 2970 (s), 1673 (m), 1590 (m); ^1H NMR (600 MHz, CDCl_3): *trans*-isomer, δ 5.82~5.76 (m, 2H), 4.99 (d, $J = 13.5$ Hz, 2H), 4.89 (d, $J = 9.7$ Hz, 2H), 2.16~2.06 (m, 6H), 1.94~1.92 (m, 2H), 1.82~1.81 (m, 2H), 1.60~1.58 (m, 2H), 1.49~1.48 (m, 2H), 0.92 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 139.4, 136.2, 114.6, 56.4, 43.8, 33.2, 25.2, 24.7, 23.1; HRMS calcd for $\text{C}_{17}\text{H}_{26}$: 230.2035, found 230.2021.

Spectral data for carbocyclic compound (15). IR(neat, cm^{-1}): 3040 (m), 2982 (s), 1660 (m), 1615 (m), 1510 (m); ^1H NMR (400 MHz, CDCl_3): δ 7.36 (d, $J = 7.6$ Hz, 2H), 7.27 (t, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 1H), 6.70 (d, $J = 6.4$ Hz, 1H), 2.70 (t, $J = 4.8$ Hz, 1H), 2.62 (t, $J = 5.2$ Hz, 1H), 2.56 (ddd, $J = 7.2, 4.8, 1.6$ Hz, 1H), 2.30 (d, $J = 7.2$ Hz, 1H), 2.08~1.99 (m, 5H), 1.73 (d, $J = 9.2$ Hz, 1H), 1.62~1.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 145.4, 142.1, 135.2, 133.4, 131.0, 128.2, 126.5, 124.5, 42.3, 41.6, 40.4, 28.8, 24.5, 23.3, 23.2, 23.1; HRMS calcd for $\text{C}_{18}\text{H}_{20}$: 236.1565, found 236.1562.

Spectral data for carbocyclic compounds (16). IR(neat, cm^{-1}): 3086 (m), 2974 (s), 1668 (m), 1614 (m), 1506 (m); ^1H NMR (600 MHz, CDCl_3): δ 7.35 (d, $J = 7.2$ Hz, 2H), 7.26 (d, $J = 7.2$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 6.73 (d, $J = 5.4$ Hz, 1H), 2.54~2.53 (m, 1H), 2.42~2.31 (m, 3H), 2.03~1.95 (m, 7H), 1.58~1.52 (m, 4H), 1.29~1.28 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 143.2, 142.0, 133.7, 132.8, 132.2, 128.1, 126.4, 124.4, 51.7, 47.4, 46.9, 31.7, 30.4, 30.2, 24.8, 23.4, 23.3, 23.2, 22.9, 14.1; HRMS calcd for $\text{C}_{22}\text{H}_{28}$: 292.2191, found 292.2169.

Spectral data for carbocyclic compound (17A/17B): IR(neat, cm^{-1}): 3020 (m), 2978 (s), 1665 (m), 1612 (m); ^1H NMR (600 MHz, CDCl_3): isomer **17A**, δ 4.58 (s, 2H), 2.36 (d, $J = 14.1$ Hz, 2H), 2.08~2.01 (m, 4H), 1.97~1.60 (m, 4H), 1.60~1.50 (m, 4H), 1.00 (s, 3H), 0.97 (s, 3H);

isomer **17B**, (selected peaks), δ 5.73~5.71 (m, 1H), 2.36 (m, 1H), 1.88 (s, 3H), 1.01 (s, 3H), 0.95 (s, 3H); the remaining peaks are overlapped with those of isomer **17A**; ^{13}C NMR (150 MHz, CDCl_3): **17A** and **17B** isomers, δ 146.0, 144.9, 136.9(2 $\times$ C), 133.8, 131.9, 126.6, 112.0, 52.8, 51.4(2 $\times$ CH), 51.2, 44.9, 42.8, 31.2(2 $\times$ CH₂), 31.1, 27.4, 27.2, 24.9, 24.4(2 $\times$ CH₂), 23.7, 23.4, 23.3, 23.2(2 $\times$ CH₂), 23.1, 21.5, 20.8; HRMS calcd for $\text{C}_{15}\text{H}_{22}$: 202.1722, found 202.1708.

Spectral data for 1,2,3a,4,6,7,8,9-octahydro-1-(prop-1-en-2-yl)indeno[1-b]furan (18): IR(neat, cm^{-1}): 3060 (m), 2985 (s), 1660 (m), 1610 (m); ^1H NMR (600 MHz, CDCl_3): major isomer, δ 5.12 (brs, 1H), 4.79 (s, 1H), 4.73 (s, 1H), 4.13 (dd, $J = 7.8, 2.6$ Hz, 1H), 3.82~3.78 (m, 2H), 2.72~2.71 (m, 1H), 2.56~2.52 (m, 1H), 2.35~2.34 (m, 1H), 2.20~2.19 (m, 1H), 2.18~2.15 (m, 1H), 1.82~1.78 (m, 2H), 1.71 (s, 3H), 1.67~1.63 (m, 2H), 1.29~1.24 (m, 1H), 1.16~1.14 (m, 1H), minor isomer, selected peaks: 5.28~5.22 (m, 1H), 4.83~4.81 (m, 1H), 4.22 (d, $J = 5.6$ Hz, 1H), 3.77~3.70 (m, 2H), 2.81 (d, $J = 5.2$ Hz, 1H), 1.55 (s, 3H); the remaining peaks are overlapped with those of the major isomer; ^{13}C NMR (150 MHz, CDCl_3): δ 146.7, 145.9, 119.9, 113.4, 90.7, 72.7, 62.7, 56.5, 40.1, 37.1, 28.1, 27.9, 23.8, 20.3; HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{O}$: 204.1514, found 204.1514.

Spectral data for 4-butyl-1,2,3a,4,6,7,8,9-octahydro-1-(prop-1-en-2-yl)indeno[1-b]furan (19): IR(neat, cm^{-1}): 3030 (m), 2990 (s), 1665 (s), 1604 (m); ^1H NMR (600 MHz, CDCl_3): major isomer, δ 5.11 (s, 1H), 4.81 (s, 1H), 4.74 (s, 1H), 3.84~3.78 (m, 2H), 3.72~3.70 (m, 1H), 2.69~2.68 (m, 1H), 2.53~2.52 (m, 1H), 2.19~2.16 (m, 1H), 2.13~2.10 (m, 1H), 1.84~1.82 (m, 1H), 1.78~1.76 (m, 1H), 1.71 (s, 3H), 1.66~1.63 (m, 2H), 1.36~1.24 (m, 8H), 0.73 (t, $J = 7.2$ Hz, 3H), minor isomer, selected peaks: δ 5.28 (s, 1H), 4.83~4.82 (m, 1H), 2.74 (d, $J = 4.8$ Hz, 1H), 1.78 (s, 3H); the remaining peaks are overlapped with those of the major isomer; ^{13}C NMR (150 MHz, CDCl_3): δ 146.6, 145.1, 125.3, 113.5, 97.4, 92.3, 72.7, 62.5, 56.3, 50.0, 41.5, 35.3, 29.8, 28.0, 23.7, 22.8, 20.4, 14.0; HRMS calcd for $\text{C}_{18}\text{H}_{28}\text{O}$: 260.2140, found 260.2135.

NOE-map of compound **23**

	irradiation (δ ppm)	enhancement(%)
<p>19</p>	H ^b (δ 5.11)	H ^g (δ 2.53, 2.11%); H ⁱ (δ 2.17, 2.86%); H ^{k,l} (δ 1.59~1.36, 5.46%)
	H ^c (δ 4.79)	H ^b (δ 4.74, 4.90%); H ^d (δ 2.69, 5.03%)
	H ^b (δ 4.74)	H ^c (δ 4.79, 2.93%); H ^a (δ 1.71, 3.47%)
	H ^e (δ 3.85)	H ^d (δ 2.69, 2.61%); H ^a (δ 1.71, 1.10%)
	H ^d (δ 2.69)	H ^c (δ 4.79, 5.10%); H ^e (δ 3.85, 4.90%); H ^l (δ 1.83, 4.60%)
	H ^g (δ 2.53)	H ^b (δ 5.11, 2.15%); H ^f (δ 3.70, 0.84%); H ^a (δ 1.71, 1.07%); H ^{k,l} (δ 1.59~1.36, 7.22%)

Spectral data for 1,2,3,4,6,6a-Hexahydrobenzo[b]indeno[1,7a-d]furan (20). IR(neat, cm⁻¹): 3015 (m), 2985 (s), 1660 (m), 1616 (m), 1514 (m); ¹H NMR (600 MHz, CDCl₃): δ 7.10 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.35~5.34 (m, 1H), 3.56 (d, *J* = 8.4 Hz, 1H), 2.88~2.83 (m, 1H), 2.43~2.42 (m, 1H), 2.41~2.36 (m, 1H), 2.27~2.26 (m, 1H), 2.18~2.16 (m, 1H), 1.94~1.87 (m, 2H), 1.73~1.70 (m, 1H), 1.54~1.49 (m, 1H), 1.32~1.23 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 158.2, 143.3, 132.2, 128.1, 124.7, 122.6, 119.9, 109.7, 100.3, 48.5, 39.4, 37.4, 27.1, 26.3, 22.5; HRMS calcd for C₁₅H₁₆O: 212.1201, found 212.1213.

Spectral data for 6-butyl-1,2,3,4,6,6a-hexahydrobenzo[b]indeno[1,7a-d]furan (21). IR(neat, cm⁻¹): 3012 (s), 2987 (s), 1663 (m), 1607 (m), 1520 (m); ¹H NMR (600 MHz, CDCl₃): δ 7.11 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.2 Hz, 1H), 5.36 (s, 1H), 3.10 (s, 1H), 2.65~2.64 (m, 1H), 2.36~2.35 (m, 1H), 2.29~2.21 (m, 2H), 1.94~1.89 (m, 2H), 1.75~1.72 (m, 1H), 1.52~1.39 (m, 8H), 0.95 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 142.4, 131.8, 128.2, 128.0, 124.6, 119.9, 109.8, 100.0, 55.6, 53.9, 39.0, 36.6, 30.5, 27.1, 26.3, 22.8, 22.6, 14.0; HRMS calcd for C₁₉H₂₄O: 268.1827, found 268.1826.

NOE-map of compound **21**

	irradiation (δ , ppm)	enhancement(%)
H ^a (δ 7.11)	H ^b (δ 6.80, 1.23%); H ^e (δ 3.10, 0.58%); H ^f (δ 2.65, 0.66%)
	H ^d (δ 6.73)	H ^c (δ 7.08, 0.93%)
	H ^g (δ 5.39)	H ^f (δ 2.65, 1.04%); H ^h (δ 2.36, 0.87%); H ⁱ (δ 1.50, 0.81%); H ^k (δ 1.42, 0.78%)
	H ^e (δ 3.10)	H ^a (δ 7.11, 0.50%); H ^f (δ 2.65, 0.51%); H ⁱ (δ 2.24, 0.65%); H ^{j,k} (δ 1.52~1.39, 4.64%)
	H ^f (δ 2.65)	H ^a (δ 7.11, 0.70%); H ^g (δ 5.39, 1.07%); H ^e (δ 3.10, 0.55%); H ^{j,k} (δ 1.52~1.39, 3.56%)

Spectral data for 2,3,3a,4,6,7,8,9-octahydro-2-methyl-2-phenylindeno[1-b]furan (22):

IR(neat, cm^{-1}): 2990 (s), 1644 (m), 1600 (m), 1510 (m); ^1H NMR (600 MHz, CDCl_3): major isomer, δ 7.39 (d, J = 8.0 Hz, 2H), 7.23 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 4.94~4.93 (m, 1H), 2.64~2.60 (m, 1H), 2.38~2.29 (m, 4H), 2.15~2.12 (m, 1H), 1.97~1.89 (m, 2H), 1.85~1.78 (m, 2H), 1.64~1.61 (m, 1H), 1.47 (s, 3H), 1.25~1.16 (m, 2H); minor isomer (selected peaks), δ 7.46 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 5.12~5.11 (m, 1H), 2.57~2.56 (m, 1H), 2.48~2.44 (m, 1H); the remaining peaks are overlapped with those of major isomer; ^{13}C NMR (150 MHz, CDCl_3): δ 149.3, 148.9, 147.2, 146.2, 127.8, 127.6, 127.5, 126.1, 126.0, 125.9, 125.1, 124.8, 119.3, 118.5, 95.9, 95.3, 84.6, 84.4, 48.0, 47.6, 45.8, 45.2, 39.5, 38.0, 36.9, 36.4, 31.1, 30.5, 27.8, 27.5, 26.9, 26.5, 23.0, 22.8; HRMS calcd for $\text{C}_{18}\text{H}_{22}\text{O}$: 254.1671, found 254.1671.

Spectral data for 4-butyl-2,3,3a,4,6,7,8,9-octahydro-2-methyl-2-phenylindeno[1-b]

furan (23): IR(neat, cm^{-1}): 2992 (s), 1654 (m), 1606 (m), 1515 (m); ^1H NMR (600 MHz, CDCl_3): major isomer, δ 7.44 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 4.99 (s, 1H), 2.44~2.32 (m, 4H), 2.09~2.01 (m, 4H), 1.99~1.88 (m, 4H), 1.52 (s, 3H), 1.37~1.24 (m, 6H), 0.92 (t, J = 7.2 Hz, 3H); minor isomer (selected peaks), δ 7.51 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.23 (t, J = 8.0 Hz, 1H), 5.22 (s, 1H), 2.69~2.66 (m, 1H), 2.22~2.19 (m, 2H), the remaining peaks are overlapped with those of major isomer; ^{13}C NMR (150 MHz, CDCl_3): δ 149.5, 148.9, 146.7, 145.0, 127.8, 127.5, 126.1, 125.9, 125.1, 124.8, 124.3, 95.0, 84.8, 84.7, 53.2, 52.5, 50.3, 47.2, 47.1, 41.3, 40.1, 36.3, 36.2, 31.2, 30.9, 30.4, 30.3, 27.6, 27.5, 26.9, 26.5, 23.0, 22.8, 14.1; HRMS calcd for $\text{C}_{22}\text{H}_{30}\text{O}$: 310.2297, found

310.2291.

Spectral data for compound (24): IR(neat, cm^{-1}): 3015 (m), 2985 (s), 1640 (m), 1600 (m), 1506 (m); ^1H NMR (400 MHz, CDCl_3): δ 7.30 (d, $J = 2.0$ Hz, 1H), 6.18 (d, $J = 2.0$ Hz, 1H), 5.25~5.24 (m, 1H), 4.71 (d, $J = 14.0$ Hz, 1H), 4.60 (d, $J = 14.0$ Hz, 1H), 4.45 (t, $J = 8.4$ Hz, 1H), 2.51~2.46 (m, 1H), 2.39~2.37 (m, 2H), 2.26~2.14 (m, 2H), 2.04~1.90 (m, 2H), 1.74~1.70 (m, 1H), 1.47~1.43 (m, 1H), 1.32~1.25 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.5, 144.4, 141.3, 119.3, 113.2, 106.9, 86.7, 60.1, 47.7, 38.5, 30.3, 28.7, 26.8, 23.4; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$: 216.1150, found 216.1150.

Spectral data for compound (25): IR(neat, cm^{-1}): 3020 (m), 2988(s), 1650 (m), 1620 (m), 1514 (m); ^1H NMR (400 MHz, CDCl_3): δ 7.29 (d, $J = 2.0$ Hz, 1H), 6.17 (d, $J = 2.0$ Hz, 1H), 5.19 (s, 1H), 4.68 (d, $J = 14.0$ Hz, 1H), 4.60 (d, $J = 14.0$ Hz, 1H), 3.97 (d, $J = 8.4$ Hz, 1H), 2.75~2.71 (m, 1H), 2.42~2.33 (m, 2H), 2.19~2.16 (m, 1H), 2.03~1.90 (m, 2H), 1.74~1.69 (m, 1H), 1.57~1.55 (m, 1H), 1.48~1.24 (m, 7H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 153.5, 142.6, 141.0, 123.9, 112.6, 106.6, 92.7, 60.0, 47.8, 40.7, 38.6, 33.3, 29.9, 28.3, 26.3, 23.1, 22.9, 14.0; HRMS calcd for $\text{C}_{18}\text{H}_{24}\text{O}_2$: 272.1776, found 272.1782.

Spectral data for compound (26): IR(neat, cm^{-1}): 3015 (m), 2985(s), 1645 (m), 1616 (m), 1530 (m); ^1H NMR (400 MHz, CDCl_3): δ 7.12 (d, $J = 5.2$ Hz, 1H), 6.75 (d, $J = 5.2$ Hz, 1H), 5.22 (s, 1H), 4.81 (d, $J = 14.4$ Hz, 1H), 4.75 (d, $J = 14.4$ Hz, 1H), 4.02 (d, $J = 8.4$ Hz, 1H), 2.82~2.77 (m, 1H), 2.43~2.36 (m, 2H), 2.17~2.13 (m, 1H), 2.01~1.90 (m, 2H), 1.78~1.74 (m, 1H), 1.63~1.50 (m, 2H), 1.46~1.28 (m, 6H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.3, 138.2, 131.3, 124.6, 122.9, 122.4, 92.4, 61.8, 48.1, 40.3, 39.8, 33.0, 29.9, 27.6, 25.9, 22.9, 22.5, 14.0; HRMS calcd for $\text{C}_{18}\text{H}_{24}\text{OS}$: 288.1548, found 288.1555.

Spectral data for 2-((*E*)-4-hydroxybut-1-enyl)cyclohex-1-enecarbaldehyde (27). IR(neat, cm^{-1}): 3300 (brs), 2933 (m), 2858 (m), 1670 (s), 1615 (s), 1045 (s); ^1H NMR (400 MHz, CDCl_3): δ 10.19 (s, 1H), 6.99 (d, $J = 15.6$ Hz, 1H), 5.98 (dt, $J = 15.6, 6.8$ Hz, 1H), 3.66 (t, $J = 6.4$ Hz, 2H), 2.73 (brs, 1H), 2.40 (q, $J = 6.4$ Hz, 2H), 2.34 (t, $J = 5.6$ Hz, 2H), 2.18 (t, $J = 5.6$ Hz, 2H), 1.58~1.50 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.0, 152.5, 134.2, 133.0, 127.2, 61.5, 36.6, 27.6, 22.7, 21.7, 21.3; HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$: 180.1150, found 180.1145.

Spectral data for compound 28A. IR(neat, cm^{-1}): 2930 (s), 2858 (m), 1665 (s), 1160 (s), 1145 (s); ^1H NMR (400 MHz, CDCl_3): δ 4.88 (d, $J = 3.6$ Hz, 1H), 3.95 (s, 1H), 3.74~3.68 (m, 1H), 3.42~3.36 (m, 1H), 3.27 (ddd, $J = 9.6, 6.4, 3.6$ Hz, 1H), 3.03 (ddd, $J = 9.6, 7.2, 3.6$ Hz, 1H), 2.63~2.56 (m, 1H), 2.15~1.72 (m, 6H), 1.67~1.48 (m, 5H), 0.86 (dd, $J = 7.6, 3.6$ Hz, 3H), 0.84 (dd, $J = 7.6, 3.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 139.2, 138.8, 92.5, 88.9, 75.8, 66.2, 46.5, 32.4, 28.6, 23.2(2x CH_2), 22.4(2x CH_2), 19.5, 19.4; HRMS calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2$: 236.1776, found 236.1776.

NOE-map of compound **28A**

irradiation (δ ppm)	enhancement(%)
H^a (δ 4.88)	H^b (δ 2.60, 6.17%)
H^b (δ 2.63~2.56)	H^a (δ 4.88, 7.71%)

Spectral data for compound 28B. IR(neat, cm^{-1}): 2930 (s), 2858 (m), 1665 (s), 1161 (s), 1148 (s); ^1H NMR (400 MHz, CDCl_3): δ 4.69 (d, $J = 6.4$ Hz, 1H), 4.07 (d, $J = 6.8$ Hz, 1H), 3.76 (ddd, $J = 16.0, 7.6, 3.6$ Hz, 1H), 3.42 (dt, $J = 15.2, 6.4$ Hz, 1H), 3.30 (dd, $J = 9.2, 6.8$ Hz, 1H), 3.11 (dd, $J = 9.2, 6.8$ Hz, 1H), 2.94~2.87 (m, 1H), 2.20~2.08 (m, 2H), 2.00~1.93 (m, 1H), 1.92~1.82 (m, 3H), 1.73~1.56 (m, 5H), 0.90 (d, $J = 6.4$ Hz, 3H), 0.89 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 140.0, 135.8, 88.0, 84.2, 77.4, 66.7, 42.8, 28.8, 26.1, 23.2, 22.9, 22.6, 22.5, 19.5(2x CH_3); HRMS calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2$: 236.1776, found 236.1780.

NOE-map of compound **28B**

irradiation (δ ppm)	enhancement(%)
H^a (δ 4.69)	H^b (δ 2.90, 5.94%)
H^b (δ 2.94~2.87)	H^a (δ 4.69, 7.08%), H^c (δ 4.07, 5.92%)
H^c (δ 4.07)	H^b (δ 2.90, 5.82%)

Spectral data for 2-(buta-1,3-dienyl)cyclohex-1-enecarbaldehyde (29)

IR (neat, cm^{-1}): 2878 (w), 1733 (s), 1620 (m); ^1H NMR (600 MHz, CDCl_3): major isomer (*trans*): δ 10.30 (s, 1H), 7.18 (d, $J = 14.8$ Hz, 1H), 6.51~6.40 (m, 2H), 5.36 (d, $J = 15.7$ Hz, 1H), 5.25 (d, $J = 9.1$ Hz, 1H), 2.42~2.40 (m, 2H), 2.28~2.26 (m, 2H), 1.70~1.53 (m, 4H); cis isomer: δ 9.69 (s, 1H), 6.32~6.26 (m, 2H), 5.95 (d, $J = 9.7$ Hz, 1H), 5.31~5.28 (m, 1H), 5.17~5.15 (m, 1H), other peaks are overlapped with the *trans* isomer: ^{13}C NMR (150 MHz, CDCl_3): δ 193.2, 190.3, 151.3, 136.8, 135.5, 134.2, 134.1, 132.2, 127.7, 127.4, 120.8, 120.5, 31.6, 27.2, 23.1, 22.9, 21.9, 21.8, 21.7, 21.5, 21.4, 21.3; HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: 162.1045, found 162.1044.

Spectral data for 1,3-bis(but-3-enyloxy)-2,3,4,5,6,7-hexahydro-2-vinyl-1H-indene (30)

IR (neat, cm^{-1}): 2920 (s), 1640 (m), 1210 (s); ^1H NMR (600 MHz, CDCl_3): δ 5.94~5.91 (m, 1H), 5.82~5.77 (m, 2H), 5.18 (d, $J = 16.6$ Hz, 1H), 5.06~5.03 (m, 3H), 4.99 (dd, $J = 10.2$ Hz, $J = 1.4$ Hz, 2H), 3.93 (d, $J = 3.2$ Hz, 2H), 3.58~3.54 (m, 2H), 3.46~3.42 (m, 2H), 2.61 (quin, $J = 4.4$ Hz, 1H), 2.30~2.26 (m, 4H), 2.18~2.15 (m, 2H), 1.88~1.85 (m, 2H), 1.67~1.54 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 140.6, 138.1(2 $\times$ C), 135.4, 115.9(2 $\times$ CH_2), 115.2(2 $\times$ CH), 88.6(2 $\times$ CH), 68.0(2 $\times$ CH_2), 55.8, 34.5(2 $\times$ CH_2), 23.2(2 $\times$ CH_2), 22.3(2 $\times$ CH_2); HRMS calcd for $\text{C}_{19}\text{H}_{28}\text{O}_2$: 288.2089, found 288.2082.

Spectral data for 6-(but-3-enyloxy)-3,5a,6,7,8,9,10,10b-octahydro-2H-indeno[1,2-b]

oxepin (31) IR (neat, cm^{-1}): 2910 (s), 1648 (m), 1230 (s); ^1H NMR (600 MHz, CDCl_3): δ 6.12~6.09 (m, 1H), 5.89~5.77 (m, 2H), 5.08~4.99 (m, 2H), 4.08 (t, $J = 3.4$ Hz, 1H), 3.97 (qd, $J = 11.8$ Hz, $J = 2.6$ Hz, 1H), 3.82~3.81 (m, 1H), 3.57~3.45 (m, 3H), 2.91 (m, 1H), 2.57~2.52 (m, 1H), 2.33~2.29 (m, 1H), 2.19~2.11 (m, 4H), 1.88~1.81 (m, 2H), 1.67~1.60 (m, 2H), 1.57~1.51 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 137.8, 137.6, 135.3, 134.5, 130.9, 116.2, 87.0, 86.0, 69.0, 68.2, 55.2, 34.6, 31.9, 23.0, 22.4, 22.4, 22.3; HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: 260.1776, found 260.1770.

Spectral data for 2-butyl-2,3,4,5,6,7-hexahydro-1,3-diisopropoxy-1H-indene (32).

IR(neat, cm^{-1}): 2942 (s), 2866 (m), 1670 (m); ^1H NMR (400 MHz, CDCl_3): δ 3.73 (brs, 2H), 3.68~3.62 (m, 2H), 2.23~2.19 (m, 2H), 1.86~1.82 (m, 3H), 1.64~1.55 (m, 4H), 1.46~1.32 (m, 6H), 1.12 (d, $J = 6.4$ Hz, 12H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.5, 87.0, 69.8, 52.0, 32.7, 29.4, 23.5, 23.3, 22.9, 22.7, 22.5, 13.9; HRMS calcd for $\text{C}_{19}\text{H}_{34}\text{O}_2$: 294.2559, found 294.2576.

Spectral data for 2,3,4,5,6,7-hexahydro- N^1,N^3 -ditosyl-1H-indene-1,3-diamine (33-*cis*/*trans*). IR(neat, cm^{-1}): 3210 (s), 2920 (m), 1665 (m), 1480 (m), 1335 (s); ^1H NMR (600 MHz, CDCl_3): *cis*-isomer, δ 7.67 (d, $J = 8.4$ Hz, 4H), 7.25 (d, $J = 8.4$ Hz, 4H), 5.31 (d, $J = 9.6$ Hz, 2H), 3.89 (br, 2H), 2.40 (s, 6H), 1.91~1.88 (m, 2H), 1.64~1.59 (m, 4H), 1.46~1.43 (m, 4H); *trans*-isomer, δ 7.67 (d, $J = 8.4$ Hz, 4H), 7.23 (d, $J = 8.4$ Hz, 4H), 4.76 (d, $J = 8.8$ Hz, 2H), 4.15 (br, 2H), 2.41 (s, 6H), 2.24~2.20 (m, 2H), 1.74 (t, $J = 5.6$ Hz, 2H), 1.61~1.57 (m, 2H), 1.46~1.43 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): *cis*-isomer, δ 143.3, 138.0, 137.8, 129.6, 126.9, 59.3, 39.8, 22.9, 22.1, 21.5; *trans*-isomer, δ 143.2, 138.5, 137.9, 129.7, 126.9, 59.7, 40.6, 22.8, 22.1, 21.5; HRMS calcd for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4\text{S}_2$: 460.1490, found 460.1506.

Spectral data for 2,3,4,5,6,7-hexahydro-2,2-dimethyl- N^1,N^3 -ditosyl-1H-indene-1,3-diamine (34-*cis*/*trans*). IR(neat, cm^{-1}): 3210 (s), 2920 (m), 1665 (m), 1492 (m), 1314 (s); ^1H NMR (600 MHz, CDCl_3): *cis*-isomer, δ 7.79 (d, $J = 8.4$ Hz, 4H), 7.29 (d, $J = 8.4$ Hz, 4H), 4.71 (d, $J = 9.6$ Hz, 2H), 3.59 (d, $J = 9.6$ Hz, 2H), 2.41 (s, 6H), 1.63~1.60 (m, 4H), 1.45~1.40 (m, 4H), 0.84 (s, 3H), 0.70 (s, 3H); *trans*-isomer, δ 7.69 (d, $J = 8.4$ Hz, 4H), 7.26 (d, $J = 8.4$ Hz, 4H), 4.33 (d, $J = 9.6$ Hz, 2H), 3.73 (d, $J = 9.6$ Hz, 2H), 2.39 (s, 6H), 1.62~1.59 (m, 4H), 1.44~1.39 (m, 4H), 0.77 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): *cis*-isomer, δ 143.1, 138.3, 136.4, 129.7, 126.9, 68.3, 43.4, 27.7, 23.1, 22.8, 22.2, 19.0; *trans*-isomer, δ 143.3, 138.5, 137.0, 129.7, 126.9, 68.3, 43.4, 23.1, 22.8, 22.2, 21.5; HRMS calcd for $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_2$: 488.1803, found 488.1788.

Spectral data for 2,3,4,5,6,7-hexahydro-1,3-bis(phenylthio)-1H-indene (35-cis/trans). (*cis*-isomer), IR(neat, cm^{-1}): 2920 (s), 1640 (m), 1600 (m), 1510 (m); ^1H NMR (400 MHz, CDCl_3): *cis*-isomer, δ 7.30~7.18 (m, 10H), 3.85~3.82 (m, 2H), 2.95~2.91 (m, 1H), 2.45~2.20 (m, 3H), 1.91~1.87 (m, 2H), 1.64~1.59 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): *cis*-isomer, δ 138.2(2 $\times$ C), 135.1(2 $\times$ C), 131.4(4 $\times$ CH), 128.6(4 $\times$ CH), 126.6(2 $\times$ CH), 54.2(2 $\times$ CH), 40.9, 24.3(2 $\times$ CH₂), 22.4(2 $\times$ CH₂); HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{S}_2$: 338.1163, found 338.1161. (*trans*-isomer), IR(neat, cm^{-1}): 2932 (s), 1633 (m), 1592 (m), 1510 (m); ^1H NMR (400 MHz, CDCl_3): *trans*-isomer, δ 7.30~7.18 (m, 10H), 4.07~4.05 (m, 2H), 2.47 (t, $J = 6.4\text{Hz}$, 2H), 2.48~2.45 (m, 2H), 1.94~1.91 (m, 2H), 1.64~1.59 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): *trans*-isomer, δ 137.9(2 $\times$ C), 136.7(2 $\times$ C), 130.3(4 $\times$ CH), 128.6(4 $\times$ CH), 126.1(2 $\times$ CH), 54.8 (2 $\times$ CH), 40.5, 24.5(2 $\times$ CH₂), 22.4(2 $\times$ CH₂); HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{S}_2$: 338.1163, found 338.1160.

Spectral data for 2,3,4,5,6,7-hexahydro-2,2-dimethyl-1H-indene (36). IR(neat, cm^{-1}): 2930 (s), 2835 (m), 1665 (s); ^1H NMR (400 MHz, CDCl_3): δ 2.01 (s, 4H), 1.86~1.84 (m, 4H), 1.58~1.56 (m, 4H), 1.04 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 132.6, 51.6, 36.7, 30.4, 25.9, 23.1; HRMS calcd for $\text{C}_{11}\text{H}_{18}$: 150.1409, found 150.1401.

Spectral data for 2,3,4,5,6,7-hexahydro-2,2-dimethyl-1,3-bis(2-methylallyl)-1H-indene (37). IR(neat, cm^{-1}): 3050 (s), 2940 (s), 2820 (m), 1660 (m), 1640 (m); ^1H NMR (400 MHz, CDCl_3): δ 4.71 (s, 4H), 2.28~2.26 (m, 2H), 2.10~1.92 (m, 6H), 1.81~1.78 (m, 2H), 1.73 (s, 6H), 1.60~1.57 (m, 2H), 1.49~1.46 (m, 2H), 0.90 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.0, 136.8, 110.9, 53.0, 44.5, 36.9, 25.2, 24.1, 23.2, 22.4; HRMS calcd for $\text{C}_{19}\text{H}_{30}$: 258.2348, found 258.2347.

Spectral data for 1-(2-methylcyclopent-1-enyl)benzene (38). IR(neat, cm^{-1}): 3020 (s), 2920 (m), 1640 (m), 1610 (m), 1512 (m); ^1H NMR (400 MHz, CDCl_3): δ 7.35~7.25 (m, 4H), 7.23~7.15 (m, 1H), 2.74~2.67 (m, 2H), 2.52~2.40 (m, 2H), 1.92~1.84 (m, 2H), 1.83 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.7, 135.2, 134.7, 127.9, 127.5, 125.9, 40.0, 37.2, 21.8, 15.4; HRMS calcd for $\text{C}_{12}\text{H}_{14}$: 158.1096, found 158.1097.

Spectral data for 2,4,5,6-tetrahydro-1-methoxy-2,2-dimethyl-1H-indene (s4): IR(neat, cm^{-1}): 2940 (s), 2888 (m), 1635 (m); ^1H NMR (400 MHz, CDCl_3): δ 5.70 (t, $J = 1.6\text{Hz}$, 1H), 5.25 (s, 1H), 3.83 (s, 1H), 3.49 (s, 3H), 2.38~2.19 (m, 2H), 2.19~2.10 (m, 2H), 1.70~1.60 (m, 2H), 1.13 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 144.8, 136.4, 135.7, 119.6, 89.5, 58.7, 46.6, 28.7, 25.0, 25.0, 22.7, 22.0; HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: 178.1358, found 178.1358.

Spectral data for 2,4,5,6-tetrahydro-4-methoxy-2,2-dimethyl-1H-indene (s5): IR(neat, cm^{-1}): 2922 (m), 2870 (s), 1650 (m); ^1H NMR (400 MHz, CDCl_3): δ 5.67 (s, 1H), 5.40 (brs, 1H), 3.98 (t, $J = 4.8\text{ Hz}$, 1H), 3.36 (s, 3H), 2.32~2.24 (m, 2H), 2.24~2.20 (m, 1H), 2.12~2.05 (m, 1H), 1.82~1.76 (m, 2H), 1.11 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.1, 141.0, 137.4, 115.3, 74.4, 55.7, 44.0, 43.2, 29.2, 28.9, 28.2, 22.3; HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}$: 178.1358, found 178.1355.