Supporting Information

Lewis Acid-Mediated Cycloaddition of Methylenecyclopropanes with Aldehydes and Imines: A Facile Access to Indene, THF, and Pyrrolidine Skeletons *via* Homoallylic Rearrangement Protocol

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Experimental Procedures

General Methods.

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnegan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses. The commercially obtained aldehydes were purified by dissolved in dichloromethane (DCM) and was washed with NaHCO_3 aqueous solution and redistilled in *vacuo* or recrystallisation. All reactions were monitored by TLC plate with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. The MCPs **1** were prepared using the modified procedure of literature.¹ Deuterated benzaldehyde $\text{C}_6\text{H}_5\text{C(O)D}$ was purchased from Aldrich Co.

1. General Procedure for the Reaction of MCPs with Aldehydes Produces Indene system (Method A)

Under argon atmosphere, MCPs **1** (0.5 mmol) and aldehyde (1.0 mmol) was dissolved in 1.5 mL of DCM, then $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.1 mmol) was added into the solution. The reaction mixture was stirred for 24 h at room temperature and then was quenched by the addition of NaHCO_3 aqueous solution. The organic compound was extracted with DCM (3 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was passed through a silica gel column chromatography (SiO_2 , hexane/ethyl acetate as an eluent) to afford the product.

2. General Procedure for the Reaction of MCPs with Imines Produces Indene System (Method B)

Under argon atmosphere, MCPs **1** (0.5 mmol) and imine (0.75 mmol) was dissolved in 1.5 mL of DCM, then $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.1 mmol) was added into the solution. The reaction mixture was stirred for 24 h at room temperature and then was quenched by the addition of NaHCO_3 aqueous solution. The organic compound was extracted with DCM (3 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was passed through a silica gel column chromatography (SiO_2 , hexane/ethyl acetate as an eluent) to afford the product.

3. General Procedure for the Reaction of MCPs with Aldehydes Produces THF System (Method C)

Under argon atmosphere, MCPs **1** (0.5 mmol) and aldehyde (1.0 mmol) was dissolved in 1.5 mL

(1) Utimoto, K.; Tamura, M.; Sisido, K. *Tetrahedron*. **1973**, 29, 1169.

of DCM, the solution was cooled to $-20\text{ }^{\circ}\text{C}$, then $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.1 mmol) was added into the solution. The reaction was monitored by TLC plate. When the starting material **1** was completely consumed, then reaction was quenched by the addition of NaHCO_3 aqueous solution. The organic compound was extracted with DCM (3 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was passed through a silica gel column chromatography (SiO_2 , hexane/ethyl acetate as an eluent) to afford the product.

4. General Procedure for the Reaction of MCPs with Imine Produces Pyrrolidine System (Method D)

Under argon atmosphere, MCPs **1** (0.5 mmol) and imine (0.75 mmol) was dissolved in 2.0 mL of DCM, the solution was cooled to $-20\text{ }^{\circ}\text{C}$, then $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.1 mmol) was added into the solution. The reaction was monitored by TLC plate. When the starting material **1** was completely consumed, the reaction was quenched by the addition of NaHCO_3 aqueous solution. The organic compound was extracted with DCM (3 x 10 mL). The organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was passed through a silica gel column chromatography (SiO_2 , hexane/ethyl acetate as an eluent) to afford the product.

The preparation and spectroscopic data of compounds in Table 1 and Scheme 2.

2-(2-Chloroethyl)-1,3-diphenyl-1H-indene (**2'**):

Compound **2'** was prepared according to the Scheme 2 in main text. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2'** in 15% yield as a colorless oil.

IR (neat): ν 3318, 2921, 1488, 1039, 745, 501 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.57-2.62 (m, 1H, H-CH), 3.01-3.05 (m, 1H, H-CH), 3.51-3.59 (m, 2H, CH_2), 4.70 (s, 1H, CH), 7.15-7.55 (m, 14H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 30.39, 43.65, 57.12, 120.06, 123.89, 125.42, 126.82, 127.10, 127.65, 128.24, 128.65, 128.96, 129.06, 134.58, 139.25, 142.25, 143.81, 144.84, 148.51; MS (EI) m/z : 330 (M^+), 281, 267, 203, 165; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{19}\text{Cl}$: 330.1175, found: 330.1147.

2-[1-(4-Chlorophenyl)-3-phenyl-1*H*-inden-2-yl]ethanol (2a):

Compound **2a** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2a** in 65% yield as a colorless oil.

IR (neat): ν 3318, 2921, 1488, 1039, 745, 501 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.24-2.31 (m, 1H, H-CH), 2.76-2.81 (m, 1H, H-CH), 3.61-3.65 (m, 2H, CH_2), 4.62 (s, 1H, CH), 7.04-7.53 (m, 13H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 30.43, 56.70, 62.16, 119.94, 123.77, 125.27, 126.91, 127.57, 128.59, 128.98, 129.07, 129.60, 132.58, 134.54, 138.24, 141.81, 144.20, 144.86, 147.65; MS (EI) m/z : 346 (M^+), 328, 315, 302, 293, 280, 202; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{19}\text{ClO}$: 346.1124, found: 346.1109.

2-[1-(4-Bromophenyl)-3-phenyl-1*H*-inden-2-yl]ethanol (2b):

Compound **2b** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2b** in 78% yield as a colorless oil.

IR (neat): ν 3352, 3053, 2952, 1598, 1485, 1265, 1071, 703 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.23-2.29 (m, 1H, H-CH), 2.71-2.78 (m, 1H, H-CH), 3.61 (t, J = 6.9 Hz, 2H, CH_2), 4.57 (s, 1H, CH), 6.94-7.45 (m, 13H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 30.78, 57.11, 62.49, 120.27, 120.98, 124.10, 125.61, 127.24, 127.90, 128.92, 129.40, 130.32, 132.25, 134.87, 139.13, 142.17, 144.49, 145.21, 147.91; MS (EI) m/z : 390 (M^+), 372, 359, 332, 307, 290, 280, 205; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{19}\text{BrO}$: 390.0619, found: 390.0640.

2-(3-Phenyl-1-*p*-tolyl-1*H*-inden-2-yl)ethanol (2c):

Compound **2c** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2c** in 34% yield as a colorless oil.

IR (neat): ν 3396, 3022, 2922, 1598, 1511, 1038, 734 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ

2.31 (s, 3H, Me), 2.35-2.37 (m, 1H, H-CH), 2.76-2.80 (m, 1H, H-CH), 3.64 (t, $J = 6.9$ Hz, 2H, CH₂), 4.59 (s, 1H), 6.97-7.48 (m, 13H, Ar); ¹³C NMR (75 MHz, CDCl₃): δ 21.09, 30.65, 57.10, 62.23, 119.77, 123.81, 125.13, 126.64, 127.45, 128.11, 128.56, 129.16, 129.57, 134.83, 136.46, 136.53, 141.49, 144.69, 144.92, 148.25; MS (EI) m/z : 326 (M^+), 295, 281, 265, 252, 239, 202; HRMS (EI) Calcd. for C₂₄H₂₂O: 326.1671, found: 326.1675.

2-[1-(4-Methoxy-phenyl)-3-phenyl-1H-inden-2-yl]ethanol (2d):

We could not collect the spectroscopic data of **2d** because only trace of compound **2d** was isolated.

2-[1-(2,4-Dichlorophenyl)-3-phenyl-1H-inden-2-yl]ethanol (2e):

Compound **2e** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2e** in 75% yield as a colorless oil.

IR (neat): ν 3342, 3061, 2953, 1587, 1470, 1100, 908 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 2.23-2.28 (m, 1H, H-CH), 2.83-2.87 (m, 1H, H-CH), 3.66-3.73 (m, 2H, CH₂), 5.31 (s, 1H, CH), 6.56 (d, $J = 8.4$ Hz, 1H, Ar), 7.05-7.25 (m, 6H, Ar), 7.41-7.53 (m, 5H, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 30.88, 52.54, 62.29, 120.50, 123.94, 125.73, 127.39, 128.00, 128.13, 128.90, 129.39, 129.58, 129.78; MS (EI) m/z : 380 (M^+), 362, 349, 327, 314, 292, 278; HRMS (EI) Calcd. for C₂₃H₁₈Cl₂O: 380.0735, found: 380.0720.

2-[1-(4-Bromophenyl)-6-methoxy-3-(4-methoxyphenyl)-1H-inden-2-yl]ethanol (2f):

Compound **2f** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2f** in 91% yield as a colorless oil.

IR (neat): ν 3438, 2953, 2907, 1605, 1510, 1247, 829 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.22-2.27 (m, 1H, H-CH), 2.74-2.78 (m, 1H, H-CH), 3.61-3.65 (m, 2H, CH_2), 3.74 (s, 3H, OMe), 3.89 (s, 3H, OMe), 4.53 (s, 1H, CH), 6.73-6.80 (m, 2H, Ar), 6.96-7.02 (m, 4H, Ar), 7.10 (d, J = 8.4 Hz, 1H, Ar), 7.38-7.42 (m, 4H, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 30.38, 55.17, 55.39, 56.51, 62.09, 110.26, 112.13, 113.91, 120.24, 120.50, 126.90, 129.97, 130.10, 131.83, 138.04, 139.06, 140.75, 141.31, 149.26, 158.06, 158.80; MS (EI) m/z : 450 (M^+), 419, 205, 119, 84; HRMS (EI) Calcd. for $\text{C}_{25}\text{H}_{23}\text{BrO}_3$: 450.0831, found: 450.0823.

2-[1-(4-Chlorophenyl)-6-methoxy-3-(4-methoxyphenyl)-1H-inden-2-yl]ethanol (2g):

Compound **2g** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2g** in 95% yield as a colorless oil.

IR (neat): ν 3437, 2953, 2835, 1625, 1510, 1279, 1247, 1034 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.19-2.24 (m, 1H, H-CH), 2.71-2.76 (m, 1H, H-CH), 3.59 (t, J = 6.3 Hz, 2H, CH_2), 3.71 (s, 3H, OMe), 3.83 (s, 3H, OMe), 4.52 (s, 1H, CH), 6.75-7.40 (m, 11H, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 30.40, 55.19, 55.41, 56.45, 62.13, 110.31, 112.13, 113.93, 120.26, 126.94, 128.90, 129.59, 130.12, 132.45, 138.06, 138.53, 140.77, 141.37, 149.36, 158.09, 158.83; MS (EI) m/z : 406 (M^+), 375, 361, 340, 251, 239, 84; HRMS (EI) Calcd. for $\text{C}_{25}\text{H}_{23}\text{ClO}_3$: 406.1336, found: 406.1319.

2-[1-(4-Bromophenyl)-6-methyl-3-*p*-tolyl-1H-inden-2-yl]ethanol (2h):

Compound **2h** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2h** in 68% yield as a colorless oil.

IR (neat): ν 3374, 3023, 2920, 1510, 1484, 1012 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.20-2.28 (m, 1H, H-CH), 2.27 (s, 3H, Me), 2.41 (s, 3H, Me), 2.73-2.78 (m, 1H, H-CH), 3.59-3.61 (m, 2H, CH_2), 4.52 (s, 1H, CH), 6.94-7.40 (m, 11H, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 21.34,

21.36, 30.55, 56.66, 62.28, 119.71, 120.61, 124.69, 127.61, 128.87, 129.33, 130.08, 131.76, 131.95, 135.04, 137.28, 139.22, 141.75, 142.40, 142.72, 147.93; MS (EI) m/z : 418 (M^+), 387, 374, 321, 308, 293; HRMS (EI) Calcd. for $C_{25}H_{23}BrO$: 418.0932, found: 418.0886.

2-(1-Isopropyl-3-phenyl-1H-inden-2-yl)ethanol (2i):

Compound **2i** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2i** in 66% yield as a colorless oil.

IR (neat): ν 2958, 2862, 1489, 1088, 1048, 828 cm^{-1} ; 1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.53 (d, J = 6.6 Hz, 3H, Me), 1.32 (d, J = 6.6 Hz, 3H, Me), 1.60-1.63 (br., s, 1H, OH), 2.42-2.50 (m, 2H, CH_2), 2.87-2.92 (m, 1H, H-CH), 3.51 (d, J = 3.3 Hz, 1H, CH), 3.69-3.76 (m, 1H, H-CH), 7.12-7.22 (m, 3H, Ar), 7.34-7.51 (m, 6H, Ar); MS (EI) m/z : 346 (M^+), 303, 227, 199, 127; HRMS (EI) Calcd. for $C_{20}H_{22}Cl_2O$: 346.0891, found: 346.0907.

Deuterium **2-d**: 1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.29-2.38 (m, 1H, H-CH), 2.75-2.85 (m, 1H, H-CH), 3.66 (t, J = 6.9 Hz, 2H, CH_2), 7.09-7.49 (m, 14H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.66, 50.42 (t, J = 24.3 Hz), 62.25, 119.83, 123.87, 125.17, 126.74, 126.96, 127.50, 128.23, 128.59, 128.87, 129.15, 134.77, 139.62, 141.72, 142.30, 144.52, 145.0, 148.12.

^1H NMR spectrum of **2-d**.

***N*-[2-(1,3-Diphenyl-1*H*-inden-2-yl)-ethyl]-4-methylbenzenesulfonamide (**2j**):**

Compound **2j** was prepared according to method B. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2j** in 75% yield as a colorless oil.

IR (neat): ν 3290, 3061, 2922, 1613, 1485, 1320, 910 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.16-2.23 (m, 1H, H-CH), 2.47 (s, 3H, Me), 2.58-2.63 (m, 1H, H-CH), 2.58-2.63 (m, 1H, H-CH), 2.90-2.99 (m, 1H, H-CH), 4.35 (s, 1H, CH), 4.40 (t, J = 6.0 Hz, 1H, NH), 6.96-7.42 (m, 18H, Ar);

^{13}C NMR (75 MHz, CDCl_3) δ 21.25, 26.85, 42.18, 56.69, 119.66, 123.58, 125.12, 126.52, 126.71, 126.78, 127.40, 127.91, 128.47, 128.65, 128.74, 129.31, 134.15, 136.32, 138.88, 141.87, 142.97,

143.38, 144.36, 147.70; MS (EI) m/z : 465 (M^+), 310, 294, 282, 203, 155, 91; HRMS (EI) Calcd. for $C_{30}H_{27}NO_2S$: 465.1762, found: 465.1789.

***N*-{2-[1-(4-Chlorophenyl)-3-phenyl-1*H*-inden-2-yl]-ethyl}-4-methylbenzenesulfonamide (2k):**

Compound **2k** was prepared according to method B. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2k** in 71 % yield as a colorless oil.

IR (neat): ν 3284, 3023, 1598, 1489, 1159, 1092 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.15-2.20 (m, 1H, H-CH), 2.38 (s, 3H, Me), 2.59-2.64 (m, 1H, H-CH), 2.93-2.97 (m, 2H, CH_2), 4.28 (t, J = 6.0 Hz, 1H, NH), 4.36 (s, 1H, CH), 6.91-7.56 (m, 17H, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 21.45, 27.03, 42.34, 56.14, 120.00, 123.70, 125.47, 126.85, 126.92, 127.70, 128.69, 128.86, 129.00, 129.46, 129.52, 132.65, 134.11, 136.43, 137.68, 142.37, 143.04, 143.29, 144.45, 147.44; MS (EI) m/z : 499 (M^+), 328, 316, 279, 203, 184, 155; HRMS (EI) Calcd. for $C_{30}H_{26}\text{ClNO}_2\text{S}$: 499.1373, found: 499.1390.

4-Methyl-*N*-{2-[3-phenyl-1-(4-trifluoromethylphenyl)-1*H*-inden-2-yl]-ethyl}benzenesulfonamide (2l):

Compound **2l** was prepared according to method B. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2l** in 73 % yield as a colorless oil.

IR (neat): ν 3283, 3024, 1618, 1417, 1325, 1161, 708 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.11-2.16 (m, 1H, H-CH), 2.37 (s, 3H, Me), 2.62-2.67 (m, 1H, H-CH), 2.92-2.98 (m, 2H, CH_2), 4.38 (t, J = 6.0 Hz, 1H, NH), 4.48 (s, 1H, CH), 7.08-7.47 (m, 17H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 21.44, 27.06, 42.41, 56.46, 120.16, 123.80, 124.24 (d, $J_{\text{C-F}}$ = 271 Hz), 125.61, 125.86 (d, $J_{\text{C-F}}$ = 3.2 Hz), 125.89, 127.11, 127.82, 128.53, 128.62, 128.77, 129.05, 129.16 (d, $J_{\text{C-F}}$ = 32 Hz), 129.58, 134.06, 136.51, 142.78, 142.88, 143.38, 143.66, 144.57; MS (EI) m/z : 533 (M^+), 378, 362, 350, 203, 184, 155; HRMS (EI) Calcd. for $C_{31}H_{26}\text{F}_3\text{NO}_2\text{S}$: 533.1636, found: 533.1632.

***N*-{2-[1-(2,3-Dichlorophenyl)-3-phenyl-1*H*-inden-2-yl]ethyl}-4-methylbenzenesulfonamide (2m):**

Compound 2m was prepared according to method B. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexanes = 1/10) to give the product **2m** in 71% yield as a colorless oil.

IR (neat): ν 3278, 3022, 1598, 1418, 1094, 703 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.09-2.16 (m, 1H, H-CH), 2.36 (s, 3H, Me), 2.65-2.70 (m, 1H, H-CH), 2.90-3.05 (m, 2H, CH_2), 4.31 (t, $J = 6.0$ Hz, 1H, NH), 5.06 (s, 1H, CH), 6.44-6.47 (m, 1H, Ar), 6.94-7.56 (m, 15H, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 21.49, 27.12, 42.34, 52.96, 120.30, 123.57, 125.65, 126.29, 126.92, 126.95, 127.16, 127.77, 127.91, 128.71, 128.90, 129.17, 129.58, 133.00, 136.26, 139.39, 142.54, 143.32, 143.42, 144.42, 133.95, 147.02; MS (EI) m/z : 533 (M^+), 350, 278, 203, 184, 155, 91; HRMS (EI) Calcd. for $\text{C}_{30}\text{H}_{25}\text{Cl}_2\text{NO}_2\text{S}$: 533.0983, found: 533.0989.

***N*-{2-[1-(3-Fluorophenyl)-3-phenyl-1*H*-inden-2-yl]ethyl}-4-methylbenzenesulfonamide (2n):**

Compound 2n was prepared according to method B. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **2n** in 75% yield as a colorless oil.

IR (neat): ν 3283, 3061, 2925, 1613, 1485, 1327, 910 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.15-2.23 (m, 1H, H-CH), 2.60-2.65 (m, 1H, H-CH), 2.37 (s, 3H, Me), 2.61-2.65 (m, 1H, H-CH), 2.93-2.98 (m, 1H, H-CH), 4.36 (s, 1H, CH), 4.40 (br., s, 1H, NH), 6.60-6.63 (m, 1H, Ar), 6.84-7.56 (m, 16H, Ar); MS (EI) m/z : 483 (M^+), 328, 312, 300, 184, 155; HRMS (EI) Calcd. for $\text{C}_{30}\text{H}_{26}\text{FNO}_2\text{S}$: 483.1668, found: 483.1711.

5-(4-Chlorophenyl)-2,2-diphenyl-3,4-dihydro-2*H*-pyran (3a):

Compound 3a was prepared according to method A. It was purified by a flash column

chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **3a** in 10 % yield as a colorless oil.

IR (neat): ν 2926, 1638, 1462, 1164, 1005, 825 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.27 (t, J = 6.3 Hz, 2H, CH_2), 2.66 (t, J = 6.3 Hz, 2H, CH_2), 7.12-7.45 (m, 15H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 30.88, 52.54, 62.29, 120.50, 123.94, 125.73, 127.39, 128.00, 128.13, 128.90, 129.39, 129.58, 129.78; MS (EI) m/z : 346 (M^+), 317, 228, 180, 165; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{19}\text{ClO}$: 346.1124, found: 346.1111.

5-(4-Bromophenyl)-2,2-diphenyl-3,4-dihydro-2H-pyran (3b):

We can not measure its spectroscopic data of **3b** because the yield of **3b** is too low.

5-(4-Methoxyphenyl)-2,2-diphenyl-3,4-dihydro-2H-pyran (3c):

Compound **3c** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **3c** in 30 % yield as a colorless oil.

IR (neat): ν 3028, 2940, 1636, 1449, 1160, 1006 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.28 (t, J = 6.3 Hz, 2H, CH_2), 2.29 (s, 3H, Me), 2.65 (t, J = 6.3 Hz, 2H, CH_2), 7.04-7.45 (m, 15H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 20.97, 31.83, 80.99, 112.96, 123.84, 125.91, 127.10, 128.24, 129.01, 135.41, 136.09, 140.08, 144.59; MS (EI) m/z : 326 (M^+), 308, 297, 180, 165; HRMS (EI) Calcd. for $\text{C}_{24}\text{H}_{22}\text{O}$: 362.1671, found: 362.1681.

5-(4-Methoxyphenyl)-2,2-diphenyl-3,4-dihydro-2H-pyran (3d):

Compound **3d** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: EtOAc/hexane = 1/10) to give the product **3d** in 45 % yield as a colorless oil.

IR (neat): ν 3020, 1646, 1513, 1245, 1162, 758 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.26 (t, J = 6.3 Hz, 2H, CH_2), 2.64 (t, J = 6.3 Hz, 2H, CH_2), 3.74 (s, 3H, OMe), 6.79 (d, J = 6.9 Hz, 2H,

Ar), 7.06-7.45 (m, 13H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 21.12, 31.78, 55.24, 80.84, 112.67, 113.74, 125.04, 125.89, 127.09, 128.24, 131.62, 139.45, 144.59, 157.88; MS (EI) m/z : 342 (M^+), 180, 162, 133; HRMS (EI) Calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_2$: 342.1620, found: 342.1636.

Deuterium **3-d**: ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.31 (t, $J = 6.6$ Hz, 2H, CH_2), 2.66 (t, $J = 6.6$ Hz, 2H, CH_2), 7.12-7.45 (m, 15H, Ar). ^{13}C NMR (75 MHz, CDCl_3): δ 20.83, 31.79, 81.04, 112.85, 123.88, 125.78, 127.14, 128.33, 138.95, 140.37 (t, $J = 28.5$ Hz), 144.50.

The mechanistic explanation of the formation of **3** by classical carbon cation.

R= aromatic group

¹³C NMR spectrum of **3-d**.

The regional enlargement of the ^{13}C NMR spectrum of **3-d**.

XH-1
 STANDARD 1H OBSERVE
 Archive directory: /export/home/ASU/vnmrsws/data
 Sample directory: auto_08NOV2003
 Pulse Sequence: ghmqc
 Solvent: cdcl3
 Acquisition temperature
 File: xu-103
 Mercury-300BB "DMC300"
 Relax delay 1.000 sec
 Relax time 2.100 sec
 Width 4807.7 Hz
 20 Width 12820.5 Hz
 20 Width 12820.5 Hz
 2 x 512 increments
 OBSERVE H1, 300.0279787 MHz
 DECOUPLE C13, 75.4477345 MHz
 Recycle delay 1.000 sec
 on during acquisition
 off during delay
 Data collected
 DATA PROCESSING
 Gauss apodization 0.098 sec
 F1 DATA PROCESSING 0.074 sec
 C13 apodization 0.074 sec
 FT size 2048 x 8192
 Total time 6 hr, 46 min, 40 sec

The HMQC spectrum of **3-d**.

The preparation and spectroscopic data of compounds in Table 2.

3-Benzhydrylidene-2-butyltetrahydrofuran (4a):

Compound 4a was prepared according to method C. It was purified by a flash column chromatography on silica gel (eluent: CH₂Cl₂/hexane = 1/5) to afford the product 4a in 45% yield as a colorless oil.

IR (neat): ν 2956, 2858, 1492, 1443, 1265, 1075, 739 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 0.73 (t, J = 7.2 Hz, 3H, Me), 0.80-1.28 (m, 6H, CH₂), 2.49-2.56 (m, 1H, H-CH), 2.84-2.90 (m, 1H, H-CH), 3.65-3.73 (m, 1H, H-CH), 4.08 (td, J = 2.4, 8.4 Hz, 1H, H-CH), 4.75-4.77 (m, 1H, CH), 7.16-7.34 (m, 10H, Ar); ¹³C NMR (75 MHz, CDCl₃): δ 13.85, 22.26, 26.99, 32.54, 33.62, 67.18, 80.01, 126.58, 126.77, 127.89, 128.35, 128.89, 129.14, 133.57, 141.73, 141.89, 142.69; MS (EI) m/z : 292 (M⁺), 235, 207, 129, 91; HRMS (EI) Calcd. for C₂₁H₂₄O: 292.1827, found: 292.1849.

3-Benzhydrylidene-2-isopropyltetrahydrofuran (4b):

Compound 4b was prepared according to method C. It was purified by a flash column chromatography on silica gel (eluent: CH₂Cl₂/hexane = 1/5) to afford the product 4b in 58% yield as a white solid.

Mp 70-72 °C. IR (neat): ν 3029, 2942, 2860, 1590, 1489, 1389, 1090, 1013, 824 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 0.90 (m, 6H, Me), 1.35-1.42 (m, 1H, CH), 2.43-2.48 (m, 1H, H-CH), 2.79-2.85 (m, 1H, H-CH), 3.60-3.68 (m, 1H, H-CH), 4.05 (td, J = 2.4, 8.4 Hz, 1H, H-CH), 4.71-4.73 (m, 1H, CH), 7.08-7.35 (m, 10H, Ar); ¹³C NMR (75 MHz, CDCl₃): δ 15.39, 19.76, 30.25, 34.28, 67.39, 84.34, 126.65, 126.78, 127.88, 128.38, 129.01, 129.12, 134.10, 141.43, 141.95, 142.95; MS (EI) m/z : 278 (M⁺), 235, 207, 129, 91; HRMS (EI) Calcd. for C₂₀H₂₂O: 278.1671, found: 278.1654. Element Analysis for C₂₀H₂₂O: C 86.29, H 7.97, found: C 86.12, H 8.16%.

3-Di-*p*-tolylmethylene-2-isopropyltetrahydrofuran (4c):

Compound **4c** was prepared according to method C. It was purified by a flash column chromatography on silica gel (eluent: CH₂Cl₂/hexane = 1/5) to afford the product **4c** in 54% yield as a colorless oil.

IR (neat): ν 2961, 2868, 1509, 1265, 1055, 739 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 0.76 (d, J = 6.9 Hz, 6H, Me), 1.40-1.45 (m, 1H, CH), 2.31 (s, 3H, Me), 2.33 (s, 3H, Me), 2.44-2.52 (m, 1H, H-CH), 2.77-2.83 (m, 1H, H-CH), 3.61-3.69 (m, 1H, H-CH), 4.05-4.11 (m, 1H, H-CH), 4.69-4.71 (m, 1H, CH), 7.02-7.11 (m, 8H, Ar); ¹³C NMR (75 MHz, CDCl₃): δ 15.36, 19.74, 21.09, 21.16, 30.15, 34.25, 67.36, 84.32, 128.48, 128.87, 128.91, 128.95, 128.97, 133.82, 136.16, 139.11, 140.31, 140.46; MS (EI) m/z : 306 (M⁺), 263, 143, 128, 119; HRMS (EI) Calcd. for C₂₂H₂₆O: 306.1984, found: 306.1992.

3-[Bis(4-chlorophenyl)methylene]-2-isopropyltetrahydrofuran (4d):

Compound **4d** was prepared according to method C. It was purified by a flash column chromatography on silica gel (eluent: CH₂Cl₂/hexane = 1/5) to afford the product **4d** in 50% yield as a colorless oil.

IR (neat): ν 3359, 2959, 1462, 1366, 1040, 738 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 0.78-0.82 (m, 6H, Me), 1.38-1.43 (m, 1H, CH), 2.42-2.49 (m, 1H, H-CH), 2.75-2.81 (m, 1H, H-CH), 3.62-3.70 (m, 1H, H-CH), 4.08-4.13 (m, 1H, H-CH), 4.65 (s, 1H, CH), 7.04-7.30 (m, 8H, Ar); MS (EI) m/z : 346 (M⁺), 303, 227, 199, 127; HRMS (EI) Calcd. for C₂₀H₂₀Cl₂O: 346.0891, found: 346.0907.

3-(1-Butylpentyldiene)-2-isopropyltetrahydrofuran (4e):

Compound **4e** was prepared according to method C. It was purified by a flash column chromatography on silica gel (eluent: CH₂Cl₂/hexane = 1/5) to afford the product **4e** in 41% yield as a colorless oil.

IR (neat): ν 2957, 2860, 1466, 1061, 758 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 0.93 (t, J = 7.2 Hz, 6H, Me), 0.98 (d, J = 6.9 Hz, 6H, Me), 1.16-1.61 (m, 12H, CH₂), 2.34-2.41 (m, 2H, CH₂), 2.51 (td, J = 2.1, 7.2 Hz, 2H, CH₂), 4.86 (dt, J = 9.3, 2.1 Hz, 1H, CH); ¹³C NMR (75 MHz, CDCl₃): δ 14.11, 22.78, 23.15, 23.18, 25.92, 29.52, 30.36, 39.55, 65.52, 85.76, 127.13, 141.29; MS (EI) m/z : 238 (M⁺), 195, 181, 57, 41; HRMS (EI) Calcd. for C₁₆H₃₀O: 238.2297, found: 238.2270.

2-Butyl-3-(1-butylpentylidene)tetrahydrofuran (4f):

Compound 4f was prepared according to method C. It was purified by a flash chromatography on silica gel (eluent: CH₂Cl₂/hexane = 1/5) to give the product 4f in 45% yield as a colorless oil.

IR (neat): ν 2957, 2860, 1466, 1061, 758 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 0.85-0.92 (m, 9H, Me), 1.17-1.55 (m, 16H, CH₂), 1.99-2.04 (m, 2H, CH₂), 2.49 (t, J = 7.2 Hz, 2H, CH₂), 3.85 (t, J = 7.2 Hz, 2H), 5.02 (t, J = 7.2 Hz, 1H, CH); ¹³C NMR (75 MHz, CDCl₃): δ 13.96, 14.13, 22.26, 23.21, 25.99, 29.57, 30.64, 31.67, 39.59, 65.50, 85.97, 119.68, 143.75; MS (EI) m/z : 252 (M⁺), 195, 139, 85, 57, 41; HRMS (EI) Calcd. for C₁₇H₃₂O: 252.2453, found: 252.2447.

3-Benzhydrylidene-2-phenyl-1-(toluene-4-sulfonyl)pyrrolidine (4g):

Compound 4g was prepared according to method D. It was purified by a flash column chromatography on silica gel (eluent: 10% V/V of EtOAc/hexanes) to afford the product 4g in 41% yield as a colorless oil.

IR (neat): ν 3027, 2924, 1596, 1493, 1348, 1161, 700 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 2.47 (s, 3H, Me), 2.56-2.64 (m, 1H, H-CH), 2.88-2.93 (m, 1H, H-CH), 3.28-3.37 (m, 1H, H-CH), 3.69-3.76 (m, 1H, H-CH), 5.35 (s, 1H, CH), 6.70-7.59 (m, 19H, Ar); ¹³C NMR (75 MHz, CDCl₃): δ 21.54, 30.24, 47.91, 64.47, 127.21, 127.33, 127.75, 127.96, 128.12, 128.19, 128.49, 128.29, 129.03, 129.56, 132.88, 134.32, 137.31, 137.47, 139.99, 140.75, 140.85, 143.64; MS (EI) m/z : 465 (M⁺), 388, 310, 282, 232, 205, 129, 91; HRMS (EI) Calcd. for C₃₀H₂₇NO₂S: 465.1762, found: 465.1721.

3-Benzhydrylidene-2-(4-chlorophenyl)-1-(toluene-4-sulfonyl)pyrrolidine (4h):

Compound 4h was prepared according to method D. It was purified by a flash column chromatography on silica gel (eluent: 10% V/V of EtOAc / hexane) to afford the product 4h in 40% yield as a colorless oil.

IR (neat): ν 3024, 1597, 1490, 1348, 1162, 1092, 758 cm⁻¹; ¹H NMR (300 MHz, TMS, CDCl₃): δ 2.47 (s, 3H, Me), 2.54-2.62 (m, 1H, H-CH), 2.85-2.91 (m, 1H, H-CH), 3.33-3.42 (m, 1H, H-CH),

3.69-3.73 (m, 1H, H-CH), 5.43 (s, 1H, CH), 6.72-7.59 (m, 18H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 21.54, 30.24, 47.61, 65.09, 126.86, 127.05, 127.16, 127.73, 127.94, 128.09, 128.35, 128.83, 129.04, 129.51, 134.74, 136.88, 137.64, 140.88, 141.11, 141.24, 143.40; MS (EI) m/z : 499 (M^+), 422, 388, 344, 316, 207; HRMS (EI) Calcd. for $\text{C}_{30}\text{H}_{26}\text{ClNO}_2\text{S}$: 499.1373, found: 499.1390.

3-Benzhydrylidene-2-(4-bromophenyl)-1-(toluene-4-sulfonyl)pyrrolidine (4i):

Compound 4i was prepared according to method D. It was purified by a flash column chromatography on silica gel (eluent: 10% V/V of EtOAc/hexane) to afford the product **4i** in 43% yield as a colorless oil.

IR (neat): ν 3022, 1486, 1348, 1162, 666 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.47 (s, 3H, Me), 2.56-2.65 (m, 1H, H-CH), 2.84-2.92 (m, 1H, H-CH), 3.28-3.37 (m, 1H, H-CH), 3.69-3.76 (m, 1H, H-CH), 5.34 (s, 1H, CH), 6.70-7.35 (m, 18H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 21.52, 30.19, 47.88, 64.45, 121.04, 127.17, 127.28, 127.69, 127.91, 128.45, 128.48, 128.75, 128.99, 129.51, 131.01, 134.26, 137.36, 140.45, 140.69, 140.78, 143.61; MS (EI) m/z : 543 (M^+), 465, 388, 360, 207, 129, 91; HRMS (EI) Calcd. for $\text{C}_{30}\text{H}_{26}\text{BrNO}_2\text{S}$: 543.0868, found: 543.0869.

3-Benzhydrylidene-1-(toluene-4-sulfonyl)-2-(4-trifluoromethylphenyl)pyrrolidine (4j):

Compound 4j was prepared according to method D. It was purified by a flash column chromatography on silica gel (eluent: 10% V/V of EtOAc/hexane) to give the product **4j** as a colorless oil, yield 45%.

IR (neat): ν 3056, 2926, 1618, 1493, 1159, 910 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.41 (s, 3H, Me), 2.61-2.68 (m, 1H, H-CH), 2.89-3.01 (m, 1H, H-CH), 3.31-3.39 (m, 1H, H-CH), 3.75-3.82 (m, 1H, H-CH), 5.44 (s, 1H, CH), 6.69-7.37 (m, 18H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 21.46, 30.27, 48.13, 64.57, 124.04 (d, $J_{\text{C-F}} = 270.3$ Hz), 124.50 (d, $J_{\text{C-F}} = 3.9$ Hz), 127.03, 127.38, 127.69, 127.93, 128.55, 128.77, 129.01, 129.10 (d, $J_{\text{C-F}} = 3.2$ Hz), 129.32, 129.53, 134.15, 137.35, 137.71, 140.69, 143.74; MS (EI) m/z : 533 (M^+), 456, 388, 370, 350, 207, 129, 91; HRMS (EI) Calcd. for $\text{C}_{31}\text{H}_{26}\text{F}_3\text{NO}_2\text{S}$: 533.1636, found: 533.1639.

3-Benzhydrylidene-2-(2,3-dichlorophenyl)-1-(toluene-4-sulfonyl)pyrrolidine (4k):

Compound 4k was prepared according to method D. It was purified by a flash column chromatography on silica gel (eluent: 10% V/V of EtOAc/hexane) to give the product **4k** as a colorless oil, yield 48%.

IR (neat): ν 3056, 1598, 1443, 1350, 1163, 702 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.41 (s, 3H, Me), 2.64-2.73 (m, 1H, H-CH), 3.21-3.27 (m, 1H, H-CH), 3.27-3.46 (m, 1H, H-CH), 3.46-3.91 (m, 1H, H-CH), 5.59 (s, 1H, CH), 6.64-7.53 (m, 17H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 21.53, 31.53, 48.49, 63.74, 126.56, 127.05, 127.13, 127.42, 127.62, 128.06, 128.39, 128.43, 128.89, 129.18, 129.23, 129.51, 131.81, 132.71, 134.19, 128.15, 138.67, 140.71, 141.25, 143.47; MS (EI) m/z : 533 (M^+), 378, 207, 129, 91, 65; HRMS (EI) Calcd. for $\text{C}_{30}\text{H}_{25}\text{Cl}_2\text{NO}_2\text{S}$: 533.0983, found: 533.0992.

3-[Bis(4-chlorophenyl)methylene]-2-(4-bromophenyl)-1-(toluene-4-sulfonyl)pyrrolidine (4l):

Compound 4l was prepared according to method D. It was purified by a flash column chromatography on silica gel (eluent: 10% V/V of EtOAc/hexane) to give the product **4l** as a colorless oil, yield 54%.

IR (neat): ν 3020, 2927, 1489, 1218, 1091, 778, 669 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.47 (s, 3H, Me), 2.53-2.62 (m, 1H, H-CH), 2.84-2.91 (m, 1H, H-CH), 3.32-3.40 (m, 1H, H-CH), 3.69-3.75 (m, 1H, H-CH), 5.28 (s, 1H, CH), 6.62-6.84 (m, 6H, Ar), 7.71-7.30 (m, 8H, Ar), 7.55-7.57 (m, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 21.56, 30.37, 47.67, 64.45, 121.31, 127.64, 128.28, 128.44, 128.81, 129.50, 130.02, 130.31, 131.17, 133.32, 133.50, 134.33, 135.04, 138.67, 138.78, 138.88, 139.93, 143.74; MS (EI) m/z : 611 (M^+), 458, 275, 184, 163, 125, 91; HRMS (EI) Calcd. for $\text{C}_{30}\text{H}_{24}\text{BrCl}_2\text{NO}_2\text{S}$: 611.0088, found: 611.0111.

3-Benzhydrylidene-2-isopropyl-1-(toluene-4-sulfonyl)pyrrolidine (4m):

Compound **4m** was prepared according to method A. It was purified by a flash column chromatography on silica gel (eluent: 10% V/V of EtOAc/hexane) to give the product **4m** as a colorless oil, yield 55%.

IR (neat): ν 3055, 2963, 1598, 1493, 1162, 733, 549 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 0.66 (d, J = 7.2 Hz, 3H, Me), 0.86 (d, J = 7.2 Hz, 3H, Me), 1.93-1.99 (m, 1H, CH), 2.23-2.25 (m, 1H, H-CH), 2.49 (s, 3H, Me), 2.72-2.77 (m, 1H, H-CH), 3.30-3.40 (m, 1H, H-CH), 3.55-3.63 (m, 1H, H-CH), 4.47 (d, J = 4.8 Hz, 1H, CH), 6.76-6.79 (m, 2H, Ar), 6.92-6.96 (m, 2H, Ar), 7.14-7.38 (m, 8H, Ar), 7.75-7.78 (m, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 18.74, 21.55, 31.25, 34.78, 48.28, 66.80, 126.90, 127.00, 127.87, 127.89, 128.20, 129.02, 129.42, 129.57, 129.59, 134.99, 136.81, 141.87, 142.12, 143.48; MS (EI) m/z : 431 (M^+), 388, 232, 203, 91, 43; HRMS (EI) Calcd. for $\text{C}_{27}\text{H}_{29}\text{NO}_2\text{S}$: 433.1919, found: 433.1918.

The preparation and spectroscopic data of compounds in Scheme 3.

3-Benzhydrylidene-2-(4-chlorophenyl)tetrahydrofuran (**4n**):

IR (neat): ν 3061, 2953, 1587, 1470, 1100, 908 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.72-2.79 (m, 1H, H-CH), 3.02-3.14 (m, 1H, H-CH), 3.82-3.89 (m, 1H, H-CH), 4.22-4.27 (m, 1H, H-CH), 5.54 (s, 1H, CH), 6.79-7.31 (m, 14H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 29.67, 33.37, 67.92, 81.63, 126.86, 126.95, 127.95, 128.31, 128.45, 128.72, 129.22, 132.87, 136.05, 140.07, 141.24, 141.27, 141.88; MS (EI) m/z : 346 (M^+), 314, 292, 278; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{19}\text{ClO}$: 346.1124, found: 346.1120.

3-(4-Chlorobenzylidene)-2,2-diphenyltetrahydrofuran (**5a**):

a colorless solid. m.p. 150-152 $^{\circ}\text{C}$; IR (neat): ν 2933, 2863, 1700, 1363, 1222, 703 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.94 (td, J = 6.9, 2.4 Hz, 2H, CH_2), 4.04 (t, J = 6.9 Hz, 2H, CH_2), 5.99

(t, $J = 2.4$ Hz, 1H, =CH), 7.20-7.38 (m, 14H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 31.24, 64.99, 91.39, 124.30, 127.48, 127.93, 127.99, 128.48, 129.59, 132.55, 135.61, 143.32, 146.34; MS (EI) m/z : 346 (M^+), 317, 269, 235, 203; Element Analysis: Calcd. for $\text{C}_{23}\text{H}_{19}\text{ClO}$: C 79.64, H 5.52. Found: C 79.28, H 5.71%.

The reactions that have not been stated in the main text due to the limitation of space.

Scheme SI-1

2-[1-(4-Bromophenyl)-6-chloro-3-(4-chlorophenyl)-1H-inden-2-yl]ethanol (2o):

IR (neat): ν 3380, 2927, 2883, 1486, 1091, 820 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.21-2.26 (m, 1H, H-CH), 2.69-2.74 (m, 1H, H-CH), 3.69 (t, $J = 6.9$ Hz, 2H, CH_2), 4.58 (s, 1H, CH), 6.93-7.46 (m, 11H, Ar); MS (EI) m/z : 458 (M^+), 429, 407, 361, 313, 276, 236, 202; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{17}\text{BrCl}_2\text{O}$: 457.9840, found: 457.9851.

3-[Bis(4-chlorophenyl)methylene]-2-(4-bromophenyl)tetrahydrofuran (4o):

IR (neat): ν 3029, 2942, 2860, 1590, 1489, 1389, 1090, 1013, 824 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.68-2.74 (m, 1H, H-CH), 3.00-3.05 (m, 1H, H-CH), 3.80-3.85 (m, 1H, H-CH),

4.21-4.26 (m, 1H, H-CH), 5.45 (s, 1H, CH), 6.75-6.86 (m, 4H, Ar), 7.06-7.27 (m, 8H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 33.37, 60.71, 81.59, 121.32, 128.17, 128.51, 128.68, 129.87, 130.43, 130.96, 132.88, 132.95, 133.66, 139.06, 139.69, 139.69, 139.94, 142.61; MS (EI) m/z : 457 (M^+), 431, 397, 349, 277, 183; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{17}\text{BrCl}_2\text{O}$: 457.9840, found: 457.9843.

3-(4-Bromobenzylidene)-2,2-bis(4-chlorophenyl)tetrahydrofuran (5b):

IR (neat): ν 2951, 2877, 1592, 1488, 1398, 1093, 823 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.94 (td, $J = 6.9, 2.4$ Hz, 2H, CH_2), 4.01 (t, $J = 6.9$ Hz, 2H, CH_2), 5.93 (t, $J = 2.4$ Hz, 1H, =CH), 7.13-7.47 (m, 12H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 30.95, 64.96, 90.42, 120.97, 124.63, 128.15, 129.14, 129.14, 129.16, 129.77, 131.41, 133.53, 135.42, 141.34, 145.58; MS (EI) m/z : 457 (M^+), 397, 349, 303, 277, 180; HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{17}\text{BrCl}_2\text{O}$: 457.9840, found: 457.9863.

Some special cases in this novel annulation reaction.

It should be noticed that the reaction could give some different products when some special substrates were used.

1. The reaction MCP **1a** with *p*-nitrobenzaldehyde:

5-Benzhydrylidene-2,4-bis(4-nitrophenyl)-[1,3]dioxepane (6):

a colorless solid. m.p. 145-147 °C; IR (neat): ν 3055, 1598, 1523, 1348, 1266, 739, 704 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 2.45-2.53 (m, 1H, H-CH), 2.69-2.74 (m, 1H, H-CH), 3.61-3.69 (m, 1H, H-CH), 4.07-4.13 (m, 1H, H-CH), 6.06 (s, 2H, 2CH), 7.19-8.30 (m, 18H, Ar); ^{13}C NMR (75 MHz, CDCl_3): δ 31.74, 70.41, 79.92, 100.20, 123.46, 123.53, 127.27, 127.34, 127.55, 128.21, 128.39, 128.79, 129.04, 136.15, 140.97, 141.20, 145.57, 146.07, 147.23, 147.93, 148.30; MS (EI) m/z : 490, 357, 340, 323, 313, 205, 191; Anal. Calcd. for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_6$: C 86.29, H 7.97. found: C 86.12, H 8.16%.

2. The reaction of aliphatic MCP **1e** with arylaldehydes:

The reaction of aliphatic MCP **1e** with arylaldehydes gives product **7** in DCM at room temperature for 24 h.

3-(4-Bromobenzylidene)-2,2-dibutyltetrahydrofuran (**7**):

IR (neat): ν 2932, 2861, 1488, 1073, 1009 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 0.87 (t, J = 7.2 Hz, 6H, Me), 1.27–1.37 (m, 8H, CH_2), 1.57-1.68 (m, 4H, CH_2), 2.81 (td, J = 6.9, 2.1 Hz, 2H, CH_2), 3.95 (t, J = 6.9 Hz, 2H, CH_2), 6.06 (s, 1H, =CH), 7.20 (d, J = 8.1 Hz, 2H, Ar), 7.46 (d, J = 8.1 Hz, 2H, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 13.82, 22.89, 25.67, 32.42, 39.30, 65.60, 87.37, 118.38, 119.74, 129.36, 130.63, 131.05, 132.09, 136.56, 147.88; MS (EI) m/z : 350 (M^+), 293, 237, 214, 171; HRMS (EI) Calcd. for $\text{C}_{29}\text{H}_{27}\text{BrO}$: 350.1245, found: 350.1278.

The derivation of indene **2** and ORTEP draws of X-Ray diffraction for typical compounds.

In order to verify the indene structure of **2**, we tried to prepare the derivatives of compound **2a** by the reactions with Ac_2O /pyridine and MeI/NaH , respectively (Scheme SI-4). The corresponding

derivatives were obtained in good yields.

The acetylation of **2a** with Ac_2O gives product **2a-1** as a colorless oil in 90% yield. IR (neat): ν 3062, 2958, 1739, 1489, 1237, 1037 cm^{-1} ; ^1H NMR (300 MHz, TMS, CDCl_3): δ 1.98 (s, 3H, Me), 2.28-2.32 (m, 1H, H-CH), 2.82-2.89 (m, 1H, H-CH), 4.06-4.14 (m, 2H, CH_2), 4.60 (s, 1H, CH), 7.02-7.53 (m, 14H, Ar); MS (EI) m/z : 388 (M^+), 328, 293, 278, 215, 203; HRMS (EI) Calcd. for $\text{C}_{25}\text{H}_{21}\text{ClO}_2$: 388.1230, found: 388.1256.

The methylation of **2a** gives a mixture of products **2a-2** and **2a-3** (1:1) in 85% yield as a colorless oil. IR (neat): ν 3062, 2966, 2928, 2826, 1598, 1490, 1261, 1041, 756 cm^{-1} ; MS (EI) m/z : 374 (M^+), 329, 316, 279, 251, 217, 202; HRMS (EI) Calcd. for $\text{C}_{25}\text{H}_{23}\text{ClO}$: 374.1437, found: 374.1430. ^1H NMR (300 MHz, TMS, CDCl_3): one isomer: δ 1.76 (s, 3H, Me), 2.49-2.56 (m, 2H, CH_2), 2.85-3.09 (m, 2H, CH_2), 3.03 (s, 3H, OMe), 7.04-7.49 (m, 14H, Ar); another isomer: δ 1.77 (s, 3H, Me), 2.49-2.56 (m, 2H, CH_2), 2.85-3.09 (m, 2H, CH_2), 3.04 (s, 3H, OMe), 7.04-7.49 (m, 14H, Ar).

ORTEP draw of **3d**:

The X-ray data of **3d** has been deposited in CCDC with number 210600. Empirical Formula: $C_{24}H_{22}O_2$; Formula Weight: 342.42; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.347 x 0.282 x 0.086 mm; Crystal System: Monoclinic; Lattice Type: primitive; Lattice Parameters: $a = 7.2745(13) \text{ \AA}$, $b = 8.0146(15) \text{ \AA}$, $c = 15.813(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.298(4)^\circ$, $\gamma = 90^\circ$, $V = 920.4(3) \text{ \AA}^3$; Space group: $P2(1)$; Zvalue= 2; $D_{calc} = 1.236 \text{ g/cm}^3$; $F_{000} = 364$; $\mu(\text{MoK}\alpha) = 1.98 \text{ cm}^{-1}$; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0563, 0.1094.

ORTEP draw of **4b**:

The X-ray data of **4b** has been deposited in CCDC with number 210598. Empirical Formula: $C_{20}H_{22}O$; Formula Weight: 278.38; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.460 x 0.273 x 0.213 mm; Crystal System: Monoclinic; Lattice Type: primitive; Lattice Parameters: $a = 15.3994(13) \text{ \AA}$, $b = 9.0725(8) \text{ \AA}$, $c = 24.337(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 106.141(2)^\circ$, $\gamma = 90^\circ$, $V = 3266.1(5) \text{ \AA}^3$; Space group: $P2(1)/c$; Zvalue= 8; $D_{calc} = 1.132 \text{ g/cm}^3$; $F_{000} = 1200$; $\mu(\text{MoK}\alpha) = 1.98 \text{ cm}^{-1}$; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0412, 0.0565.

ORTEP draw of **5a**:

The X-ray data of **5a** has been deposited in CCDC with number 210599. Empirical Formula: $C_{23}H_{19}OCl$; Formula Weight: 346.83; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.328 x 0.245 x 0.202 mm; Crystal System: Monoclinic; Lattice Type: primitive; Lattice Parameters: $a = 10.0390(7) \text{ \AA}$, $b = 19.8339(14) \text{ \AA}$, $c = 9.2205(7) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.7300(10)^\circ$, $\gamma = 90^\circ$, $V = 1775.6(2) \text{ \AA}^3$; Space group: $P2(1)/c$; Zvalue= 4; $D_{calc} = 1.297 \text{ g/cm}^3$; $F_{000} = 728$; $\mu(\text{MoK}\alpha) = 1.98 \text{ cm}^{-1}$; Diffractometer: Rigaku AFC7R; Residuals: R; R_w : 0.0545, 0.1228.

ORTEP draw of **6**:

The X-ray data of **6** has been deposited in CCDC with number 210597. Empirical Formula: $C_{31}H_{26}N_2O_6Cl_2$; Formula Weight: 593.44; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.375 x 0.323 x 0.306 mm; Crystal System: triclinic; Lattice Type: primitive; Lattice Parameters: $a = 8.8296(7)$ Å, $b = 9.0971(8)$ Å, $c = 19.3280(16)$ Å, $\alpha = 86.203(2)^\circ$, $\beta = 80.525(2)^\circ$, $\gamma = 73.713(2)^\circ$, $V = 1469.5(2)$ Å³; Space group: P-1; Z value= 2; $D_{calc} = 1.341$ g/cm³; $F_{000} = 616$; $\mu(\text{MoK}\alpha) = 1.98$ cm⁻¹; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0882, 0.2680.