Lewis Acid Catalyzed Tandem Diels–Alder Reaction/Retro-Claisen Rearrangement as an Equivalent of an Inverse-Electron-Demand Hetero-Diels–Alder Reaction

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General Information

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Low temperature (-78 °C) was maintained using dry ice/acetone and (-40 °C or -20 °C) using immersion cooler. Hexanes, THF and ether were distilled over sodium and benzophenone, or purified by passage through a bed of activated alumina. Dichloromethane was purified by passage through a bed of activated alumina. Purification of reaction products was carried out by flash chromatography using silica gel 60 (230-400 mesh). ¹H NMR spectra were measured at 300, 400 or 500 MHz spectrometers and are reported in ppm using TMS as an internal standard (TMS at 0.00 ppm). Data reported as (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad; coupling constant(s) in Hz; integration). ¹³C NMR spectra were recorded at 75 or 125 MHz spectrometer and reported in ppm using solvent as an internal standard (CDCl₃ at 77.0 ppm).

Experimental Procedures and Physical Data

1. Syntheses of 2-Aryl- α,β -Unsaturated Aldehydes.

2-Phenylacrylaldehyde (1b).¹ To the solution of α -methyl styrene (2.75 g, 23 mmol) in 50 mL benzene was added SeO₂ (3.10 g, 28 mmol). The resulting white suspension was refluxed for 1 h. After cooled down, the mixture was concentrated to ca 10 mL and filtered through celite and washed with pentane. The combined filtrate was concentrated and purified on silica gel (1% - 3% ether/pentane) gave desired product. The yield was not determined since it is unstable and the compound was used immediately. ¹H NMR (500 MHz, CDCl₃) δ 9.83 (s, CHO, 1H), 7.48-7.25 (m, 5H), 6.64 (s, 1H), 6.20 (s, 1H), 1.51 (m, 2H).

¹ Laitalainen, T.; Kuronen, P.; Hesso, A. *Organic Preparations and Procedures International* **1993**, 25(5), 597.

2-(2-Methoxyphenyl)acrylaldehyde (1c).² To a stirred solution of oxalyl chloride (1.63 mL, 18.8 mmol) in dichloromethane (45 mL) is added dimethyl sulfoxide (1.82 mL, 37.7 mmol) dropwise at -78°C , and after 20 min, 2-(2-methoxyphenyl) ethanol (1.00 g, 6.3 mmol) followed by triethylamine (9.56 mL, 69.1 mmol) are added at the same temperature. After having stirred at room temperature for 30 min, methylene-N,N-dimethylammonium chloride (1.17 g, 12.6 mmol) is added to the mixture and the stirring is continued for 15 h at the room temperature. The mixture is taken up into dichloromethane (90 mL), washed with saturated NaHCO_3 and brine, dried over MgSO_4 , and purified on silica gel (7% - 10% ether/pentane) gave desired product 636 mg (60% y). ^1H NMR (500 MHz, CDCl_3) δ 9.71 (s, CHO, 1H), 7.37-6.92 (m, 4H), 6.37 (s, 1H), 6.29 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 192.4, 156.8, 147.0, 133.8, 130.4, 130.1, 124.1, 120.7, 110.9, 55.5; IR (neat) 2838, 1698 (C=O), 1493, 1246, 1025 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$ $[\text{M}]^+$, required m/z : 162.0675, found m/z : 162.0679

2-(4-Methoxyphenyl)acrylaldehyde (1d).² Similar procedure as **1d**. However, **1d** was very easy to dimerize and gave **11**. Thus **1d** was not full characterized. ^1H NMR (400 MHz, CDCl_3) δ 9.80 (s, CHO, 1H), 7.44 (d, $J = 8.8$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.60 (s, 1H), 6.10 (s, 1H), 3.83 (s, 3H).

3,4-dihydro-2,5-bis(4-methoxyphenyl)-2H-pyran-2-carbaldehyde (11). ^1H NMR (500 MHz, CDCl_3) δ 9.51 (d, $J = 1.0$ Hz, 1H), 7.41 (m, 2H), 7.19 (m, 2H), 7.09 (s, 1H), 6.93 (m, 2H), 6.84 (d, $J = 8.5$ Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 2.62-2.56 (m, 1H), 2.43-2.36 (m, 1H), 2.31-2.18 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.8, 159.7, 158.4, 139.0, 131.0, 128.4, 127.0, 125.5, 114.6, 114.3, 113.9, 83.9, 55.3, 27.7, 20.6; IR (neat) 1734, 1635, 1510, 1248, 1021, 828 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{O}$ $[\text{M}+1]^+$, required m/z : 325.1434, found m/z : 325.1432.

² Inomata, K.; Samizu, K.; Tomita, S.; Yanase, M.; Suzuki, M.; Iwabuchi, Y.; Takumichi, S.; Ogasawara, K. *Chem. Lett.* **1989**, 1283.

(E)-2-Phenyloct-2-enal (1f).³ A suspension of Pd(OAc)_2 (808 mg, 3.60 mmol, 12 mol%) in degassed t-BuOH (10 mL) was treated with tributylphosphine (2.60 mL, 10.40 mmol, 36 mol%) under argon, resulting in rapid formation of the yellow Pd(0). After addition of heptanal (18 mL, 150 mmol, 5.0 eq), the mixture was stirred at rt for 20 min, while the color of the solution changed from yellow to black. Styrene oxide (3.6 g, 30.0 mmol) was added, the solution was refluxed under argon for 48 h. Extracted with ether, washed with NaHCO_3 , water and brine successively. Dried (MgSO_4), concentrated and purified on silica gel (0% to 3% EtOAc/hexanes) gave desired product 2.0 g (33% y). ^1H NMR (500 MHz, CDCl_3) δ 9.61 (s, CHO, 1H), 7.42-7.14 (m, 5H), 6.73 (t, J = 7.5 Hz, 1H), 2.35 (q, 8.0 Hz, 2H), 1.51 (m, 2H), 1.32-1.25 (m, 4H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 193.7, 156.7, 143.9, 132.6, 129.4, 128.1, 127.8, 31.4, 29.7, 28.4, 22.3, 13.8.

(E)-2,4-Diphenylbut-2-enal (1h).³ A suspension of Pd(OAc)_2 (300 mg, 3 mol%) in degassed t-BuOH (20 mL) was treated with tributylphosphine (0.99 mL, 3.90 mmol, 9 mol%) under argon, resulting in rapid formation of the yellow Pd(0). Styrene oxide (5.1 mL, 44.7 mmol) was added, after heat for a while, the orange yellow solution turned to deep color very soon and the solution was refluxed under argon for 9 h. Extracted with ether, washed with NaHCO_3 , water and brine successively. Dried (MgSO_4), concentrated and purified on silica gel (7:1 hexanes-EtOAc) gave desired product 2.20 g (44% y). The physical and spectral data were identical to those previously reported for this compound:³ ^1H NMR (400 MHz, CDCl_3): δ 9.66 (s, CHO, 1H), 7.47-7.14 (m, 10H), 6.87 (t, J = 7.6 Hz, 1H), 3.69 (d, J = 7.6 Hz, 2H).

³ Kim, J. H.; Kulawiec, R. J. *J. Org. Chem.* **1996**, *61*, 7656.

(E)-2,4-Bis(4-fluorophenyl)but-2-enal (1i)³ A suspension of Pd(OAc)₂ (320 mg, 1.42 mmol, 4 mol%) in degassed t-BuOH (10 mL) was treated with tributylphosphine (1.06 mL, 4.26 mmol, 12 mol%) under argon, resulting in rapid formation of the yellow Pd(0). *p*-Fluorostyrene oxide (5.00 g, 36.20 mmol) was added, after heat for a while, the orange yellow solution turned to deep color very soon and the solution was refluxed under argon for 27 h. Extracted with ether, washed with NaHCO₃, water and brine successively. Dried (MgSO₄), concentrated and purified on silica gel (10% to 20% EtOAc/hexanes) gave desired product 1.20 g (26% y). The physical and spectral data were identical to those previously reported for this compound:³ ¹H NMR (500 MHz, CDCl₃): δ 9.64 (s, CHO, 1H), 7.22-6.98 (m, 8H), 6.83 (t, *J* = 7.5 Hz, 1H), 3.65 (d, *J* = 7.5 Hz, 2H).

1-Tetralone phenylsulphonylhydrazone.⁴ A solution of phenylsulfonylhydrazide (2.63 g, 15.30 mmol) and 1-tetralone (2.20 g, 15.40 mmol) in CH₃CN (30 mL) was treated with concentrated HCl (2 mL) and then the resultant mixture stirred at room temperature for 24 h. Concentrated and recrystallized from EtOH gave desired product 2.69 g (60%).¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.62-7.52 (m, 3H), 7.27-7.19 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.48 (t, *J* = 6.5 Hz, 2H), 1.91 (m, 2H), 1.70 (br, 1H).

⁴ (a) Shea, K. J.; Stoddard, G. J.; England, W. P.; Haffner, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 2635; (b) Song, Z.; Beak, P. *J. Am. Chem. Soc.* **1990**, *112*, 8126.

3, 4-Dihydronaphthalene-1-carbaldehyde (1j).⁴ To a stirred solution of (2.60 g, 8.70 mmol) of the hydrazone in 50 mL of THF at -78 °C was added 18 mL of 1.6 M n-BuLi solution in hexane dropwise. The red-purple solution was left at -78 °C for 1.5 h, allowed to warm to rt for 1.5 h, and cooled to -78 °C, and (4.20 mL, 58.00 mmol) of anhydrous DMF was added. Then the mixture was allowed to warm to rt and stood for 2 h before workup with 10% HCl and ether. The product was isolated by chromatography with 5% EtOAc as the eluent in 43 % yield (590 mg). The physical and spectral data were identical to those previously reported for this compound:⁴ ¹H NMR (500 MHz, CDCl₃): δ 9.69 (s, 1H), 8.20 (m, 1H), 7.28-7.17 (m, 3H), 7.02 (t, *J* = 5.0 Hz, 1H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.59 (td, *J* = 8.0, 4.5 Hz, 2H).

1-(Phenylsulfonyl)indole-3-carbaldehyde (1k).⁵ To a solution of indocarboxaldehyde (1.12 g, 7.71 mmol) in ethanol (50 mL) at room temperature, KOH pellets were added (0.54g, 9.64 mmol), and the mixture was stirred until total solubilization. The ethanol was completely removed in vacuum and acetone (50 mL) added followed by benzenesulfonyl chloride (0.98 mL, 7.71 mmol). A precipitate was formed instantly. The solid was filtered and the solution concentrated in vacuum. Crystals precipitated out and were filtered and washed with ethanol, yielding 1.32 g (60%). The physical and spectral data were identical to those previously reported for this compound:⁵ ¹H NMR (500 MHz, CDCl₃): δ 10.11 (s, 1H), 8.26 (m, 2H), 7.97 (m, 3H), 7.64-7.36 (m, 5 H).

⁵ (a) Ottoni, O.; Cruz, R.; Alves, R. *Tetrahedron* **1998**, 54, 13915. (b) Gribble, G. W.; Jiang, J.; Liu, Y. *J. Org. Chem.* **2002**, 67, 1001.

3-phenylbut-3-en-2-one (11).² Similar procedure as **1b**. The physical and spectral data were identical to those previously reported for this compound.⁶ ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.29 (m, 5H), 6.18 (s, 1H), 5.97 (s, 1H), 2.45 (s, 3H).

2. [4+2] Cycloaddition Between Cyclopentadiene and Aldehydes.

A 15 mL one-necked round flask was charged with 2-phenyl-2-butenal **1a** (0.42 g, 2.78 mmol) and CH₂Cl₂ (5 mL) followed by cooling for 10 min at -40 °C. Dimethylaluminum chloride (0.14 mL, 0.14 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.92 g, 13.95 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -40 °C for 20 h. The reaction was quenched by addition of 3 mL saturated NaHCO₃ solution, extracted with ether (2×), and the combined extracts were washed with water and brine, dried over MgSO₄, and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2a** as colorless oil 418 mg (71% yield); mixture of **4a** and **5a** as colorless oil 23 mg (4% yield).

(4S*,4aR*,7aR*)-4,4a,5,7a-tetrahydro-4-methyl-3-phenylcyclopenta[b]pyran (2a). ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.16 (m, 5H), 6.63 (s, 1H), 6.16 (m, 1H), 6.00 (m, 1H), 4.84 (br d, *J* = 6.0 Hz, 1H), 3.16 (m, 1H), 2.68 (m, 1H), 2.42-2.32 (m, 2H), 1.00 (d, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.1, 139.0, 137.1, 131.5, 128.1, 126.9, 125.8, 118.2, 80.6, 43.4, 33.1, 27.8, 16.6; IR (neat) 2931, 1639, 1176, 761, 701 cm⁻¹; HRMS (EI) calcd for C₁₅H₁₆O [M]⁺, required *m/z*: 212.1196, found *m/z*: 212.1198. Diastereoselectivity (*exo-endo* ratio) was determined by ¹H NMR analysis (H₁) of the crude mixture : δ 6.63 (s, 1H, *endo*, major), δ 6.83 (s, 1H, *exo*, minor).

(1R*,2R*,3S*,4S*)-3-methyl-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (4a). ¹H NMR (500 MHz, CDCl₃) δ 9.33 (s, CHO, 1H), 7.38-7.18 (m, 5H), 6.39 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.17

⁶ Filho, E. P. S.; Rodrigues, A. R.; Moran, P. J. S. *Tetrahedron Asymmetry* **2001**, *12*, 847.

(dd, $J = 5.5, 3.0$ Hz, 1H), 3.47 (br s, 1H), 2.63 (br s, 1H), 2.60 (m, 1H), 2.00 (d, $J = 8.5$ Hz, 1H), 1.65 (d, $J = 8.5$ Hz, 1H), 0.64 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 198.9, 141.6, 136.7, 133.1, 129.4, 128.4, 126.9, 67.0, 51.1, 47.2, 44.8, 37.9, 20.2; IR (neat) 2968, 1712 (C=O), 1463, 704 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}$ $[\text{M}]^+$, required m/z : 212.1196, found m/z : 212.1196. Diastereoselectivity (*exo-endo* ratio) was determined by ^1H NMR analysis (CHO) of the crude mixture : δ 9.33 (s, 1H, *endo*, major), δ 9.66 (s, 1H, *exo*, minor).

A 15 mL one-necked round flask was charged with 2-phenylacrylaldehyde **1b** (0.35 g, 2.65 mmol) and CH_2Cl_2 (5 mL) followed by cooling for 10 min at -40°C . Dimethylaluminum chloride (0.27 mL, 0.27 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.88 g, 13.25 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -40°C for 20 h. The reaction was quenched by addition of 3 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2b** as colorless oil 262 mg (50% yield); mixture of **4b** and **5b** as colorless oil 183 mg (35% yield).

(4*aS, 7*aR**)-4,4*a*,5,7*a*-tetrahydro-3-phenylcyclopenta[*b*]pyran (**2b**).** ^1H NMR (500 MHz, CDCl_3) δ 7.31-7.14 (m, 5H), 6.98 (s, 1H), 6.05 (m, 1H), 5.93 (m, 1H), 4.90 (br d, $J = 6.5$ Hz, 1H), 2.73 (m, 1H), 2.64 (dd, $J = 16.5, 7.0$ Hz, 1H), 2.54 (dd, $J = 16.5, 7.0$ Hz, 1H), 2.33-2.26 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.6, 139.7, 135.7, 132.2, 128.4, 125.7, 124.1, 112.4, 80.4, 38.2, 35.9, 24.8; IR (neat) 2926, 1642, 1163, 756, 695 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}$ $[\text{M}]^+$, required m/z : 198.1039, found m/z : 198.1043.

(1*R, 2*R**, 4*R**)-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (**4b**).** ^1H NMR (500 MHz, CDCl_3) δ 9.38 (s, CHO, 1H), 7.37-7.25 (m, 5H), 6.33 (dd, $J = 6.0, 3.0$ Hz, 1H), 6.13 (dd, $J = 6.0, 3.0$ Hz, 1H), 3.64 (br s, 1H), 2.99 (br s, 1H), 2.36 (d, $J = 11.5$ Hz, 1H), 2.02 (dd, $J = 11.5, 4.0$ Hz, 1H), 1.57 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.7, 140.5, 132.8, 128.9, 128.4, 127.1, 64.8, 47.7, 47.1, 43.7, 36.7; IR (neat) 2972, 1719 (C=O), 1640, 1493, 1164, 699 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}$ $[\text{M}]^+$, required m/z : 198.1039, found m/z : 198.1032.

(1*R, 2*S**, 4*R**)-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (**5b**).** ^1H NMR (500 MHz, CDCl_3) δ 9.55 (s, CHO, 1H), 7.35-7.21 (m, 5H), 6.18 (dd, $J = 5.5, 3.0$ Hz, 1H), 5.95 (dd, $J = 5.5, 3.0$ Hz, 1H), 3.61 (br s, 1H), 2.98 (br s, 1H), 2.69 (dd, $J = 11.5, 4.0$ Hz, 1H), 1.60 (dd, $J = 12.0, 3.0$ Hz, 1H), 1.54 (m, 1H), 1.44 (d, $J = 9.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.2, 139.6,

133.5, 129.1, 128.7, 127.0, 65.1, 46.9, 46.8, 42.1, 33.6; IR (neat) 2971, 1717 (C=O), 1492, 700 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}$ $[\text{M}]^+$, required m/z : 198.1039, found m/z : 198.1046.

A 10 mL one-necked round flask was charged with 2-(2-methoxyphenyl)acrylaldehyde **1c** (110 mg, 0.68 mmol) and CH_2Cl_2 (2 mL) followed by cooling for 10 min at -20°C . Dimethylaluminum chloride (68 μL , 0.068 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (224 mg, 3.39 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -20°C for 20 h. The reaction was quenched by addition of 3 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 2-7% pentane/diethyl ether as eluent to give **2c** as colorless oil 48 mg (51% yield); mixture of **4c** and **5c** as colorless oil 86 mg (56% yield, *endo* : *exo* = 3 : 1).

(4a*R, 7a*S**)-4,4a,5,7a-tetrahydro-3-(2-methoxyphenyl)cyclopenta[b]pyran (2c).** ^1H NMR (500 MHz, CDCl_3) δ 7.21–6.84 (m, 4H), 6.78 (s, 1H), 6.03 (m, 1H), 5.91 (m, 1H), 4.96 (br d, J = 6.5 Hz, 1H), 3.81 (s, 3H), 2.74–2.67 (m, 1H), 2.63 (dd, J = 16.0, 7.0 Hz, 1H), 2.51 (dd, J = 16.0, 7.0 Hz, 1H), 2.35–2.29 (m, 1H), 2.26 (dd, J = 16.5, 4.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.3, 143.4, 135.3, 132.3, 129.4, 128.9, 127.4, 120.6, 112.7, 110.9, 81.1, 55.4, 38.2, 36.2, 26.5; IR (neat) 2930, 1646, 1490, 1238, 1156, 751 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$, required m/z : 228.1145, found m/z : 228.1151.

2-(2-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (4c). ^1H NMR (500 MHz, CDCl_3) δ 9.46 (s, CHO, 1H), 7.38–6.84 (m, 4H), 6.36 (dd, J = 5.5, 3.0 Hz, 1H), 6.03 (dd, J = 5.5, 3.0 Hz, 1H), 3.74 (s, 3H), 3.50 (br s, 1H), 2.98 (br s, 1H), 2.70 (dd, J = 12.5, 2.5 Hz, 1H), 1.85 (dd, J = 13.0, 3.0 Hz, 1H), 1.71 (d, J = 8.5 Hz, 1H), 1.57 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.0, 157.4, 139.9, 132.7, 132.4, 128.1, 126.9, 120.6, 110.8, 59.1, 55.3, 48.7, 48.0, 43.4, 37.2; IR (neat) 2970, 1718 (C=O), 1488, 1245, 1027, 754 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$, required m/z : 228.1145, found m/z : 228.1149. Diastereoselectivity (*exo-endo* ratio) was determined by ^1H NMR analysis (CHO) of the crude mixture : δ 9.46 (s, 1H, *endo*, major), δ 9.64 (s, 1H, *exo*, minor).

A 10 mL one-necked round flask was charged with 2-(4-methoxyphenyl)acrylaldehyde **1d** (50 mg, 0.31 mmol) and CH_2Cl_2 (2 mL) followed by cooling for 10 min at -40°C . Dimethylaluminum chloride (31 μL , 0.031 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (102 mg, 1.54 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -40°C for 20 h. The reaction was quenched by addition of 2 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2d** as colorless oil 40 mg (61% yield); mixture of **4d** and **5d** as colorless oil 18 mg (28% yield, *endo* : *exo* = 7 : 1).

(4aR*,7aS*)-4,4a,5,7a-tetrahydro-3-(4-methoxyphenyl)cyclopenta[b]pyran (2d). ^1H NMR (500 MHz, CDCl_3) δ 7.19 (d, J = 8.5 Hz, 2H), 6.88 (br, 1H), 6.84 (d, J = 8.5 Hz, 2H), 6.05 (m, 1H), 5.92 (m, 1H), 4.87 (br d, J = 6.5 Hz, 1H), 3.79 (s, 3H), 2.71 (m, 1H), 2.64-2.52 (m, 2H), 2.30-2.25 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.0, 141.3, 135.6, 132.4, 132.3, 125.3, 113.9, 112.4, 80.4, 55.3, 38.3, 36.0, 25.3; IR (neat) 2929, 1645, 1513, 1246, 1158, 826 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$, required m/z : 228.1145, found m/z : 228.1148.

2-(2-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (4d). ^1H NMR (500 MHz, CDCl_3) δ 9.34 (s, CHO, 1H), 7.27 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.32 (dd, J = 6.0, 3.0 Hz, 1H), 6.13 (dd, J = 5.5, 3.0 Hz, 1H), 3.81 (s, 3H), 3.59 (br s, 1H), 2.98 (br s, 1H), 2.32 (d, J = 11.5 Hz, 1H), 1.98 (dd, J = 12.0, 3.5 Hz, 1H), 1.56 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.7, 158.6, 140.4, 132.8, 132.1, 129.4, 114.3, 64.1, 55.3, 47.6, 47.3, 43.7, 36.5; IR (neat) 1718 (C=O), 1511, 1251 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$, required m/z : 228.1145, found m/z : 228.1138. Diastereoselectivity (*exo*-*endo* ratio) was determined by ^1H NMR analysis (CHO) of the crude mixture : δ 9.34 (s, 1H, *endo*, major), δ 9.51 (s, 1H, *exo*, minor).

A 15 mL one-necked round flask was charged with 2-phenyl-2-pentenal **1e** (0.38 g, 2.30 mmol) and CH_2Cl_2 (5 mL) followed by cooling for 10 min at -40°C . Dimethylaluminum chloride (0.12 mL, 0.12 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.76 g, 11.50 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -40°C for 20 h. The reaction was quenched by addition of 3 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2e** as colorless oil 270 mg (52% yield); mixture of **4e** and **5e** as colorless oil 62 mg (12% yield).

(4*R,4*aS**,7*aS**)-4-ethyl-4,4*a*,5,7*a*-tetrahydro-3-phenylcyclopenta[*b*]pyran (**2e**).** ^1H NMR (500 MHz, CDCl_3) δ 7.30-7.15 (m, 5H), 6.57 (s, 1H), 6.19 (m, 1H), 6.02 (m, 1H), 4.82 (m, 1H), 2.93 (m, 1H), 2.76 (m, 1H), 2.42-2.31 (m, 2H), 1.67 (m, 1H), 1.02 (m, 1H), 0.92 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.4, 139.3, 137.5, 131.6, 128.0, 127.5, 125.8, 117.4, 80.6, 41.2, 34.8, 32.2, 23.7, 12.3; IR (neat) 2961, 1637, 1492, 1173, 761, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}$ $[\text{M}]^+$, required m/z : 226.1352, found m/z : 226.1353. Diastereoselectivity (*exo-endo* ratio) was determined by ^1H NMR analysis (H_1) of the crude mixture : δ 6.57 (s, 1H, *endo*, major), δ 6.84 (s, 1H, *exo*, minor).

(1*R,2*R**,3*S**,4*S**)-3-ethyl-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (**4e**).** ^1H NMR (500 MHz, CDCl_3) δ 9.31 (s, CHO, 1H), 7.38-7.17 (m, 5H), 6.36 (dd, $J = 5.5, 3.0$ Hz, 1H), 6.19 (dd, $J = 5.5, 3.0$ Hz, 1H), 3.43 (br s, 1H), 2.89 (br s, 1H), 2.32 (m, 1H), 1.95 (d, $J = 8.5$ Hz, 1H), 1.65 (d, $J = 8.5$ Hz, 1H), 1.20-1.14 (m, 1H), 0.88 (t, $J = 7.5$ Hz, 3H), 0.42-0.35 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 198.9, 141.6, 136.9, 133.5, 129.5, 128.4, 126.9, 67.2, 47.3, 46.1, 45.4, 45.1, 26.5, 13.3; IR (neat) 2970, 1721 ($\text{C}=\text{O}$), 1446, 704 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}$ $[\text{M}]^+$, required m/z : 226.1352, found m/z : 226.1349. Diastereoselectivity (*exo-endo* ratio) was determined by ^1H NMR analysis (CHO) of the crude mixture : δ 9.31 (s, 1H, *endo*, major), δ 9.66 (s, 1H, *exo*, minor).

A 15 mL one-necked round flask was charged with 2-Phenyloct-2-enal **1f** (0.15 g, 0.74 mmol) and CH_2Cl_2 (2 mL) followed by cooling for 10 min at -20°C . Dimethylaluminum chloride (0.12 mL, 0.12 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.25 g, 3.71 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -20°C for 20 h. The reaction was quenched by addition of 1 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2f** as colorless oil 101 mg (51% yield); mixture of **4f** and **5f** as colorless oil 57 mg (29% yield).

(4R*,4aS*,7aS*)-4,4a,5,7a-tetrahydro-4-pentyl-3-phenylcyclopenta[b]pyran (2f). ^1H NMR (500 MHz, CDCl_3) δ 7.30-7.15 (m, 5H), 6.57 (d, $J = 2.0$ Hz, 1H), 6.20 (m, 1H), 6.02 (m, 1H), 4.81 (dd, $J = 5.5, 2.0$ Hz, 1H), 3.05-3.00 (m, 1H), 2.74 (m, 1H), 2.43-2.31 (m, 2H), 1.62-1.55 (m, 1H), 1.44-1.39 (m, 1H), 1.30-1.14 (m, 5H), 1.01-0.98 (m, 1H), 0.84 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.5, 139.3, 137.6, 131.6, 128.0, 127.5, 125.8, 117.4, 80.5, 41.6, 33.0, 32.4, 31.9, 30.7, 27.4, 22.6, 14.0; IR (neat) 2928, 1638, 1170, 761, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{24}\text{O}$ $[\text{M}]^+$, required m/z : 268.1822, found m/z : 268.1822.

(1R*,2R*,3S*,4S*)-3-pentyl-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (4f). ^1H NMR (500 MHz, CDCl_3) δ 9.31 (s, CHO, 1H), 7.38-7.16 (m, 5H), 6.35 (dd, $J = 5.5, 3.0$ Hz, 1H), 6.18 (dd, $J = 5.5, 3.0$ Hz, 1H), 3.42 (br s, 1H), 2.85 (br s, 1H), 2.39 (dt, $J = 11.5, 1.5$ Hz, 1H), 1.95 (d, $J = 8.5$ Hz, 1H), 1.64 (m, 1H), 1.39-1.10 (m, 7H), 0.82 (t, $J = 7.0$ Hz, 3H), 0.44-0.36 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.0, 141.6, 136.8, 133.4, 129.5, 128.4, 126.9, 67.1, 47.3, 46.8, 45.1, 43.5, 33.5, 31.9, 28.7, 22.6, 14.0; IR (neat) 2930, 1723 (C=O), 1455, 704 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{24}\text{O}$ $[\text{M}]^+$, required m/z : 268.1822, found m/z : 268.1823.

(1R*,2S*,3R*,4S*)-3-pentyl-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (5f). ^1H NMR (500 MHz, CDCl_3) δ 9.35 (s, CHO, 1H), 7.33-7.14 (m, 5H), 6.50 (dd, $J = 5.5, 3.0$ Hz, 1H), 6.22 (dd, $J = 5.5, 3.0$ Hz, 1H), 3.41 (br s, 1H), 3.08-3.04 (m, 1H), 2.96 (br s, 1H), 1.54 (m, 1H), 1.33 (d, $J = 9.0$ Hz, 1H), 1.30-1.11 (m, 7H), 0.84 (t, $J = 7.0$ Hz, 3H), 0.27 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.7, 138.4, 136.1, 134.2, 130.7, 128.2, 127.1, 68.3, 47.0, 46.4, 45.0, 41.8, 32.0, 31.7, 28.3, 22.7, 14.0; IR (neat) 2927, 1717 (C=O), 1445, 702 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{24}\text{O}$ $[\text{M}]^+$, required m/z : 268.1822, found m/z : 268.1822.

A 15 mL one-necked round flask was charged with 5-methyl-2-phenylhex-2-enal **1g** (0.47 g, 2.39 mmol) and CH₂Cl₂ (5 mL) followed by cooling for 10 min at -20 °C. Dimethylaluminum chloride (0.48 mL, 0.48 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.79 g, 12.0 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -20 °C for 20 h. The reaction was quenched by addition of 1 mL saturated NaHCO₃ solution, extracted with ether (2×), and the combined extracts were washed with water and brine, dried over MgSO₄, and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2g** as colorless oil 297 mg (49% yield); mixture of **4g** and **5g** as colorless oil 109 mg (18% yield).

(4R*,4aS*,7aS*)-4,4a,5,7a-tetrahydro-4-isobutyl-3-phenylcyclopenta[b]pyran (2g). ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.14 (m, 5H), 6.58 (d, *J* = 2.0 Hz, 1H), 6.20 (m, 1H), 6.03 (m, 1H), 4.80 (m, 1H), 3.16 (m, 1H), 2.71 (m, 1H), 2.43-2.29 (m, 2H), 1.73-1.64 (m, 1H), 1.33 (ddd, *J* = 14.0, 10.5, 4.0 Hz, 1H), 1.02 (ddd, *J* = 14.0, 11.0, 3.5 Hz, 1H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.7, 139.3, 137.7, 131.6, 128.1, 127.5, 125.8, 117.3, 80.4, 41.6, 39.8, 32.5, 30.4, 25.3, 24.0, 21.4; IR (neat) 2953, 1639, 1465, 1173, 1008, 760, 700 cm⁻¹; HRMS (EI) calcd for C₁₈H₂₂O [M]⁺, required *m/z*: 254.1665, found *m/z*: 254.1664.

(4S*,4aS*,7aS*)-4,4a,5,7a-tetrahydro-4-isobutyl-3-phenylcyclopenta[b]pyran (3g). ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.15 (m, 5H), 6.84 (s, 1H), 6.10-6.07 (m, 1H), 5.96-5.93 (m, 1H), 4.92 (dt, *J* = 6.5, 2.0 Hz, 1H), 2.74-2.69 (m, 2H), 2.50-2.43 (m, 1H), 2.32-2.26 (m, 1H), 1.76-1.71 (m, 1H), 1.53-1.41 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 142.7, 139.8, 137.4, 131.5, 128.4, 125.7, 124.7, 117.4, 78.6, 44.7, 41.4, 37.8, 33.2, 25.6, 23.5, 22.0; IR (neat) 2956, 2923, 1635, 1173, 1151, 759 cm⁻¹; HRMS (EI) calcd for C₁₈H₂₂O [M]⁺, required *m/z*: 254.1665, found *m/z*: 254.1664.

(1R*,2R*,3S*,4S*)-3-isobutyl-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (4g). ¹H NMR (500 MHz, CDCl₃) δ 9.31 (s, CHO, 1H), 7.40-7.15 (m, 5H), 6.35 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.18 (dd, *J* = 5.5, 3.0 Hz, 1H), 3.42 (br s, 1H), 2.81 (br s, 1H), 2.55-2.52 (m, 1H), 1.95 (d, *J* = 8.5 Hz, 1H), 1.65 (d, *J* = 8.5 Hz, 1H), 1.60-1.50 (m, 1H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.82-0.77 (m, 1H), 0.75 (d, *J* = 6.0 Hz, 3H), 0.50-0.43 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 198.9, 141.5, 137.0, 133.5, 129.5, 128.4, 126.9, 67.2, 47.39, 47.37, 45.2, 42.7, 41.3, 27.0, 24.1, 21.4; IR (neat) 2956, 1722 (C=O) cm⁻¹; HRMS (EI) calcd for C₁₈H₂₂O [M]⁺, required *m/z*: 254.1665, found *m/z*: 254.1668.

(1*R,2*S**,3*R**,4*S**)-3-isobutyl-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (5g).** ¹H NMR (500 MHz, CDCl₃) δ 9.35 (s, CHO, 1H), 7.35-7.13 (m, 5H), 6.50 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.21 (dd, *J* = 6.0, 3.0 Hz, 1H), 3.41 (br s, 1H), 3.18 (dt, *J* = 12.5, 4.0 Hz, 1H), 2.94 (br s, 1H), 1.56-1.51 (m, 2H), 1.35 (d, *J* = 9.0 Hz, 1H), 1.02 (t, *J* = 6.0 Hz, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H), 0.33 (ddd, *J* = 16.5, 13.0, 3.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 200.0, 138.6, 134.1, 130.7, 128.2, 127.1, 68.2, 47.1, 46.5, 45.1, 40.8, 39.7, 26.8, 24.3, 21.2; IR (neat) 2955, 1717 (C=O), 1465, 702 cm⁻¹; HRMS (EI) calcd for C₁₈H₂₂O [M]⁺, required *m/z*: 254.1665, found *m/z*: 254.1664.

A 15 mL one-necked round flask was charged with 2,4-Diphenylbut-2-enal **1h** (0.17 g, 0.76 mmol) and CH₂Cl₂ (3 mL) followed by cooling for 10 min at -40 °C. Dimethylaluminum chloride (0.08 mL, 0.08 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.26 g, 3.85 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -40 °C for 20 h. The reaction was quenched by addition of 1 mL saturated NaHCO₃ solution, extracted with ether (2×), and the combined extracts were washed with water and brine, dried over MgSO₄, and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2h** as colorless oil 153 mg (70% yield); mixture of **4h** and **5h** as colorless oil 23 mg (11% yield).

(4*R,4*aS**,7*aS**)-4-benzyl-4,4a,5,7a-tetrahydro-3-phenylcyclopenta[*b*]pyran (2h).** ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.15 (m, 10H), 6.38 (d, *J* = 2.0 Hz, 1H), 6.13-6.11 (m, 1H), 6.98-5.96 (m, 1H), 4.80-4.77 (m, 1H), 3.51-3.46 (m, 1H), 3.07 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.60-2.40 (m, 2H), 2.34-2.29 (m, 1H), 2.18 (dd, *J* = 14.0, 11.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 144.1, 140.7, 138.8, 137., 131.4, 128.6, 128.3, 128.1, 127.7, 126.0, 125.9, 116.8, 81.0, 41.0, 36.8, 34.8, 32.7; IR (neat) 3024, 2928, 1637, 1493, 1166, 700 cm⁻¹; HRMS (EI) calcd for C₂₁H₂₀O [M]⁺, required *m/z*: 288.1509, found *m/z*: 288.1511.

(1*R,2*R**,3*S**,4*S**)-3-benzyl-2-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (4h).** ¹H NMR (500 MHz, CDCl₃) δ 9.35 (s, CHO, 1H), 7.40-7.09 (m, 10H), 6.23-6.18 (m, 2H), 3.51 (br s, 1H), 2.83-2.79 (m, 1H), 2.64 (br s, 1H), 2.56 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.11 (d, *J* = 8.5 Hz, 1H), 1.69-1.66 (m, 1H), 1.57-1.53 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 198.5, 141.7, 141.4, 136.5, 133.6, 129.5, 128.9, 128.6, 128.2, 127.2, 125.8, 67.0, 47.6, 46.3, 44.8, 44.6, 40.2; IR (neat) 2975, 1719 (C=O), 1494, 704 cm⁻¹; HRMS (EI) calcd for C₂₁H₂₀O [M]⁺, required *m/z*: 288.1509, found

m/z : 288.1512. Diastereoselectivity (*exo-endo* ratio) was determined by ^1H NMR analysis (CHO) of the crude mixture : δ 9.35 (s, 1H, *endo*, major), δ 9.40 (s, 1H, *exo*, minor).

A 10 mL one-necked round flask was charged with 2,4-Bis(4-fluorophenyl)but-2-enal **1i** (0.23 g, 0.89 mmol) and CH_2Cl_2 (2 mL) followed by cooling for 10 min at -20°C . Dimethylaluminum chloride (0.09 mL, 0.09 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.30 g, 4.46 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -20°C for 20 h. The reaction was quenched by addition of 1 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2i** as colorless oil 144 mg (50% yield); mixture of **4i** and **5i** as colorless oil 89 mg (31% yield).

(4*R,4*aS**,7*aS**)-4-(4-fluorobenzyl)-3-(4-fluorophenyl)-4,4*a*,5,7*a*-tetrahydro-cyclopenta[*b*]pyran (**2i**).** ^1H NMR (500 MHz, CDCl_3) δ 7.14-6.92 (m, 8H), 6.58 (d, J = 1.5 Hz, 1H), 6.12 (m, 1H), 5.96 (m, 1H), 4.82 (br d, J = 5.5 Hz, 1H), 3.35 (m, 1H), 2.93 (dd, J = 14.0, 5.0 Hz, 1H), 2.54-2.27 (m, 3H), 2.20 (dd, J = 14.0, 11.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.3 (d, J = 24.5 Hz), 160.4 (d, J = 24.7 Hz), 144.08 (d, J = 1.1 Hz), 137.2, 136.1 (d, J = 3.4 Hz), 134.6 (d, J = 3.4 Hz), 131.5, 129.9, 129.8, 129.1, 129.0, 116.2, 115.2, 115.1, 115.0, 114.9, 81.3, 41.1, 36.0, 35.4, 32.8; IR (neat) 2929, 1640, 1508, 1223, 1160, 832 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{18}\text{F}_2\text{O}$ $[\text{M}]^+$, required m/z : 324.1320, found m/z : 324.1320.

(1*R,2*R**,3*S**,4*S**)-3-(4-fluorobenzyl)-2-(4-fluorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (**4i**).** ^1H NMR (500 MHz, CDCl_3) δ 9.32 (s, CHO, 1H), 7.24-6.91 (m, 8H), 6.25-6.19 (m, 2H), 3.47 (br s, 1H), 2.75 (dd, J = 12.0, 3.0 Hz, 1H), 2.61 (br s, 1H), 2.47 (dd, J = 14.0, 4.5 Hz, 1H), 2.05 (d, J = 8.5 Hz, 1H), 1.68 (t, J = 9.0 Hz, 1H), 1.56 (d, J = 12.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 198.2, 162.5 (d, J = 79.3 Hz), 160.6 (d, J = 75.3 Hz), 141.6, 136.7 (d, J = 3.4 Hz), 133.6, 132.0 (d, J = 3.4 Hz), 131.1, 130.9, 130.1, 130.0, 115.7, 115.5, 115.1, 115.0, 66.4, 47.9, 46.2, 44.6, 44.5, 39.4; IR (neat) 2975, 1719 (C=O), 1509, 1226, 834 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{18}\text{F}_2\text{O}$ $[\text{M}]^+$, required m/z : 324.1320, found m/z : 324.1329. Diastereoselectivity (*exo-endo* ratio) was determined by ^1H NMR analysis (CHO) of the crude mixture : δ 9.32 (s, 1H, *endo*, major), δ 9.36 (s, 1H, *exo*, minor).

A 10 mL one-necked round flask was charged with **1j** (50 mg, 0.32 mmol) and CH_2Cl_2 (1 mL) followed by cooling for 10 min at -40°C . Dimethylaluminum chloride (0.16 mL, 0.16 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.11 g, 1.58 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -40°C for 20 h. The reaction was quenched by addition of 1 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2j** as colorless oil 21 mg (30% yield); mixture of **4j** and **5j** as colorless oil 42 mg (60% yield).

(2j) ^1H NMR (500 MHz, CDCl_3) δ 7.39 (d, $J = 8.0$ Hz, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 7.10-7.00 (m, 3H), 6.08 (m, 1H), 5.92 (m, 1H), 5.02 (m, 1H), 2.94-2.75 (m, 4H), 2.33-2.23 (m, 2H), 2.02-1.96 (m, 1H), 1.50-1.41 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.3, 137.5, 135.6, 133.3, 131.2, 128.9, 126.2, 125.0, 120.7, 112.2, 82.5, 42.9, 33.3, 32.1, 30.1, 26.7; IR (neat) 2962, 1631, 1167, 756 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}$ $[\text{M}]^+$, required m/z : 224.1196, found m/z : 224.1197.

(4j) ^1H NMR (500 MHz, CDCl_3) δ 9.35 (s, CHO, 1H), 7.51 (d, $J = 7.5$ Hz, 1H), 7.30-7.16 (m, 3H), 6.35 (dd, $J = 5.5, 3.0$ Hz, 1H), 6.20 (dd, $J = 5.5, 3.0$ Hz, 1H), 3.54 (br s, 1H), 2.69-2.64 (m, 2H), 2.58-2.46 (m, 2H), 2.32-2.27 (m, 1H), 1.49 (d, $J = 9.0$ Hz, 1H), 1.43 (m, 1H), 1.26-1.17 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.5, 141.9, 139.6, 134.4, 132.9, 128.4, 127.5, 126.9, 126.8, 63.1, 49.7, 48.0, 45.1, 41.5, 30.0, 29.9; IR (neat) 2940, 1718 (C=O), 1451, 739 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}$ $[\text{M}]^+$, required m/z : 224.1196, found m/z : 224.1192.

(5j) ^1H NMR (500 MHz, CDCl_3) δ 9.45 (s, CHO, 1H), 7.31-7.08 (m, 4H), 6.21 (dd, $J = 5.5, 3.0$ Hz, 1H), 5.99 (dd, $J = 5.5, 3.0$ Hz, 1H), 3.64 (br s, 1H), 3.03-2.97 (m, 1H), 2.94 (br s, 1H), 2.56 (dt, $J = 15.0, 3.5$ Hz, 1H), 2.49 (td, $J = 14.0, 3.5$ Hz, 1H), 2.20-2.14 (m, 1H), 1.61-1.52 (m, 2H), 0.83 (qd, $J = 12.5, 3.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.9, 141.3, 138.2, 135.3, 134.6, 128.0, 127.9, 126.8, 126.7, 62.7, 48.1, 47.1, 46.3, 42.0, 30.1, 27.2; IR (neat) 2936, 1714 (C=O), 1451, 742 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{O}$ $[\text{M}]^+$, required m/z : 224.1196, found m/z : 224.1192.

A 10 mL one-necked round flask was charged with **1k** (0.12 g, 0.42 mmol) and CH_2Cl_2 (3 mL) followed by cooling for 10 min at -20°C . Dimethylaluminum chloride (0.09 mL, 0.09 mmol, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (0.14 g, 2.10 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -20°C for 40 h. The reaction was quenched by addition of 1 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 5-10% pentane/diethyl ether as eluent to give mixture of **4k** and **5k** as white solid 59 mg (40% yield).

(5k) ^1H NMR (500 MHz, CDCl_3) δ 9.44 (s, CHO, 1H), 7.74-6.99 (m, 9H), 6.17 (dd, $J = 5.5, 3.0$ Hz, 1H), 5.64 (dd, $J = 5.5, 3.0$ Hz, 1H), 4.87 (d, $J = 4.5$ Hz, 1H), 3.53 (br s, 1H), 3.36 (br s, 1H), 1.53 (m, 1H), 1.46 (d, $J = 9.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.1, 144.5, 136.0, 135.3, 133.3, 129.4, 129.0, 127.1, 124.2, 124.1, 115.6, 69.3, 68.4, 48.7, 48.1, 44.7; IR (neat) 1711 (C=O), 1357, 1168 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{17}\text{NO}_3\text{S} [\text{M}]^+$, required m/z : 351.0924, found m/z : 351.0936. Diastereoselectivity (*exo-endo* ratio) was determined by ^1H NMR analysis (CHO) of the crude mixture : δ 9.13 (s, 1H, *endo*, minor), δ 9.44 (s, 1H, *exo*, major).

A 10 mL one-necked round flask was charged with **11** (65 mg, 0.44 mmol) and CH_2Cl_2 (2 mL) followed by cooling for 10 min at -40°C . Dimethylaluminum chloride (0.044 mL, 1.0 M in hexanes) was added dropwise to the stirred solution. After 15 min, an aliquot of freshly distilled precooled cyclopentadiene (145 mg, 2.20 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at -40°C for 20 h. The reaction was quenched by addition of 1 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and

concentrated. The crude product was purified by column chromatography on silica gel using 2% pentane/diethyl ether as eluent to give **4l** as colorless oil 89 mg (95% yield, >98% de).

(4l) ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.21 (m, 5H), 6.31 (dd, $J = 5.5, 3.0$ Hz, 1H), 6.04 (dd, $J = 5.5, 3.0$ Hz, 1H), 3.65 (br s, 1H), 2.92 (br s, 1H), 2.56 (dd, $J = 12.0, 3.0$ Hz, 1H), 1.89 (s, 3H), 1.81 (dd, $J = 12.0, 3.5$ Hz, 1H), 1.65-1.58 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 207.2, 143.5, 140.7, 132.2, 128.8, 127.4, 126.6, 65.6, 48.2, 47.6, 43.5, 37.8, 26.6; IR (neat) 2975, 1707 (C=O), 1494, 1335, 1223 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}$ $[\text{M}]^+$, required m/z : 212.1196, found m/z : 212.1194.

A 25 mL one-necked round flask was charged with **1d** (0.53 g, 3.51 mmol) and CH_2Cl_2 (4 mL) at room temperature. Dimethylaluminum chloride (3.51 mL, 1.0 M in hexanes) was added dropwise to the stirred solution. After 5 min, an aliquot of freshly distilled cyclopentadiene (1.17 g, 17.58 mmol) was then added by syringe to the reaction mixture giving a clear yellow solution. The resulting mixture was kept stirring at room temperature for 40 min. The reaction was quenched by addition of 5 mL saturated NaHCO_3 solution, extracted with ether (2 $\times$), and the combined extracts were washed with water and brine, dried over MgSO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using 3% to 7% pentane/diethyl ether as eluent to give **6** as colorless oil 190 mg (26% yield) and **7** as colorless oil 230 mg (31% yield).

(1R*,3S*,4S*,5S*)-3-methyl-4-phenylbicyclo[3.2.1]oct-6-en-2-one (6). ^1H NMR (500 MHz, CDCl_3) δ 7.33-7.21 (m, 5H), 6.20 (dd, $J = 5.5, 2.5$ Hz, 1H), 6.17 (dd, $J = 5.5, 2.5$ Hz, 1H), 3.61 (br s, 1H), 3.14 (m, 1H), 2.61 (m, 1H), 2.50-2.45 (m, 1H), 2.20 (d, $J = 11.5$ Hz, 1H), 1.88-1.81 (m, 1H), 1.16 (d, $J = 8.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 215.0, 139.6, 138.3, 135.9, 128.5, 127.7, 126.5, 58.7, 49.6, 44.1, 43.4, 31.9, 18.3; IR (neat) 2937, 1702 (C=O), 1449, 721, 698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}$ $[\text{M}]^+$, required m/z : 212.1196, found m/z : 212.1200.

(3aS*,4S*,5R*,9bS*)-3a,4,5,9b-tetrahydro-4-methyl-3H-cyclopenta[a]naphthalene-5-carbaldehyde (7). ^1H NMR (500 MHz, CDCl_3) δ 9.39 (d, $J = 5.0$ Hz, 1H), 7.37 (d, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 5.87 (m, 1H), 5.74 (m, 1H), 3.98 (m, 1H), 3.18 (dd, $J = 10.0, 5.0$ Hz, 1H), 2.74-2.67 (m, 1H), 2.40-2.29 (m, 2H), 1.95-1.89 (m, 1H), 1.05 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.3, 138.2, 134.6, 130.3, 129.4, 128.8, 128.1, 127.6, 126.0, 59.0, 47.9, 41.8, 37.7, 30.0, 18.9; IR (neat) 2906, 1723 (C=O), 1429, 747 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{16}\text{O}$ $[\text{M}]^+$, required m/z : 212.1196, found m/z : 212.1202.

To a degassed solution of (*R*)-(+)-BINOL (87 mg, 0.30 mmol) in dry dichloromethane (3 mL) was added a 0.15 mL Me₃Al (2.0 M in hexanes, 0.30 mmol), whereupon the solution turned to white suspension under the evolution of CH₄. The solution was stirred for 1 h at room temperature. After the mixture was cooled to -40 °C, 2-phenyl-2-butenal (438 mg, 3.00 mmol) was added dropwise. 10 mins later, precooled cyclopentadiene (951 mg, 15.0 mmol) was added dropwise and gave a yellow suspension. The reaction was then stirred for 20 h at -40 °C. The reaction was quenched by addition of 2 mL saturated NaHCO₃ solution, extracted with ether (2×), and the combined extracts were washed with water and brine, dried over MgSO₄, and concentrated. The crude product was purified by column chromatography on silica gel using 1-2% pentane/diethyl ether as eluent to give **2a** as colorless oil 368 mg (58% yield, 44% ee) and **4a** as colorless oil 184 mg (29% yield, 44% ee).

The enantioselective excess of **2a** was determined by HPLC (Daicel Chiralcel OD-H, hexanes/*i*-PrOH = 99:1, flow rate = 1.0 mL/min) *t*_r = 5.1 min (minor), *t*_r = 7.9 min (major). [*α*]_D = 74.9° (*c* = 2.70, CHCl₃).

The enantioselective excess of **4a** was determined in the presence of the chiral shift reagent Eu(hfc)₃.

XD-III-83-frac36-011704

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-III-83-frac36-011704

INOV-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984138 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FI size 65536

Total time 1 min, 18 sec

XD-IV-40-frac60-DA-022404

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-40-frac60-DA-022404

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984019 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 85536

Total time 1 min, 18 sec

XD-IV-71-frac37to40-033004

Pulse Sequence: szpul

Solvent: CDCl3

Ambient temperature

File: XD-IV-71-frac37to40-033004

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984083 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

2b

XD-IV-71-fraction-033004

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: XD-IV-71-fraction-033004

INOV4-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1: 499.8984016 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-71-fraction-033004

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-71-fraction-033004

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984031 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-VI-62-fr14to16-110604

Pulse Sequence: s2pul1

Solvent: CDCl3

Ambient temperature

File: XD-VI-62-fr14to16-110604

INDVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984083 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-VI-62-fr20to23-110604

Pulse Sequence: s2pul1

Solvent: D2O

Ambient temperature

File: XD-VI-62-fr20to23-110604

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 26.0 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984058 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-VI-76-HDA-111604

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-VI-76-HDA-111604

INOVIA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

ORSERVE H1 499.8384061 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-VI-76-DA-111604

Pulse Sequence: szpu1

Solvent: CDCl₃

Ambient temperature

File: XD-VI-76-DA-111604

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984043 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-20-frac25-020904

Pulse Sequence: szpu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-20-frac25-020904

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 10.000 sec

Pulse 34.6 degrees

Acq. time 1.831 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984122 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 3 min, 58 sec

XD-IV-20-frac45-020904

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-20-frac45-020904

INOVIA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 10.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984022 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 3 min, 58 sec

XD-IV-45-fraction-030204

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

File: XD-IV-45-fraction-030204

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984043 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-45-frac46-030204

Pulse Sequence: s2pul1

Solvent: CDCl3

Ambient temperature

File: XD-IV-45-frac46-030204

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984028 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-45-fraction-030204

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: XD-IV-45-fraction-030204

INOVIA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984019 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

5f

XD-IV-21-HDA-frac11-021604

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-21-HDA-frac11-021604

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984040 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

2g

XD-IV-21-HDA-frac6-021504

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

File: XD-IV-21-HDA-frac6-021504

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984019 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

3g

XD-IV-21-DA-frac20-021504

Pulse Sequence: szpul

Solvent: CDCl3

Ambient temperature

File: XD-IV-21-DA-frac20-021504

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 Repetitions

OBSERVE H1, 499.8984013 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-21-DA-feac12-021504

Pulse Sequence: szpul

Solvent: CDCl3

Ambient temperature

File: XD-IV-21-DA-feac12-021504

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

5g

XD-IV-36-fraction-022204

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-36-fraction-022204

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

32 repetitions

OBSERVE H1 499.8984083 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 2 min, 20 sec

XD-IV-36-frac24-022204

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-36-frac24-022204

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984046 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-51-fraction-031104

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

File: XD-IV-51-fraction-031104

IMOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1: 499.9984046 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-51-ffrac55-031104

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: XD-IV-51-ffrac55-031104
INOV4-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.891 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1: 499.8984025 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 18 sec

XD-IV-94-frac34-042604

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-94-frac34-042604

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984034 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-94-fraction-042604

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: XD-IV-94-fraction-042604

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1 499.8984043 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-94-frac47-042604

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: XD-IV-94-frac47-042604

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1: 499.8984028 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

Pulse Sequence: s2pu1

Solvent: CDCl₃

Ambient temperature
E170: YD-TV-EE-3-453

```
File: XD-IV-65-2-frac17-032304
      INOVA-500  "nmrdata.chem.buffalo.edu"
```

Relax. delay 2.000 sec
Pulse 34.6 decroos

Pulse 34.6 degrees

Acq. time 1.891 sec
Width 10000.0 Hz

Width 10000.0 Hz

16 repetitions
OBSERVED H1 4

OBSERVE H1, 499.8984019 MHZ
DATA PROCESSING

DATA PROCESSING
Line broadening 0.7 Hz

Line broaden
FT size 65536

Total time 1 min, 18 sec

XD-VI-53-103004

Pulse Sequence: s2pul1

Solvent: CDCl3

Ambient temperature

File: XD-VI-53-103004

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

18 repetitions

OBSERVE H1, 499.8984040 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

41

XD-III-72-fraction-010704

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: XD-III-72-fraction-010704

INQVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984028 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-III-72-frac42-010704

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: XD-III-72-frac42-010704

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8384065 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-VI-55-110204

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: XD-VI-55-110204

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984092 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

XD-IV-39-C3-frac62-022704

Pulse Sequence: szpu1

Solvent: CDCl3

Ambient temperature

File: XD-IV-39-C3-frac62-022704

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984077 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FI size 65536

Total time 1 min, 18 sec

XD-VI-71-dimer-111604

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

File: XD-VI-71-dimer-111604

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

18 repetitions

OBSERVE H1, 499.8384061 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec