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Synthetic study of optically active and C_2-symmetric novel ligand, 7,8-bis(benzyloxy)bicyclo[2.2.2]octa-2,5-diene and a tricarbonyliron complex

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The 7,8-bis(benzyloxy)bicyclo[2.2.2]octa-2,5-diene derivatives have been synthesized *via* Diels–Alder reaction of optically active 5,6-bis(benzyloxy)cyclohexa-1,3-diene and dienophiles. The corresponding tricarbonyliron complexes have also been synthesized in enantiomerically pure form.

Introduction

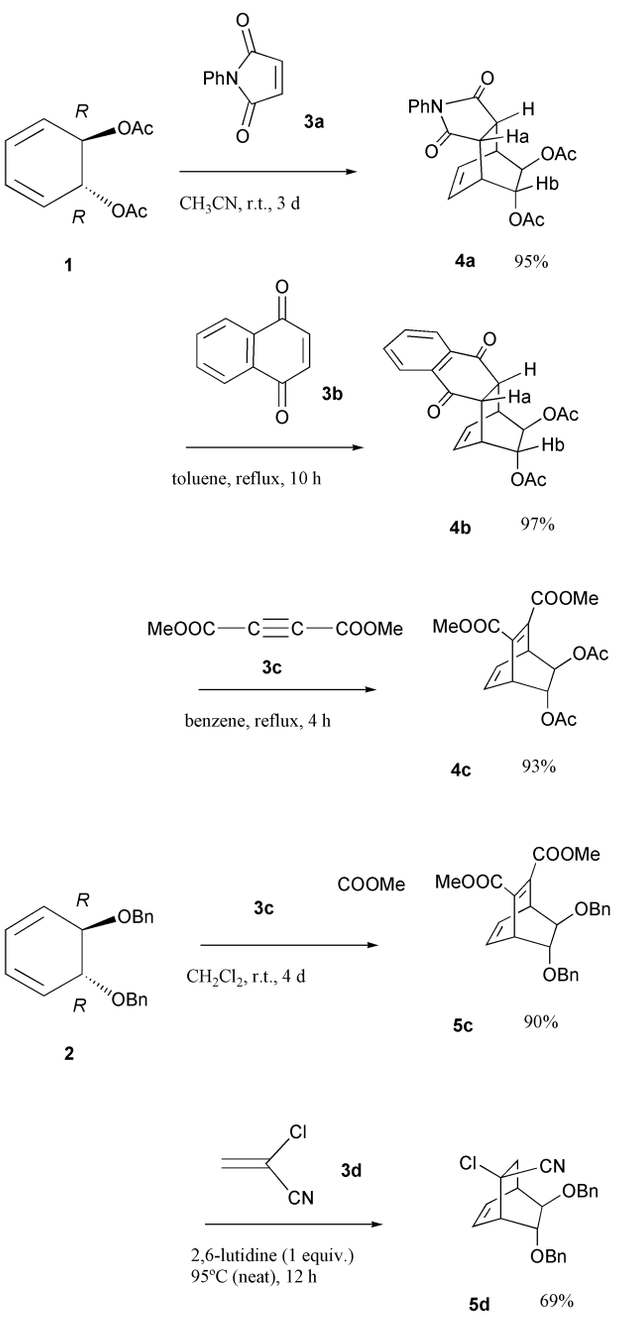
We recently, reported the asymmetric synthesis of both enantiomers of 5,6-bis(benzyloxy)cyclohexa-1,3-diene and the corresponding tricarbonyliron complex[1a] in the course of our studies on the development of asymmetric reaction using a metal catalyst with novel diene compounds as chiral ligands.[1] In this report, we describe the asymmetric synthesis of 5,6-bis(benzyloxy)bicyclo[2.2.2]oct-2-ene and 7,8-bis(benzyloxy)bicyclo[2.2.2]octa-2,5-diene derivatives, and diene-tricarbonyliron complexes. So far, synthetic studies of σ-symmetric bicyclo[2.2.2]octapolyenes have been reported *via* [4 + 2] cycloaddition,[2] however, there are few reports on Diels–Alder reactions of C_2-symmetric optically active cyclic dienes for the synthesis of this framework.

Results and discussion

The Diels–Alder reaction of optically active 5,6-disubstituted cyclohexa-1,3-dienes (**1** and **2**) with several dienophiles (**3a**–**d**) was studied. Reaction of **1** and **3a**,**b** gave [4 + 2] cycloadducts **4a** (95%) and **4b** (97%) as the sole product, respectively. The stereochemistry of the products was determined by the NOEs between Ha and Hb in the ^{1}H–^{1}H NOESY spectra. In these reactions, the selection of diene-faces may be negligible for the stereochemistry of the product, and reactivity might be enhanced by using both faces of diene because of the C_2-symmetry of **1**. The *endo*–*exo* selectivity is the key to determining the stereochemistry, and complete *endo*-selective [4 + 2] cycloaddition was observed in these cases.

The reaction of compounds **1**, **2** and dimethyl acetylenedicarboxylate (**3c**) gave cycloadducts **4c** and **5c** in 93% and 90% yields, respectively. The former required heating conditions, and the latter proceeded in CH_2Cl_2 at room temperature (Scheme 1). The reaction of **2** and **3c** in refluxing benzene gave **5c** in 72% yield. In the reactions of Scheme 1, the dienophile–diene ratios varied between 0.67 and 11, which gave satisfactory yields of products. Among them, the use of a smaller amount of **3b** (0.67 equiv.) was required because the separation of **3b** and product **4b** was difficult.

In the case of the reaction of **2** and 2-chloroacrylonitrile (**3d**), the addition of amine base was required to prevent decomposition of **2** and cycloadduct by acidic species derived from **3d** under heating conditions.[3] In this reaction, cycloadduct **5d** was obtained in 69% yield as the sole product. The structure of **5d** was determined based on further derivatization using (±)-**5d** as follows. Reduction of (±)-**5d** with $LiAlH_4$ afforded an aziridine derivative (±)-**6** (61%) accompanied by an unexpected primary amine (±)-**7** (17%). The structure of (±)-**6** and (±)-**7** was



Scheme 1

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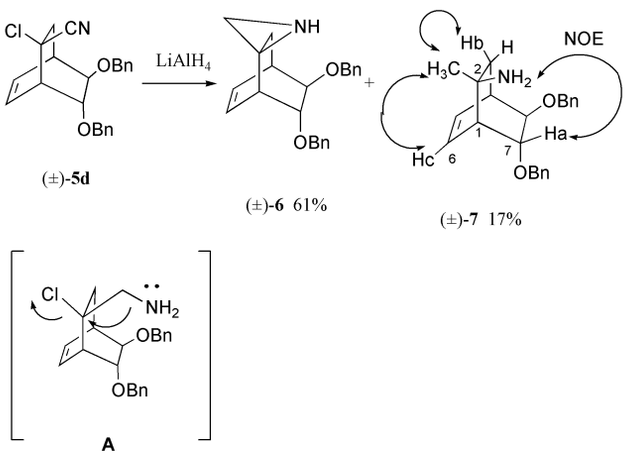
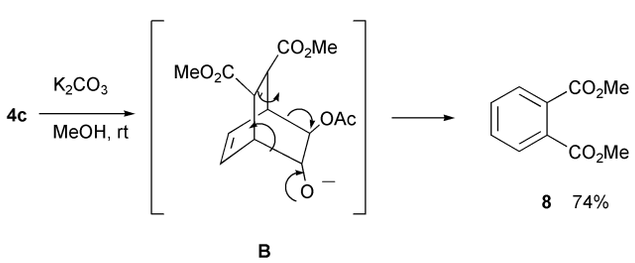
determined based on spectroscopic analyses. In ^{1}H-NMR spectrum of (±)-**6**, CH_2 in the aziridine ring were observed at δ 1.98 (1H, s) and 1.93 (1H, s). In ^{1}H-NMR spectrum of compound (±)-**7**, C_2-Me was observed at δ 1.10 (3H, s), and C_2-Me carbon in ^{13}C-CMR spectrum was observed at δ 31.7 (q). The relative stereochemistry of (±)-**7** was determined to be 1*RS*,2*SR*,4*RS*,7*RS*,8*RS* based on ^{1}H,^{1}H-NOESY spectrum, in which correlations were observed between C7–Ha and C2–NH_2, C2–Me and C3–H_b, C2–Me and C6–H_c as illustrated in Scheme 2. Considering that the reductive aziridine ring cleavage of (±)-**6** might afford (±)-**7**, the configuration at the C2-position of (±)-**7** should be derived from that of (±)-**6**. As a plausible process for the formation of (±)-**6**, $LiAlH_4$ reduction of the nitrile function of (±)-**5d** might afford an aminomethyl intermediate **A**, and further intramolecular S_N2-type substitution might construct (±)-**6**. Based on this consideration, the absolute stereochemistry of the C2-position of optically active **5d** was expected to be *R*. The above results suggest that [4 + 2] cycloaddition of **2** and **3d** proceeded in both complete *exo*-selective and regioselective manner. This *exo*-selectivity might be attributable to the steric factor instead of the secondary orbital effect.



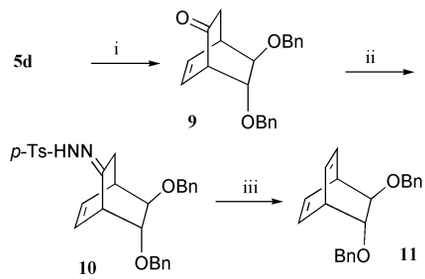
Scheme 2

Next, the solvolysis of acetate function in **4a**–**c** was performed to study the stability and the possibility of derivation of cycloadducts. Treatment of **4a**,**b** with K_2CO_3 in MeOH at room temperature afforded a complex mixture in both cases. Reaction of **4c** under the same conditions did not afford a corresponding diol but dimethyl phthalate **8** in 74% yield. This ring transformation was considered to proceed *via* retro-Diels–Alder reaction starting from the corresponding alkoxide anion **B** as shown in Scheme 3.



Scheme 3

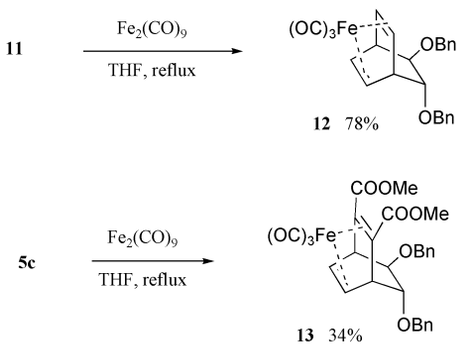
Next, compound **5d** was transformed into C_2-symmetric (7*R*,8*R*)-7,8-bis(benzyloxy)bicyclo[2.2.2]octa-2,5-diene **11** in the sequence of the following reactions. i. Conversion of **5d** into ketone **9** (83%) under basic conditions. ii. Conversion of **9** into the corresponding *p*-tosylhydrazone **10** (94%). iii. Treatment of **10** with a strong base[4] to afford the target molecule **11** (48%) (Scheme 4). Structure of **11** was supported by the following



Scheme 4 *Reagents*: i. KOH, DMSO, H_2O, 83%; ii. *p*-Ts-$NHNH_2$, MeOH, rt, 94%; iii. BuLi, THF, −78 °C, 48%.

spectroscopic analyses. In the ^{1}H-NMR spectrum, two kinds of olefinic protons and two kinds of methine protons were observed, this is attributable to the C_2-symmetric property of **11**, in addition to 11 carbon signals in the ^{13}C-NMR spectrum.

Metal-diene complex formation was studied by using compounds **5c** and **11**. In preliminary studies using diene **11** and several metal species such as $RhCl_3$, $Fe_2(CO)_9$, $Mo(CO)_6$ and $W(CO)_6$, only iron-tricarbonyl complex **12** was obtained in 78% yield under refluxing conditions in THF. In the use of $RhCl_3$ in EtOH, the reaction afforded a complex mixture, and the use of $Mo(CO)_6$ or $W(CO)_6$ afforded the recovery of substrate.[1d,5] The reaction of **5c** and $Fe_2(CO)_9$ gave a corresponding iron-tricarbonyl complex **13** in 34% yield (Scheme 5).[6] The structure of these complexes **12** and **13** was supported by spectroscopic analyses.



Scheme 5

Thus, novel diene compounds such as **4c**, **5c** and **11** have been synthesized. We plan to study further the use of these compounds as a chiral ligand of metal complex. Both enantiomers of optically active ligands were considered to be necessary to study the asymmetric reaction. For this purpose, both enantiomers of optically active compounds in this paper were prepared.

Experimental

IR spectra were measured with a JASCO A-202 and Thermo-Nicolet Avatar 320 KYD spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were measured with a JEOL JNM-GX 270 or Varian Oxford 400 or JNM-GX 500 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. Mass spectra were taken on a JEOL JMD-D-300 610 HS and JEOL JMS-SX/SX-102A spectrometer. Optical rotations were measured on a JASCO DIP-360 polarimeter and are given in 10^{-1} deg cm^2 g^{-1}. For column chromatography, silica gel (Nakarai Tesque, Silica Gel 60, 230–400 mesh) was used. All organic solvent extracts were dried over anhydrous $MgSO_4$.

Diels–Alder reaction of 1, 2 and dienophiles 3a–c

Reaction of 1 and 3a. (*R*,*R*)-5,6-Bisacetoxycyclohexa-1,3-diene **1** (180 mg, 0.9 mmol) and *N*-phenylmaleimide (**3a**, 165 mg, 0.9 mmol) were dissolved in CH_3CN (1 ml) at room

temperature, and the whole was stirred at the same temperature for 3 d. The reaction mixture was diluted with hexane (2 ml) and the resulting precipitates were recrystallized from acetone to afford **4a** (317 mg, 95%) as colorless prisms. Mp 197–198 °C; $[\alpha]_D^{24} = -61.7$ ($c = 1.4$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.49–7.36 (3H, m), 7.19 (2H, dd, $J = 1.65, 8.25$), 6.37–6.25 (2H, m), 4.85 (1H, s), 4.74 (1H, m), 3.48 (2H, d, $J = 2.97$), 3.37 (1H, dd, $J = 2.97, 8.25$), 3.24 (1H, dd, $J = 2.97, 8.25$), 2.13 (3H, s), 2.07 (3H, s); ν_{max}/cm^{-1} (KBr) 3045, 2950, 2920, 1740, 1700, 1490, 1375, 1350, 1220, 1200, 1165, 1050, 1025, 870; *m/z* (FAB) 370 $[M + H]^+$; Anal. Calcd. For $C_{20}H_{19}NO_6$: C, 65.03; H, 5.18; N, 3.79; Found: C, 65.05; H, 5.18; N, 3.79%. *Ent*-**4a**; $[\alpha]_D^{24} = +62.9$ ($c = 1.54$, $CHCl_3$).

Reaction of 1 and 3b. Compound **1** (300 mg, 1.5 mmol) and α-naphthoquinone (**3b**, 160 mg, 1 mmol) were dissolved in toluene (1 ml), and the whole was refluxed for 10 h. After cooling to room temperature, the reaction mixture was diluted with hexane (2 ml), then the resulting precipitate was recrystallized from EtOH to afford **4b** (230 mg, 97% based on **3b**, 65% based on **1**) as colorless prisms. Mp 148–149 °C; $[\alpha]_D^{24} = -52.6$ ($c = 0.76$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 8.04 (2H, dd, $J = 3.3, 5.94$), 7.73 (2H, dd, $J = 3.3, 5.94$), 6.27–6.15 (2H, m), 4.94 (1H, t, $J = 2.31$), 4.71 (1H, m), 3.63 (2H, dd, $J = 2.64, 5.94$), 3.54 (1H, dd, $J = 2.64, 10.23$), 3.38 (1H, dd, $J = 2.64, 10.23$), 2.13 (3H, s), 2.06 (3H, s); ν_{max}/cm^{-1} (KBr) 3040, 2950, 1730, 1670, 1650, 1570, 1355, 1345, 1265, 1215, 1040, 1020, 1000, 725, 700; *m/z* (FAB) 355 ($[M + H]^+$); Anal. Calcd. for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12; Found: C, 67.67; H, 5.15%. *Ent*-**4b**; $[\alpha]_D^{24} = +51.8$ ($c = 1.34$, $CHCl_3$).

Dimethyl (1*R*,4*S*,7*R*,8*R*)-7,8-bisacetoxybicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate 4c

Compound **1** (370 mg, 1.8 mmol) and dimethyl acetylenedicarboxylate **3c** (2.5 ml, 20 mmol) were dissolved in benzene (2 ml) and the whole was refluxed for 4 h. After removal of the solvent *in vacuo*, the residue was purified by silica-gel column chromatography (hexane–AcOEt = 4 : 1) to afford **4c** (563 mg, 93%) as a yellow oil. $[\alpha]_D^{22} = -96.4$ ($c = 0.93$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 6.52–6.45 (2H, m), 4.75 (1H, dd, $J = 1.65, 3.30$), 4.59 (1H, dd, $J = 1.65, 3.30$), 4.21 (2H, ddd, $J = 2.64, 5.28, 10.56$), 3.82 (3H, s), 3.79 (3H, s), 2.05 (3H, s), 2.04 (3H, s); ν_{max}/cm^{-1} (neat) 3070, 3000, 2960, 2850, 1740, 1650, 1430, 1360, 1350, 1250, 1140, 1165, 1070, 1040, 950, 890; *m/z* (FAB) 339 ($[M + H]^+$) [Calcd. For $C_{16}H_{19}O_8$: M + H. 339.108. Found: $(M + H)^+$ 339.109 (FAB)]. *Ent*-**4c**; $[\alpha]_D^{22} = +110.0$ ($c = 1.33$, $CHCl_3$).

Dimethyl (1*R*,4*S*,7*R*,8*R*)-7,8-bis(benzyloxy)bicyclo[2.2.2]-octa-2,5-diene-2,3-dicarboxylate 5c

(*R*,*R*)-5,6-Bis(benzyloxy)cyclohexa-1,3-diene **2** (600 mg, 2 mmol) and **3c** (0.5 ml, 4 mmol) were dissolved in CH_2Cl_2 (2 ml) and the whole was stirred for 4 d at room temperature. After removal of the solvent *in vacuo*, the residue was purified by column chromatography (hexane–AcOEt = 15 : 1) to afford **5c** (764 mg, 88%) as a yellow oil. $[\alpha]_D^{26} = -106.9$ ($c = 1.16$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.36–7.24 (10H, m), 6.46–6.37 (2H, m), 4.64 (1H, d, $J = 11.88$), 4.57 (1H, d, $J = 11.88$), 4.46 (1H, d, $J = 11.88$), 4.43 (1H, d, $J = 11.88$), 4.28 (1H, dd, $J = 2.64, 5.28$), 4.16 (1H, dt, $J = 2.64, 5.28$), 3.77(5) (3H, s), 3.77(1) (3H, s), 3.58 (1H, d, $J = 2.31$), 3.46 (1H, dd, $J = 1.65, 2.97$); ν_{max}/cm^{-1} (neat) 3070, 3000, 2960, 2850, 1740, 1650, 1430, 1360, 1350, 1250, 1140, 1165, 1070, 1040, 950, 890, 810, 760, 720; *m/z* (FAB) 435 ($[M + H]^+$) [Calcd. For $C_{26}H_{27}O_6$: M + H. 435.181 Found: 435.182 $(M + H)^+$ (FAB)]. *Ent*-**5c**; $[\alpha]_D^{26} = +99.3$ ($c = 1.00$, $CHCl_3$).

Reaction of 2 and 3d. A mixture of **2** (600 mg, 2 mmol), 2-chloroacrylonitrile **3d** (0.6 ml, 10 mmol) and 2,6-lutidine (0.12 ml, 2 mmol) was stirred at 95 °C for 12 h without solvent. After removal of **3d** *in vacuo*, the residue was purified by silica-gel column chromatography (hexane–AcOEt = 10 : 1) to afford **5d** (523 mg, 69%) as a yellow oil. $[\alpha]_D^{26} = -45.98$ ($c = 1.1$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.37–7.28 (10H, m), 6.40 (1H, t, $J = 6.93$), 6.12 (1H, t, $J = 6.93$), 4.60–4.42 (4H, m), 3.94 (3H, s), 3.37–3.35 (2H, m), 2.93–2.87 (2H, m), 1.87 (1H, m); ν_{max}/cm^{-1} (neat) 3060, 3030, 2950, 2860, 2240, 1600, 1480, 1445, 1350, 1200, 1080, 920, 730, 690; *m/z* (FAB) 380 ($[M + H]^+$) [Calcd. For $C_{23}H_{21}NO_2Cl$: M − H. 378.126. Found: $(M - H)^+$ 378.127 (FAB)]. *Ent*-**5d**; $[\alpha]_D^{26} = +43.8$ ($c = 1.0$, $CHCl_3$).

$LiAlH_4$ reduction of (±)-5d. A solution of (±)-**5d** (760 mg, 2 mmol) in THF (10 ml) was added dropwise to the suspension of $LiAlH_4$ (320 mg, 4 mmol) in THF (10 ml) under an Ar atmosphere at 0 °C. The reaction mixture was refluxed for 11 h. The reaction was quenched by addition of 15% aqueous sodium hydroxide. The resulting gel was filtered off and washed with THF. The combined filtrates were dried, and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate–methanol = 10 : 1) to afford (±)-**6** (163 mg, 23%) and (±)-**7** (232 mg, 33%).

(±)-**6**; 23% yield; a colorless oil; δ_H (270 MHz, $CDCl_3$) 7.35–7.23 (10H, m), 6.34–6.24 (2H, m), 4.61–4.44 (4H, m), 4.02 (1H, s), 3.49 (1H, s), 2.91 (1H, t, $J = 2.64$), 2.08 (1H, t, $J = 2.64$), 1.94 (1H, dd, $J = 2.0, 13.0$), 1.68, 1.63 (1H, each, s), 1.54 (1H, d, $J = 13.0$); ν_{max}/cm^{-1} (neat) 3300, 3060, 3032, 2946, 2866, 1496, 1454, 1361, 1205, 1097, 1074, 1028, 908, 780, 732, 698; *m/z* (FAB) 348 ($[M + H]^+$), 362 ($[M + Na]^+$); [Calcd. For $C_{23}H_{26}NO_2$: M + H. 348.196. Found: $(M+H)^+$ 348.195 (FAB)].

(±)-**7**; 33% yield; a colorless oil; δ_H (500 MHz, $CDCl_3$) 7.35–7.23 (10H, m), 6.25 (1H, t, $J = 6.87$), 6.15 (1H, t, $J = 6.87$), 4.58 (1H, d, $J = 11.9$), 4.53 (1H, d, $J = 11.9$), 4.49 (1H, d, $J = 11.9$), 4.45 (1H, d, $J = 11.9$), 4.03 (1H, s), 3.43 (1H, t, $J = 1.83$), 2.88 (1H, dd, $J = 2.97, 6.41$), 2.50 (1H, dd, $J = 2.74, 6.4$), 1.77 (1H, dd, $J = 2.28, 13.04$), 1.69 (2H, s), 1.21 (1H, dq, $J = 1.61, 13.05$), 1.10 (3H, s); δ_C (125 MHz, $CDCl_3$) 138.4 (s), 138.2 (s), 133.3 (d), 129.6 (d), 128.1 (d), 128.0 (d), 127.5 (d), 127.4 (d), 127.3 (d), 127.2 (d), 81.7 (d), 80.1 (d), 70.4 (t), 70.0 (t), 52.4 (s), 48.1 (d), 35.5 (d), 35.4 (t), 31.7 (q); ν_{max}/cm^{-1} (neat) 3366, 3289, 3050, 3030, 2940, 2866, 1586, 1496, 1453, 1364, 1205, 1094, 1074, 1028, 909, 734, 697; *m/z* (FAB) 350 ($[M + H]^+$) [Calcd. For $C_{23}H_{28}NO_2$: M + H. 350.212. Found: $(M + H)^+$ 350.212 (FAB)].

Solvolysis of 4c. K_2CO_3 (10 mg) was added to a stirred solution of **4c** (162 mg, 0.48 mmol) in MeOH (1 ml) at room temperature. After being stirred for 2 h at room temperature, water was added to the reaction mixture. The whole was extracted with ethyl acetate. The extracts were combined, dried over $MgSO_4$ and condensed *in vacuo*. The obtained residue was purified by column chromatography (hexane–AcOEt = 2 : 1) to give dimethyl phthalate **8** (70 mg, 74%).

(1*S*,4*R*,7*R*,8*R*)-7,8-Bis(benzyloxy)bicyclo[2.2.2]oct-5-en-2-one 9

Aqueous solution of 50% KOH (2 ml) was added to a stirred solution of **5d** (1.87 g, 4.9 mmol) in DMSO (5 ml) at room temperature. After being stirred for 2 d at the same temperature, the whole was poured into water (80 ml) and extracted with ether. The combined extracts were washed with brine and dried. After removal of the solvent *in vacuo*, the residue was purified by silica-gel column chromatography (hexane–AcOEt = 3 : 1) to afford **9** (1.36 g, 83%) as a yellow oil. $[\alpha]_D^{26} = +154.9$ ($c = 1.00$, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 7.38–7.26 (10H, m), 6.45 (1H, dt, $J = 1.14, 6.87$), 6.15 (1H, t, $J = 6.87$), 4.57 (2H, dd, $J = 2.75, 11.9$), 4.48 (2H, dd, $J = 3.2, 11.9$), 3.79 (1H, s), 3.69 (1H, m), 3.46 (1H, d, $J = 5.72$), 3.17 (1H, m), 2.44 (1H, dd, $J = 1.83, 18.58$), 1.96 (1H, ddd, $J = 2.06, 3.21, 18.54$); ν_{max}/cm^{-1} (neat) 3055, 3025, 2860, 1720, 1605, 1490, 1445, 1395, 1350, 1305,

1200, 1175, 1080, 1020; *m/z* (FAB) 335 ([M + H]$^+$) [Calcd. For $C_{22}H_{23}O_3$: M + H. 335.165 Found: (M + H)$^+$ 335.162 (FAB)]. *Ent*-**9**; $[a]_D^{26} = -147.6$ ($c = 1.01$, $CHCl_3$).

p-Tosylhydrazone of (1*S*,4*R*,7*R*,8*R*)-7,8-bis(benzyloxy)bicyclo-[2.2.2]oct-5-en-2-one 10

A mixed solution of **9** (250 mg, 0.75 mmol) and *p*-tosylhydrazine (140 mg, 0.75 mmol) in MeOH (2 ml) was stirred at room temperature for 1 d. After removal of the solvent *in vacuo*, the residue was purified by silica-gel column chromatography (hexane–AcOEt = 2 : 1) to afford **10** (355 mg, 94%) as colorless solids. $[a]_D^{24} = +34.7$ ($c = 1.03$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.81 (2H, d, $J = 8.25$), 7.37–7.22 (12H, m), 6.29 (1H, t, $J = 6.6$), 6.17 (1H, t, $J = 6.6$), 4.56–4.36 (4H, m), 3.59 (1H, d, $J = 4.95$), 3.54 (1H, m), 3.48 (1H, m), 3.10 (1H, m), 2.40 (3H, s), 2.34 (1H, dd, $J = 2.31$, 16.82), 1.78 (1H, dd, $J = 1.64$, 13.86); ν_{max}/cm^{-1} (KBr) 3190, 3025, 2860, 1730, 1650, 1595, 1490, 1450, 1385, 1355, 1320, 1250, 1150, 1080, 1010, 915, 810, 725, 680; *m/z* (FAB) 503 ([M + H]$^+$) [Calcd. For $C_{29}H_{31}N_2O_4S$: M + H. 503.201 Found: (M + H)$^+$ 503.202 (FAB)]. *Ent*-**10**; $[a]_D^{24} = -31.8$ ($c = 1.02$, $CHCl_3$).

(7*R*,8*R*)-7,8-Bis(benzyloxy)bicyclo[2.2.2]octa-2,5-diene 11

To a solution of **10** (500 mg, 1 mmol) in THF (40 ml) was added a 15% solution of butyllithium in hexane (12.6 ml, 4 mmol) at −78 °C under an Ar atmosphere. The whole was stirred at −78 °C for 20 min, then allowed to warm to room temperature for 2 h. The reaction was quenched by the addition of MeOH (2 ml) and saturated aqueous NH_4Cl. After removal of organic solvent *in vacuo*, the aqueous layer was extracted with CH_2Cl_2. The extracts were dried and condensed *in vacuo*. The obtained residue was purified by silica-gel column chromatography (hexane–AcOEt = 5 : 1) to give **11** (154 mg, 48%) as a yellow oil. $[a]_D^{27} = -96.1$ ($c = 1.031$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.37–7.24 (10H, m), 6.43–6.31 (4H, m), 4.52 (4H, dd, $J = 12.21$, 27.38), 3.81–3.76 (2H, m), 3.46 (1H, t, $J = 1.65$); δ_C (100 MHz, $CDCl_3$) 138.3 (s), 133.8 (d), 131.5 (d), 128.2 (d), 127.6 (d), 127.4 (d), 83.9 (d), 70.8 (t), 41.4 (d); ν_{max}/cm^{-1} (neat) 3070, 3045, 2980, 2870, 1590, 1495, 1450, 1100, 1030, 740, 705, 670; *m/z* (FAB) 317 ([M − H]$^+$) [Calcd. For $C_{22}H_{21}O_2$: M − H. 317.158 Found: (M − H)$^+$ 317.162 (FAB)]. *Ent*-**11**; $[a]_D^{27} = +94.1$ ($c = 1.0$, $CHCl_3$).

(7*R*,8*R*)-7,8-Bis(benzyloxy)bicyclo[2.2.2]octa-2,5-dienyltricarbonyliron 12

Iron nonacarbonyl (520 mg, 1.45 mmol) was added to a solution of **11** (210 mg, 0.66 mmol) in THF (15 ml) under an Ar atmosphere at room temperature. The whole was refluxed for 1 h. After cooling, the whole was passed though short silica-gel column with ether. The ether eluent was concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (hexane–ethyl acetate = 10 : 1) to give **12** (236 mg, 78%) as a yellow oil. $[a]_D^{25} = -67.0$ ($c = 1.0$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.37–7.28 (10H, m), 4.52 (2H, d, $J = 11.9$), 4.43 (2H, d, $J = 11.9$), 3.81–3.76 (2H, m), 3.14–3.09 (4H, m), 3.00–2.95 (2H, m); ν_{max} /cm^{-1} (neat) 3063 (m), 3030 (m), 2967 (m), 2867 (s), 2025 (s), 1944 (vs), 1497 (m), 1454 (m), 1357 (m), 1211 (m), 1093 (s), 1027 (m), 737 (m), 698 (s); *m/z* (FAB) 458 ([M]$^+$) [Calcd. For $C_{25}H_{22}O_5Fe$: M. 458.082 Found: M$^+$ 458.083 (FAB)]. *Ent*-**12**; $[a]_D^{25} = +61.0$ ($c = 1.3$, $CHCl_3$).

(1*R*,4*S*,7*R*,8*R*)-7,8-Bis(benzyloxy)-2,3-bis(methoxycarbonyl)-bicyclo[2.2.2]octa-2,5-dienyltricarbonyliron 13

A similar procedure described to prepare **12** using iron nonacarbonyl (1.5 g, 4 mmol) and **5c** (870 mg, 2 mmol) in 4 h reaction afforded **13** (390 mg, 34%) as a yellow oil. $[a]_D^{26} = +20.6$ ($c = 0.88$, $CHCl_3$); δ_H (270 MHz, $CDCl_3$) 7.37–7.23 (10H, m), 4.65 (1H, d, $J = 12.2$), 4.51 (1H, q, $J = 3.3$), 4.42 (2H, dd, $J = 2.64$, 12.21), 4.02 (1H, m), 3.83 (2H, dt, $J = 0.99$, 5.61), 3.75 (1H, m), 3.72 (3H, s), 3.69 (1H, m), 3.66 (3H, m), 3.61 (1H, t, $J = 2.64$), 3.11 (1H, dd, $J = 1.98$, 2.97); ν_{max} /cm^{-1} (neat) 3030 (w), 2950 (m), 2867 (w), 2051 (s), 1967 (vs), 1708 (s), 1496 (w), 1454 (m), 1436 (m), 1401 (m), 1343 (m), 1306 (m), 1235 (s), 1092 (s), 738 (m), 698 (m), 676 (m); *m/z* (FAB) 575 ([M + H]$^+$) [Calcd. For $C_{29}H_{27}O_9Fe$: M + H. 575.101 Found: (M + H)$^+$ 575.099 (FAB)]. *Ent*-**13**; $[a]_D^{26} = -19.5$ ($c = 0.88$, $CHCl_3$).

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