Supporting Information for:

Addition of Diethylzinc to Dicobalt Hexacarbonyl Complexes of -Acetylenic Aldehydes with Virtually Complete Enantioselectivity. A Formal Synthesis of (+)-Incrustoporin.

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General: All reactions were conducted under nitrogen or argon atmosphere. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Unity-300 spectrometer. ^{1}H and ^{13}C spectra were referenced relative to residual solvent peaks. In some Alkyne dicobalt complexes the carbon signals corresponding to the cluster carbons do not appear in the ^{13}C spectra and have been omitted. Infrared (IR) spectra were recorded on a Nicolette 510 FT spectrometer. High Resolution Mass Spectroscopy (HRMS) were conducted at "Unidade de Espectrometría de Masas de la Universidade de Santiago de Compostela". All anhydrous solvents were distilled under nitrogen, THF was distilled from sodium benzophenone ketyl, toluene was distilled from molten sodium and methylene chloride was distilled from CaH_2. Silica gel used for filtration and flash chromatography of cobalt complexes was previously washed through with Et_2O. Phenylpropynal and 2-octynal were obtained from commercial sources.

Dicobalthexacarbonyl complex of phenylpropynal, 7a.

Procedure A: To a solution of freshly distilled phenylpropynal (1.85 mL, 15.17 mmol) in toluene (60 mL) under nitrogen was added solid dicobaltoctacarbonyl (5.70 g, 16.68 mmol). The reaction mixture was stirred at room temperature until CO evolution ceased. Solvent removal in vacuo and column chromatography (SiO_2, hexane/AcOEt, 2%) provided 6.11 g (97%) of **7a** as a garnet solid.

R_f (SiO_2, hexane/AcOEt, 5:1): 0.59.

Mp: 48 ^{0}C.

IR (KBr): $_{max}$= 2361, 2101, 2064, 2029, 1669, 1559, 1456, 1070, 798 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6); 6.94-6.96 (m, 3H), 7.48 (d, *J*= 3.6 Hz, 2H), 10.12 (s, 1H) ppm.

^{13}C-RMN (75 MHz, C_6D_6); 129.7 (CH), 130.0 (CH), 130.5 (CH), 190.6 (CHO), 198.8 (broad, CO) ppm.

HRMS (FAB+): Calcd. for $C_{15}H_6Co_2O_7$ 415.8778, found 415.8764.

Dicobalthexacarbonyl complex of 2-octynal, 7b.

Procedure A was followed, **7b** was obtained in 92% yield as a garnet oil.

R_f (SiO_2, hexane/AcOEt, 5:1): 0.65.

IR (NaCl); $_{max}$= 2910, 2880, 2815, 2065, 2000, 1645, 1560, 1440 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6): 0.82 (s, 3H), 0.96-1.10 (m, 2H), 1.29 (s, 2H), 1.38 (s, 2H), 2.44 (s, 2H), 9.95 (s, 1H, CHO) ppm.

^{13}C-RMN (75 MHz, C_6D_6): 13.9 (CH_3), 22.5 (CH_3*C*H_2), 31.5 (*C*H_2CC), 31.8 (CH_2), 34.1 (CH_2), 38.5 (C*C*CHO), 60.0 (n-Pent*C*C), 189.4 (CHO), 199.0 (broad, CO) ppm.

HRMS (FAB+): Calcd. for $C_{14}H_{12}Co_2O_7$–H 408.9169, found 408.9158.

Dicobalthexacarbonyl complex of 4,4-dimethyl-2-pentynal, 7c.

Procedure B:[1] To a solution of *tert*-butylacetylene (488 L, 4 mmol) in THF (1mL) was added Ethylmagensium bromide 1.0M (4.8 mL, 4.8 mmol) at 0 ºC. The reaction was allowed to reach room temperature and stirred for 1h. Next, the resulting mixture was transferred via canula to a cooled (-30 ºC) solution of DMF (0.92 mL, 12.0 mmol) in THF (0.92 mL). The reaction temperature was raised to 25 ºC (1h) and then to 35 ºC (30 min). Following, the mixture was poured over H_2SO_4 5% (15 mL) and extracted with ether (15 mL). The aqueous layer was stirred overnight with ether (15 mL) and a catalytic amount of hydroquinone. Next day, the aqueous layer was extracted once more with ether (10 mL). Organic layers were combined and dried (MgSO4), and the solvent removed in vacuo. The resulting oily crude was solved in toluene 10 mL and dicobaltoctacarbonyl (1.50 g, 4.4 mmol) was added and stirred at room temperature. Formation of the alkyne dicobalt complex was monitored by TLC (30 min). Solvent removal in vacuo and flash chromatography (SiO_2, hexane/AcOEt, 1%) afforded 648 mg (41%) of **7c** as garnet oil.

R_f (SiO_2, hexane/AcOEt, 30%): 0.76.

IR (KBr); $_{max}$= 2971, 2022, 1671, 1362, 1231, 517 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6): 1.01 (s, 9H, CH_3), 9.96 (s, 1H, CHO) ppm.

^{13}C-RMN (75 MHz, C_6D_6): 32.6 (CH_3), 36.3 (C_q), 189.5 (CHO) ppm.

HRMS (FAB+): Calcd. for $C_{13}H_{10}Co_2O_7$–CO 367.9141, found 367.9148.

Dicobalthexacarbonyl complex of 1-cyclohexenylpropynal, 7d.

Procedure B was followed, **7d** was obtained in 47% yield as garnet oil.

R_f (SiO_2, hexane/AcOEt, 5:1): 0.49.

IR (film); $_{max}$= 2980, 2810, 2780, 2050, 2000, 1640, 1540, 1155, 630 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6): 1.27 (s, 2H), 1.37 (s, 2H), 1.69 (s, 2H), 2.10 (s, 2H,), 6.21 (s, 1H), 10.08 (s, 1H, CHO) ppm.

^{13}C-RMN (75 MHz, C_6D_6): 22.4 (CH_2), 23.4 (CH_2), 26.9 (CH_2), 30.9 (CH_2), 39.1 (CHOC*C*), 60.6 (CHO*C*C), 133.3 (CH), 134.1 (C_q), 190.4 (CHO), 199.2 (broad, CO) ppm.

HRMS (FAB+): Calcd. for $C_{15}H_{10}Co_2O_7$ 419.9091, found 419.9059.

Dicobalthexacarbonyl complex of *p*-tolylpropynal, 7e.

Procedure B was followed, **7e** was obtained in 89% yield as a garnet crystalline solid.

R_f (SiO_2, hexane/AcOEt, 9:1): 0.50.

Mp: 51 ^{0}C.

IR (KBr); $_{max}$= 2101, 2064, 2031, 1669, 818, 712, 513 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6); 1.94 (s, 3H), 6.82 (d, *J*= 7 Hz, 2H), 7.45 (d, *J*= 7.2 Hz, 2H), 10.16 (s, 1H, CHO) ppm.

^{13}C-RMN (75 MHz, C_6D_6); 21.4 (CH_3), 130.1 (CH), 130.4 (CH) 133.7 (C_q), 139.7 (C_q), 190.2 (CHO), 198.5 (broad, CO) ppm.

HRMS (FAB+): Calcd. for $C_{16}H_8Co_2O_7$+H 430.9012, found 430.9025.

Ethylation reaction; **typical experimental procedure**: Diethylzinc 1.0M in hexanes (1.0 mL, 1.0 mmol) was added to a solution of (*R*)-2-piperidino-1,1,2-triphenylethanol (**4**) (36 mg, 0.1 mmol) in toluene (1.0 mL) under nitrogen. The resulting mixture was stirred at room temperature for 20 min and then cooled at -10 ºC for 10 min. At this point, a solution of the corresponding complex aldehyde **7b** (205 mg, 0.5 mmol) in toluene (2 mL) is added drop wise via canula. The reaction was allowed to proceed for 4h at -10 ºC and then quenched by the addition of 0.1M HCl solution (10 mL). The two phase mixture is poured over hexane (20 mL) and the organic layer washed twice with 0.1M

HCl (2 x 10 mL), once with saturated $NaHCO_3$ (10 mL) and dried ($MgSO_4$). Solvent removal under vacuum afforded 187 mg of **8b** (98% ee) as a garnet oil. ^{1}H NMR analysis showed conv. 96%, yield being 82%. In most cases the resulting complexes could be utilized with no further purification. For characterization purposes they were purified by column chromatography (SiO_2, hexane/AcOEt).

Dicobalt hexacarbonyl complex of (*S*)-1-phenyl-pent-1-yn-3-ol, 8a.

R_f (SiO_2, hexane/AcOEt, 5:1): 0.44.

IR (KBr); $_{max}$= 3450 (broad, OH), 2975, 2925, 2100, 2060, 2020, 1655, 1600, 1440 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6): 0.84 (t, *J*= 7.3 Hz, 3H, CH_3), 1.52 (d, *J*= 5.1 Hz, 2H, CH_2), 4.53-4.57 (m, 1H, C*H*OH), 6.97-7.16 (m, 3H), 7.56 (d, *J*= 7.8 Hz, 2H) ppm.

^{13}C-RMN (75 MHz, C_6D_6): 11.0 (CH_3), 33.1 (CH_2), 73.9 (CH), 128.1 (CH), 129.1 (CH), 131.5 (CH), 138.0 (CH), 199.9 (broad, CO) ppm.

HRMS (FAB+): Calcd. for $C_{15}H_6Co_2O_7$ 4415.8778, found 415.8764.

HPLC: CHIRALCEL-OD Column. Hexane/isopropanol 97:3, 0.5 mL/min, = 254 nm, t_S= 11.4, t_R= 12.8 min

Dicobalthexacarbonyl complex of (*S*)-dec-4-yn-3-ol, 8b.

R_f (SiO_2, hexane/AcOEt, 5:1): 0.44.

IR (film); $_{max}$= 3478 (broad, OH), 2934, 2089, 2047, 2016, 1601, 1462 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6): 0.84-0.88 (m, 7H, $CH_3CH_2CH_2$), 1.17-1.21 (m, 4H, CH_2), 1.36 (d, *J*= 5.7 Hz, 1H, OH), 1.47-1.59 (m, 3H, C*H*$_3$), 2.55-2.61 (m, 2H, C*H*$_2$$CH_3$), 4.29-4.33 (m, 1H, C*H*OH) ppm.

^{13}C-RMN (75 MHz, C_6D_6): 10.9 (CH_3), 14.0 (CH_3), 22.6 (*C*H$_2$), 31.7 (CH_2), 31.8 (CH_2), 33.0 (CH_2), 33.8 (CH_2), 73.7 (CH), 99.1 (C*C*CHOH), 102.4 (n-Pent*C*C), 200.5 (broad, CO) ppm.

HRMS (FAB+): Calcd. for $C_{17}H_{12}Co_2O_7$ –CO 417.9298, found 417.9293.

HPLC: CHIRALCEL-OD Column. Hexane/isopropanol 99:1, 0.5 mL/min, = 254 nm, t_S = 9.1, t_R= 11.1 min.

Dicobalthexacarbonyl complex of (*S*)-6,6-dimethylhept-4-yn-3-ol, 8c.

R_f (SiO_2, hexane/AcOEt, 30%): 0.76.

IR (film); $_{max}$= 3480 (broad, OH), 2975, 2920, 2880, 2060, 2000, 1860, 1590, 1460 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6); 0.99 (t, *J*= 11 Hz, 3H, CH_3), 1.22 (s, 9H, CH_3), 1.66 (q, *J*= 11 Hz, 2H, CH_2), 4.30 (s, 1H, C*H*OH) ppm.

^{13}C-RMN (75 MHz, C_6D_6); 11.8 (CH_3), 33.2 ($3CH_3$), 34.0 (CH_2), 36.8 (C_q), 74.0 (CHOH), 201.4 (broad, CO) ppm.

HPLC: CHIRALCEL-OD Column. Hexane/isopropanol 98:2, 0.5 mL/min, = 254 nm, t_S= 11.0, t_R= 12.1 min.

Dicobalthexacarbonyl complex of (*S*)-1-(cyclohex-1-enyl)-pent-1-yn-3-ol, 8d.

R_f (SiO_2, hexane/AcOEt, 5:1): 0.58.

IR (film): $_{max}$= 3434 (broad, OH), 2933, 2089, 2047, 2018, 1591, 1451, 422 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6); 0.40 (broad s, 1H, OH), 0.87 (t, *J*= 7.2 Hz, 3H, CH_3), 1.31-1.50 (m, 6H, CH_2), 1.80-1.82 (m, 2H, CH_2 ethyl), 2.21 (broad s, 2H, CH_2), 4.42-4.48 (m, 1H, C*H*OH), 6.16 (broad s, 1H) ppm.

^{13}C-RMN (75 MHz, C_6D_6): 10.9 (CH_3), 22.0 (CH_2), 23.1 (CH_2), 26.4 (CH_2) 34.0 (CH_2), 30.5 (CH_2), 73.9 (CH), 130.4 (CH) ppm.

HRMS (FAB+): Calcd. for $C_{17}H_{16}Co_2O_7$ 449.9560, found 449.9560.

HPLC: CHIRALCEL-OD Column. Hexane/isopropanol 97:3, 0.5 mL/min, = 254 nm, t_S= 9.1, t_R = 10.1 min.

Dicobalhexacarbonyl complex of (*S*)-1-*p*-tolyl-pent-1-yn-3-ol, 8e.

R_f (SiO_2, hexane/AcOEt, 5:1): 0.53.

IR (KBr); $_{max}$= 3477 (broad, OH), 2927, 2089, 2051, 2020 (CO), 1659, 1601, 1497, 426 cm^{-1}.

^{1}H-RMN (300 MHz, C_6D_6); 0.85-0.90 (m, 3H, CH_3), 1.61 (d, *J*= 5 Hz, 2H, CH_2), 2.00 (s, 3H, CH_3 tolyl), 4.57-4.62 (m, 1H, C*H*OH), 6.87 (d, *J*= 8 Hz, 2H), 7.51 (d, *J*= 7.8 Hz, 2H) ppm.

^{13}C-RMN (75 MHz, C_6D_6):   11.1 (CH_3), 21.21 (CH_3 tolyl), 33.2 (CH_2), 74.1 (CH), 91.7 (Ar*C*C), 91.7 (C*C*CHOH), 129.8 (C_q), 130.0 (CH), 134.9 (C_q), 138.3 (CH), 200.1 (broad, CO) ppm.
HRMS (FAB+): Calcd. for $C_{18}H_{14}Co_2O_7$ –CO 431.9454, found 431.9456.
HPLC: CHIRALCEL-OD Column. Hexane/isopropanol 97:3, 0.5 mL/min, = 254 nm, t_S= 9.7, t_R= 11.2 min.

(*S*)-1-p-Tolylpent-1-yn-3-ol[2], 2f.

A solution of **8e** (164 mg, .35 mmol) and ceric ammonium nitrate (0.78 g, 1.4 mmol) in anhydrous methanol (4.5 mL) was stirred under nitrogen for 30 min. The reaction was quenched by addition of sat. NaCl solution. Extraction with hexane (3x15 mL), and solvent removal afforded 62 mg of crude alcohol. Purification by flash chromatography (SiO_2, hexqne/AcOEt, 2%) yielded 54 mg (87%, 99% ee) of **2f** as a colorless oil.
^{1}H-RMN (300 MHz, C_6D_6);   1.10 (t, *J*= 9 Hz, 3H), 1.84 (m, 2H), 2.37 (s, 3H), 4.57 (s, 1H), 7.12-7.15 (d, *J*= 9 Hz, 2H), 7.33-7.36 (d, *J*= 9 Hz, 2H) ppm.
HPLC: CHIRALCEL-OD Column. Hexane/isopropanol 90:10, 0.5 mL/min, = 254 nm, t_S= 18.8, t_R= 31.7 min.

References:

[1] Jones, E. R. H.; Skattebol, L.; Whiting, M. C. *J. Chem. Soc.* **1958**, 1054-1059.
[2] Rossi, R.; Bellina, F.; Biagetti, M.; Mannina, L. *Tetrahedron: Asymmetry* **1999**, *10*, 1163-1172.