Supporting Information

Preparation of Highly Substituted Tetrahydropyrans via a Metal Assisted [4+2] Dipolar Cycloaddition Reaction


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Experimental section

General Information. High resolution mass spectroscopy was carried out on a Jeol SX 102 machine, using fast atom bombardment (FAB+) ionisation technique. Nuclear magnetic resonance spectroscopy was carried out using a Brucker DPX 400 instrument. The spectra were calibrated where possible to the signals of tetramethylsilane or the small quantity of CHCl₃ present in CDCl₃. Where possible, coupling constants (J) are shown denoting the multiplicity as a singlet (s), doublet (d), triplet (t), quarter (q), multiplet (m). The size of the coupling constant is given in Hertz (Hz). Fourier transformation Infra Red spectroscopy was recorded using a Paragon 1000 Perkin Elmer FT-IR spectrophotometer in the range of 3500-600 cm⁻¹ following a standard background correction. Flash silica column chromatography was used as a standard purification procedure using Fluka Kiesel gel 60, 0.04-0.063 mm particle size. Thin layer chromatography was used where possible as a standard procedure for monitoring the course and rate of a given reaction. TLC plates used were Merck aluminium backed sheets with Kiesel gel 60 F₂₅₄ silica coating. DCM was distilled over CaH₂ for anhydrous reactions. Petrol was distilled collecting the fraction distilling below 60 °C. THF was dried over sodium/benzophenone and freshly distilled before use. Diethyl ether was purchased from Fischer Scientific (99+ %) and used without purification. Ethyl acetate was distilled over CaCl₂ for general use. Dicobalt octacarbonyl was purchased from Strem (stabilised by 1-5% hexane) and used without any further purification. Anhydrous reactions were carried out in oven-dried glassware and under an atmosphere of nitrogen. All metal carbonyl complexes were stored under a nitrogen atmosphere and kept at –18 °C in a freezer.

Butyl-3-hydroxy-5-phenylpent-4-ynoate (3)
Butyl lithium (26.1 mL, 2.5 M solution, 65.2 mmol, 1.1 eq) was added dropwise to a solution of diisopropyl amine (9.1 mL, 6.56 g, 65.2 mmol, 1.1 eq) in THF (90 mL) at 0°C. The reaction mixture was stirred for 30 minutes and 2-butylation (9.6 mL, 8.26 g, 71.1 mmol) was added at −78°C. The reaction mixture was stirred one more hour and a solution of 3-phenylpropionyaldehyde (7.62 g, 58.6 mmol) in THF (20 mL) was slowly added. After 30 minutes, the reaction was quenched with a solution of saturated ammonium chloride (25 mL). Most of the organic solvents were evaporated in vacuo. The residue was taken up in ethyl acetate (30 mL) and washed with water (30 mL). The aqueous layer was extracted with ethyl acetate (2 × 15 mL). The organic extracts were combined and dried over magnesium sulfate. Evaporation of the solvent afforded the desired compound in 99% yield (14.42 g, 58.5 mmol) as a yellow oil; Rf (15% EtOAc/petrol) 0.42; νmax (film)/cm⁻¹ 1733 (C=O), 2234 (C≡C), 2931 (ArC–H), 2978 (ArC–H) and 3444 (OH); δH (400 MHz; CDCl₃) 1.49 (9H, s, C₃H₉), 2.61 (1H, d, J 6.4 Hz, CH₂), 2.76 (1H, d, J 5.2 Hz, CH₂), 3.35 (1H, d, J 6.4 Hz, OH), 4.93 (1H, dt, J 5.2, 6.4 Hz, CHO), 7.27-7.34 (3H, m, ArC–H) and 7.40-7.45 (2H, m, ArC–H); δC (100 MHz; CDCl₃) 29 (3C₃H₉), 42.9 (CH₂), 59.5 (CH), 81.5 (OC(CH₃)₃), 84.8 (C≡C), 88.2 (C=C), 122.4 (ArC), 128.3 (2ArC), 128.5 (2ArC) and 131.7 (1ArC) and 170.8 (C=O); HRMS (EI) (M⁺), found 247.1339, C₁₅H₁₉O₃ requires 247.1334 (+1.9 ppm); m/z 247 (10%), 191 (29%), 173 (100%), 131 (44%) and 57 (59%).

5-Phenylpent-4-yne-1,3-diol (4)

Lithium borohydride (71.0 mL, 142.0 mmol, 2.0 M solution, 2.5 eq) was added over an hour to a solution of 2-butylation-3-hydroxy-5-phenylpent-4-yne (14.09 g, 57.2 mmol) in THF (200 mL). Methanol (46.3 mL, 1.1 mol, 20 eq) was then added via a syringe pump over an hour at 0°C. The reaction mixture was allowed to stir at room temperature for a further 30 min. Ice cold water (10 mL) was added and the resulting mixture was extracted from ethyl acetate (3 × 30 mL). The combined organic layers were dried over magnesium sulfate to give the title compound in 99% yield (10.04 g, 57.0 mmol) as a yellow oil; Rf (15% EtOAc/petrol) 0.13; νmax (film)/cm⁻¹ 1049 (C=O), 2230 (C=C), 2886 (ArC–H), 2953 (ArC–H) and 3341 (OH); δH (400 MHz; CDCl₃) 1.92-2.09 (2H,
m, CHCH₂), 2.33 (1H, broad s, OH), 2.99 (1H, broad s, OH), 3.85 (1H, ddd, J 4.0, 6.4, 10.8 Hz, CHHOH), 4.00 (1H, ddd, J 4.0, 7.6, 10.8 Hz, CHHOH), 4.81 (1H, dd, J 4.4, 6.4 Hz CHOH), 7.16-7.29 (3H, ArCH) and 7.31-7.42 (2H, m, ArCH); δ(C100 MHz; CDCl₃) 38.9 (CHCH₂), 60.7 (CH₂OH), 62.3 (CHOH), 85.4 (C≡C), 89.2 (C≡C), 122.4 (ArC), 128.3 (2ArCH), 128.5 (ArCH) and 131.8 (2ArCH); no mass ion could be observed.

1-(3,5-Dibromopent-1-ynyl)benzene (5)

Bromine (5.6 mL, 17.52 g, 114.7 mmol, 2.4 eq) was added dropwise to a solution of triphenylphosphine (31.33 g, 119.5 mmol, 2.5 eq) in DCM (250 mL) at 0°C. The resulting mixture was allowed to stir until the phosphonium salt precipitated (approximately 20 min). A solution of diol 303 (8.42 g, 47.8 mmol) and imidazole (8.13 g, 119.5 mmol, 2.5 eq) in DCM (150 mL) was slowly added via a cannula to the phosphonium salt at 0°C and the resulting reaction mixture was allowed to stir overnight at room temperature. The reaction mixture was quenched with ice-cold water (30 mL) and extracted from ethyl acetate (3×15 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated in vacuo. Triphenylphosphine oxide and triphenylphosphine were recrystallised thrice from cold petrol using DCM and filtered off. The filtrates were combined and the solvents were removed in vacuo affording the title compound in 99% (14.41 g, 47.8 mmol) as an orange oil; Rf (petrol) 0.24; νmax (film)/cm⁻¹ 755 (C–Br), 689 (C–Br), 2224 (C≡C), 2965 (ArC–H) and 3054 (ArC–H); δH (400 MHz; CDCl₃) 2.61 (2H, dt, J 6.4, 6.8 Hz, CHCH₂), 3.62 (2H, t, J 6.4 Hz, CH₂Br), 4.97 (1H, t, J 6.8 Hz, CHBr), 7.24-7.37 (3H, m, ArCH) and 7.40-7.47 (2H, m, ArCH); δ(C100 MHz; CDCl₃) 30.0 (CHCH₂), 35.4 (CH₂Br), 41.9 (CH₂Br), 86.6 (C≡C), 87.7 (C≡C), 121.8 (ArC), 128.4 (2ArCH), 129.1 (ArCH) and 131.9 (2ArCH); no mass ion could be observed.

Dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate (6)
Dimethyl malonate (0.9 mL, 1.08 g, 7.7 mmol, 1.1 eq) was added to a suspension of sodium hydride (620 mg, 15.4 mmol, 60% in mineral oil, 2.2 eq) in THF (140 mL) at 0°C under a nitrogen atmosphere. A solution of 1-(3,5-dibromopent-1-ynyl)benzene (2.11 g, 7.0 mmol) in THF (60 mL) was added via a cannula over 5 min and the resulting mixture was allowed to stir at room temperature for 2 hours. The reaction mixture was heated to reflux for 6 hours. Most of the solvent was evaporated in vacuo and the residue was taken up in diethyl ether (20 mL). The organic crude solution was washed with water (25 mL), dried over magnesium sulfate and concentrated in vacuo. The crude cyclobutane was purified by flash chromatography (5% ethyl acetate/petrol) affording the title compound as a yellow oil in 74% yield (1.41 g, 5.2 mmol); Rf (15% EtOAc/petrol) 0.92; \( \nu_{\text{max}} \) (film)/cm\(^{-1} \) 1754 (C=O), 1737 (C=O), 2227 (C≡C), 2953 (ArC–H) and 3001 (ArC–H); \( \delta_H \) (400 MHz; CDCl\(_3\)) 2.09-2.33 (3H, m, 1H CHCH\(_2\)C\(_3\)H\(_2\)), 2.73-2.82 (1H, m, CHCH\(_2\)C\(_3\)H\(_2\)), 3.71 (3H, s, OCH\(_3\)), 3.72 (3H, s, OCH\(_3\)), 3.95 (1H, t, J 8.8 Hz, CH), 7.17-7.24 (3H, m, ArCH) and 7.26-7.41 (2H, m, ArCH); \( \delta_C \) (100 MHz; CDCl\(_3\)) 24.4 (CH\(_3\)C\(_3\)H\(_2\)), 26.1 (CH\(_3\)C\(_3\)H\(_2\)), 31.5 (CH), 52.7 (CO\(_2\)CH\(_3\)), 52.8 (CO\(_2\)CH\(_3\)), 57.7 (C(CO\(_2\)CH\(_3\))\(_2\)), 84.4 (C≡C), 88.0 (C≡C), 123.1 (ArC), 128.0 (ArCH), 128.2 (2ArCH), 131.6 (2ArCH), 169.6 (C=O) and 171.1 (C=O); HRMS (EI) (M\(^+\)) found 273.1127, C\(_{16}\)H\(_{16}\)O\(_4\) requires 273.1121 (+0.8 ppm); m/z 273 (24%), 213 (20%), 145 (100%), 141 (37%) and 113 (61%).

**Dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate dicobalt hexacarbonyl (2)**

![Supplementary Material (ESI) for Chemical Communications](This journal is (c) The Royal Society of Chemistry 2009)

Dicobalt octacarbonyl (1.81 g, 5.3 mmol, 1.2 eq) was added to a solution of dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate (1.20 g, 4.4 mmol) in DCM (60 mL). The reaction mixture was allowed to stir for 4 hours at room temperature under a nitrogen atmosphere. The solvent was evaporated and the residue was taken up in ethyl acetate (20 mL). The resulting solution was washed with water (25 mL). The aqueous layer was extracted with ethyl acetate (2×10 mL). The combined organic layers were dried over magnesium sulfate, filtered through celite and concentrated in vacuo. The crude product was purified by flash chromatography (15 % ethyl acetate/petrol) affording the desired dicobalt hexacarbonyl complex in 97% yield (2.38 g, 4.3 mmol) as a
Typical procedure for cycloaddition reactions (7-21)

Dimethyl 2-(2-phenylethynyl)cyclobutane-1,1-dicarboxylate 6 (70 mg, 0.257 mmol) was dissolved in DCM (5 ml) in a 10 mL oven dried round-bottom flask. Activated 4 Å molecular sieves were added (150 mg). Dicobalt octacarbonyl (100 mg, 0.292, 1.14 eq) was added and the reaction mixture was allowed to stir at room temperature under nitrogen atmosphere for 1.5 hour. The aldehyde (3.0 eq) and scandium triflate (9 mg, 5 mol%) were added successively. The resulting mixture was allowed to stir at room temperature. (Refer to table for reaction times). After complete conversion of the starting material (TLC monitoring) the crude reaction mixture was filtered through a pad of celite and silica and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography on silica gel (5% ethyl acetate/petrol) for all the tetrahydropyrans synthesized.

(2R,6S) and (2S,6R)-Dicobalt hexacarbonyl 2-ethyl 3,3-dimethyl dihydro-6-(2-phenylethynyl)-2H-pyran-2,3,3(4H)-tricarboxylate (7a) isolated in 34% as a dark red oil.

Rf (15% EtOAc/petrol) 0.34; IR $\nu_{\text{max}}$ (DCM)/cm$^{-1}$ 1116 (C-O), 1732 (C=O), 2021, 2053, 2091 (C=O$_{\text{complex}}$), 2959 (ArC-H); $\delta_{\text{H}}$ (400 MHz; CDCl$_3$) 1.18 (3H, t, J 7.2 Hz, OCH$_2$CH$_3$), 1.53-1.66 (1H, m, CHCHH), 1.98-2.07 (1H, m, CHCHH), 2.21-2.31 (1H, m, CHCH$_2$CHH), 2.68 (1H, ddd, J 2.8,
4.0, 13.6 Hz, CHCH$_2$CH$_3$), 4.13-4.23 (2H, m, OCH$_2$CH$_3$), 4.63 (1H, s, OCHCO$_2$Et), 4.80 (1H, dd, J 2.5, 11.2 Hz, CH$_2$CHO), 7.18-7.29 (3H, m, ArCH) and 7.52-7.58 (2H, m, ArCH); $\delta_C$ (100 MHz; CDCl$_3$) 12.9 (OCH$_2$CH$_3$), 28.8 (CHCH$_2$), 30.5 (CHCH$_2$CH$_2$), 51.6 (OCH$_3$), 52.0 (OCH$_3$), 56.5 (C(CO$_2$CH$_3$)$_2$), 60.2 (OCH$_2$CH$_3$), 77.3 (CH$_2$CHO), 78.0 (OCHCO$_2$Et), 89.3 (CoCCC), 94.1 (CoCCC), 126.8 (ArCH), 127.7 (2ArCH), 128.9 (2ArCH), 136.6 (ArC), 167.4 (CO$_2$CH$_3$), 167.7 (CO$_2$CH$_3$), 169.4 (CO$_2$CH$_2$CH$_3$) and 198.1 (CO$_{complex}$); HRMS (FAB$^+$) (M–3CO), found 575.9890, C$_{23}$H$_{22}$Co$_2$O$_{10}$ requires 575.9877 (+2.2 ppm); m/z 548 (100%), 520 (5%) and 492 (92%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl 2-ethyl 3,3-dimethyl dihydro-6-(2-phenylethynyl)-2H-pyran-2,3,3(4H)-tricarboxylate (7b) isolated in 24% as a dark red oil.

Rf (15% EtOAc/petrol) 0.52; IR $\nu_{max}$ (DCM)/cm$^{-1}$ 1069 (C-O), 1737 (C=O), 2021, 2053, 2057 (C≡Ocomplex), and 2991 (ArC-H); $\delta_H$ (400 MHz; CDCl$_3$) 1.23 (3H, t, J 7.2 Hz, OCH$_2$CH$_3$), 1.50-1.68 (1H, m, CH$_2$CH$_2$), 1.93-2.06 (1H, m, CH$_2$CH$_2$), 2.24-2.35 (1H, m, CHCH$_2$CH$_2$), 2.57-2.66 (1H, m, CHCH$_2$CH$_2$), 3.68 (3H, s, OCH$_3$), 3.72 (3H, s, OCH$_3$), 4.18 (2H, q, J 7.2 Hz, OCH$_2$CH$_3$), 4.83 (1H, dd, J 2.4, 11.2 Hz, CH$_2$CHO), 5.42 (1H, s, OCHCO$_2$Et), 7.21-7.30 (3H, m, ArCH) and 7.50-7.56 (2H, m, ArCH); $\delta_C$ (100 MHz; CDCl$_3$) 13.0 (OCH$_2$CH$_3$), 24.0 (CHCH$_2$), 28.9 (CHCH$_2$CH$_2$), 51.9 (OCH$_3$), 52.2 (OCH$_3$), 54.3 (C(CO$_2$CH$_3$)$_2$), 60.6 (OCH$_2$CH$_3$), 72.1 (CH$_2$CHO), 75.3 (OCHCO$_2$Et), 89.0 (CoCCC), 94.9 (CoCCC), 126.8 (ArCH), 127.7 (2ArCH), 128.9 (2ArCH), 136.6 (ArC), 167.3 (CO$_2$CH$_3$), 167.6 (CO$_2$CH$_3$), 168.6 (CO$_2$Et) and 198.2 (CO$_{complex}$); HRMS (FAB$^+$) (M–2CO), found 603.9815, C$_{24}$H$_{22}$Co$_2$O$_{11}$ requires 603.9826 (–1.8 ppm); m/z 576 (17%), 548 (100%), 520 (12%) and 492 (52%).

(2S,6R) and (2R,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-methyl-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (8a) isolated in 45% as a dark red crystal.
Rf (15% EtOAc/petrol) 0.76; IR $\nu_{\text{max}}$ (DCM)/cm$^{-1}$ 1264, (C-O), 1730 (C=O), 2022, 2050, 2090 (C≡O complex) and 2953 (ArC-H); $\delta_H$(400 MHz; CDCl$_3$) 1.39 (3H, d, $J$ 6.4 Hz, CH$_3$C), 1.91-2.08 (3H, m, 2H CH$_2$CH$_2$ + 1H CHCH$_2$CHH), 2.50-2.58 (1H, m, CHCH$_2$CHH), 3.68 (3H, s, CO$_2$CH$_3$), 3.70 (3H, s, CO$_2$CH$_3$), 4.13 (1H, q, $J$ 6.4 Hz, OC$_2$HCH$_3$), 4.73 (1H, dd, $J$ 3.2, 10.0 Hz, CH$_2$CHO), 7.21-7.30 (3H, m, ArCH) and 7.46-7.51 (2H, m, ArCH); $\delta_C$(100 MHz; CDCl$_3$) 18.2 (CH$_3$C), 29.8 (CH$_2$C), 32.0 (CHCH$_2$C), 52.0 (CO$_2$CH$_3$), 52.6 (CO$_2$CH$_3$), 56.7 (C(CO$_2$CH$_3$)$_2$), 77.4 (OCH$_3$), 77.9 (CH$_2$CHO), 89.6 (CoCCCo), 96.9 (CoCCCo), 127.7 (ArCH), 128.7 (2ArCH), 129.8 (2ArCH), 137.8 (ArC), 169.4 (CO$_2$CH$_3$), 171.4 (CO$_2$CH$_3$) and 199.4 (CO complex); HRMS (FAB) (M−2CO), found 545.9782, C$_{22}$H$_{20}$Co$_2$O$_9$ requires 545.9771 (+2.1 ppm); $m/z$ 518 (5%), 490 (100%), 462 (5%) and 434 (18%); mp 112-113 °C.

(2R,6R) and (2S,6S)-Dioxygen hexacarbonyl dimethyl dihydro-2-methyl-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (8b) isolated in 28% as a dark red oil.

Rf (15% EtOAc/petrol) 0.71; IR $\nu_{\text{max}}$ (DCM)/cm$^{-1}$ 1262, (C-O), 1730 (C=O), 2028, 2050, 2089 (C≡O complex) and 2957 (ArC-H); $\delta_H$(400 MHz; CDCl$_3$) 1.29 (3H, d, $J$ 6.9 Hz, CH$_3$C), 1.44-1.57 (1H, m, CHCH), 1.92-2.01 (1H, m, CHCH), 2.25-2.35 (1H, m, CHCH$_2$CHH), 2.39-2.47 (1H, m, CHCH$_2$CHH), 3.66 (3H, s, CO$_2$CH$_3$), 3.71 (3H, s, CO$_2$CH$_3$), 4.85 (1H, dd, $J$ 2.8, 11.2 Hz, CH$_2$CHO), 4.97 (1H, q, $J$ 6.8 Hz, OCH$_3$), 7.21-7.30 (3H, m, ArCH) and 7.46-7.52 (2H, m, ArCH); $\delta_C$(100 MHz; CDCl$_3$) 14.7 (CH$_3$C), 23.7 (CHCH$_2$), 30.2 (CHCH$_2$CH$_2$), 52.8 (CO$_2$CH$_3$), 52.9 (CO$_2$CH$_3$), 57.0 (C(CO$_2$CH$_3$)$_2$), 68.6 (CH$_2$CHO), 71.2 (OCH$_3$), 90.0 (CoCCCo), 97.8 (CoCCCo), 126.9 (ArCH), 128.7 (2ArCH), 129.9 (2ArCH), 137.8 (ArC), 169.5 (CO$_2$CH$_3$), 170.0
(CO₂CH₃) and 199.4 (CO₃complex); HRMS (FAB⁺) (M−2CO), found 545.9780, C₂₂H₂₀Co₂O₉ requires 545.9771 (+1.7 ppm); m/z 518 (20%), 490 (100%) and 434 (48%).

(2R,6R) and (2S,6S) Dicobalt hexacarbonyl dimethyl dihydro-2-phenyl-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (9) isolated in 34% as a dark red solid.

Rf (15% EtOAc/petrol) 0.68; IR νmax (DCM)/cm⁻¹ 1083, 1262 (C=O), 1731, 1736 (C=O), 2020, 2051, 2091 (C≡O complex), 2848 and 2913 (ArC-H); δH (400 MHz; CDCl₃) 2.09-2.18 (2H, m, CHCH₂), 2.36-2.46 (1H, m, CHCH₂CHH), 2.72 (1H, dt, J 3.6, 13.6 Hz, CHCH₂CHH), 3.54, (3H, s, CO₂CH₃), 3.69 (3H, s, CO₂CH₃), 4.99-5.05 (1H, m, CH₂CHO), 5.27 (1H, s, OCCHAr), 7.23-7.32 (6H, m, ArC-H), 7.40-7.45 (2H, m, ArCH) and 7.55-7.60 (2H, m, ArCH); δC (100 MHz; CDCl₃) 30.0 (CHCH₂), 32.7 (CHCH₂CH₂), 51.7 (CO₂CH₃), 52.6 (CO₂CH₃), 59.1 (C(CO₂CH₃)₂), 79.2 (OCCHAr), 82.8 (CH₂CHO), 89.9 (COCCo), 96.0 (COCCo), 126.0 (2ArCH), 126.4 (2ArCH), 126.5 (ArCH), 126.8 (ArCH), 127.7 (2ArCH), 128.8 (2ArCH), 137.6 (ArC), 138.9 (ArC), 169.0 (CO₂CH₃), 171.2 (CO₂CH₃) and 198.2 (CO₃complex); HRMS (FAB⁺) m/z (M−2CO), found 607.9940, C₂₇H₂₂Co₂O₉ requires 607.9928 (+2.1 ppm); m/z 580 (90%), 552 (43%), 524 (100%) and 496 (48%); mp 114-115 °C.

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-p-tolyl-2H-pyran-3,3(4H)-dicarboxylate (10) isolated in 64% as a dark red cristal.

Rf (15% EtOAc/petrol) 0.75; IR νmax (DCM)/cm⁻¹ 1083, 1262 (C=O), 1731, (C=O), 2090, 2051, 2023 (C≡O complex) and 2952 (ArCH); δH (400 MHz; CDCl₃) 2.08-2.18 (2H, m, CHCH₂), 2.33 (3H, s, ArCH₃), 2.37-2.49 (1H, m, CHCH₂CHH), 2.72 (1H, dt, J 3.6, 13.2 Hz, CHCH₂CHH), 3.57 (3H, s,
CO\(_2\)CH\(_3\)), 3.69 (3H, s, CO\(_2\)CH\(_3\)), 4.94 (1H, dd, \(J\) 6.0, 8.2 Hz, CH\(_2\)CHO), 5.24 (1H, s, OCHAr), 7.27-7.36 (5H, m, ArCH), 7.32-7.37 (2H, m, ArCH) and 7.56-7.63 (2H, m, ArCH); \(\delta\)C(100 MHz; CDCl\(_3\)) 21.2 (ArCH\(_3\)), 30.1 (CH\(_2\)CH\(_2\)), 32.7 (CHCH\(_2\)CH\(_2\)), 51.7 (CO\(_2\)CH\(_3\)), 53.3 (CO\(_2\)CH\(_3\)), 60.4 (C(CO\(_2\)CH\(_3\))\(_2\)), 79.2 (CH\(_2\)CHO), 82.9 (OCHAr), 89.9 (CoC\(_{CCO}\)), 96.1 (CoCC\(_{Co}\)), 127.3 (1ArCH), 127.9 (4ArCH), 128.8 (2ArCH), 129.9 (2ArCH), 136.0 (ArC), 137.0 (ArC), 137.7 (ArC), 169.0 (CO\(_2\)CH\(_3\)), 171.2 (CO\(_2\)CH\(_3\)) and 199.3 (CO\(_{complex}\)); HRMS (FAB\(^+\)) (M−2CO), found 622.0096, \(\text{C}_{28}\text{H}_{24}\text{Co}_{2}\text{O}_9\) requires 622.0084 (+1.9 ppm); \(\text{m}\,/\text{z} 594 (100\%), 566 (79\%), 538 (96\%) and 510 (57\%); mp 114.1-114.8 °C.

(2\,R,\,6\,R) and (2\,S,\,6\,S)-Dicobalt heaxacarbonyl dimethyl dihydro-6-(2-phenylethylnyl)-2-otolyl-2H-pyran-3,3(4H)-dicarboxylate, (11) isolated in 43% as a dark red oil.

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\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
(\text{OC})_3\text{Co} & \quad \text{Co(OC)}_3
\end{align*}
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Rf (15\% EtOAc/petrol) 0.77; IR \(\nu_{\text{max}}\) (DCM)/cm\(^{-1}\) 1261, 1083 (C-O), 1732, (C=O), 2090, 2051, 2022 (C=O\(_{complex}\)), 2958 and 3002 (ArC-H); \(\delta\)H(400 MHz; CDCl\(_3\)) 2.01-2.08 (1H, m, CHC\(_2\)H), 2.09-2.21 (1H, m, CHC\(_2\)H), 2.27-2.39 (4H, m, 1H, CHCH\(_2\)CH\(_3\) + ArCH\(_3\)), 2.64 (1H, dt, \(J\) 4.4, 13.6 Hz, CHCH\(_2\)CH\(_3\)), 3.49 (3H, s, CO\(_2\)CH\(_3\)), 3.57 (3H, s, CO\(_2\)CH\(_3\)), 4.99 (1H, dd, \(J\) 3.6, 10.4 Hz, CH\(_2\)CHO), 5.34 (1H, s, OCHAr), 6.99-7.12 (3H, m, ArCH), 7.16-7.24 (4H, m, ArCH) and 7.44-7.52 (2H, m, ArCH); \(\delta\)C(100 MHz; CDCl\(_3\)) 20.0 (ArCH\(_3\)), 29.7 (CHCH\(_2\)), 31.9 (CHCH\(_2\)CH\(_2\)), 51.9 (CO\(_2\)CH\(_3\)), 52.6 (CO\(_2\)CH\(_3\)), 57.8 (C(CO\(_2\)CH\(_3\))\(_2\)), 78.3 (CH\(_2\)CHO), 79.3 (OCHAr), 90.1 (CoC\(_{CCO}\)), 96.3 (CoC\(_{CCO}\)), 124.8 (ArCH), 127.7 (ArCH), 127.8 (ArCH), 128.7 (2ArCH), 129.0 (ArCH), 129.8 (ArCH), 129.9 (2ArCH), 135.8 (ArC), 136.5 (ArC), 137.7 (ArC), 169.4 (CO\(_2\)CH\(_3\)), 171.0 (CO\(_2\)CH\(_3\)) and 199.3 (CO\(_{complex}\)); HRMS (FAB\(^+\)) (M−2CO), found 622.0071, \(\text{C}_{28}\text{H}_{24}\text{Co}_{2}\text{O}_9\) requires 622.0084 (−2.0 ppm); \(\text{m}\,/\text{z} 594 (76\%), 566 (72\%), 538 (100\%) and 510 (65\%); mp 114-115 °C.

(2\,R,\,6\,R) and (2\,S,\,6\,S)-Dicobalt heaxacarbonyl dimethyl dihydro-6-(2-phenylethylnyl)-2-styryl-2H-pyran-3,3(4H)-dicarboxylate (12) isolated in 82% as a dark red oil.
Rf (15% EtOAc/petrol) 0.69; IR $\nu_{\text{max}}$ (DCM)/cm$^{-1}$ 1084, 1264 (C-O), 1731 (C=O), 2021, 2050, 2088 (C=O), 2953 (Ar-C-H), 3025 and 3058 (=CH); $\delta_{\text{H}}$(400 MHz; CDCl$_3$) 1.97-2.20 (2H, m, CH(CH$_3$)$_2$), 2.64-2.55 (2H, m, CHCH$_2$CH$_2$), 3.62 (3H, s, CO$_2$CH$_3$), 3.66 (3H, s, CO$_2$CH$_3$), 4.72 (1H, d, J 5.2 Hz, OC$_3$H$_2$CH=CH), 4.84-4.90 (1H, m, CH$_2$CO), 6.49 (1H, dd, J 5.2, 16.4 Hz, CH=CHPh), 6.60 (1H, d, J 16.4 Hz, CH=CHPh), 7.11-7.30 (8H, m, ArC-H) and 7.48-7.54 (2H, m, ArC-H); $\delta_{\text{C}}$(100 MHz; CDCl$_3$) 28.8 (CH$_2$C$_{CH3}$), 30.7 (CHCH$_2$CH$_2$), 51.1 (CO$_2$CH$_3$), 51.7 (CO$_2$CH$_3$), 56.9 (C(CO$_2$CH$_3$)$_2$), 77.2 (CH$_2$CHO), 80.3 (OCHCH), 88.9 (CoC(Co), 95.5 (CoCCo), 125.5 (2ArCH), 125.9 (CH=CHPh), 126.4 (ArCH), 126.8 (ArCH), 127.4 (2ArCH), 127.8 (2ArCH), 129.2 (CH=CHPh), 129.8 (2ArCH), 136.2 (ArC), 136.7 (ArC), 168.0 (CO$_2$CH$_3$), 170.0 (CO$_2$CH$_3$) and 198.3 (CO$_{\text{complex}}$); HRMS (FAB$^+$) (M−3CO) found 606.0144, C$_{26}$H$_{24}$Co$_2$O$_8$ requires 606.0135 (+1.5 ppm); m/z 578 (80%), 550 (4%) and 522 (100%).

(2 R, 6 R) and (2 S, 6 S) - Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-((E)-1-phenylprop-1-en-2-yl)-2H-pyran-3,3(4H)-dicarboxylate (13) isolated in 84% as a dark red oil.

Rf (15% EtOAc/petrol) 0.75; IR $\nu_{\text{max}}$ (DCM)/cm$^{-1}$ 1075, 1259 (C-O), 1731, 1736 (C=O), 2021, 2050, 2089 (C=O), 2952 (Ar-C-H), 2997, 3027 and 3057 (=CH); $\delta_{\text{H}}$(400 MHz; CDCl$_3$) 1.89 (3H, s, CHCC$_3$), 2.03-2.14 (2H, m, CHCH$_2$), 2.25-2.41 (1H, m, CHCH$_2$CHH), 2.66 (1H, dt, J 3.6, 13.2 Hz, CHCH$_2$CHH), 3.71 (3H, s, CO$_2$CH$_3$), 3.74 (3H, s, CO$_2$CH$_3$), 4.82 (1H, s, OCH=), 4.94-5.00 (1H, m, CH$_2$CHO), 6.66 (1H, s, C=CHPh), 7.16-7.26 (2H, m, ArCH), 7.27-7.38 (6H, m, ArCH) and 7.57-7.63 (2H, m, ArCH); $\delta_{\text{C}}$(100 MHz; CDCl$_3$) 15.7 (CHC$_3$), 29.9 (CHCH$_3$), 32.8 (CHCH$_2$CH$_2$), 52.0 (CO$_2$CH$_3$), 52.6 (CO$_2$CH$_3$), 58.4 (C(CO$_2$CH$_3$)$_2$), 79.8 (CH$_2$CHO), 84.9 (OCHCH$_3$), 90.1 (CoCCCo), 96.2 (CoCCCo), 126.3 (ArCH), 127.2 (ArCH), 127.9 (=CHPh), 129.8 (2ArCH), 136.2 (ArC), 136.7 (ArC), 168.0 (CO$_2$CH$_3$), 170.0 (CO$_2$CH$_3$) and 198.3 (CO$_{\text{complex}}$); HRMS (FAB$^+$) (M−3CO) found 606.0144, C$_{26}$H$_{24}$Co$_2$O$_8$ requires 606.0135 (+1.5 ppm); m/z 578 (80%), 550 (4%) and 522 (100%).
128.0 (2ArCH), 128.8 (2ArCH), 129.1 (2ArCH), 129.9 (2ArCH), 135.9 (CHCCH$_3$), 137.7 (ArC), 137.9 (ArC), 169.7 (CO$_2$CH$_3$), 171.6 (CO$_2$CH$_3$) and 199.3 (CO$_{\text{complex}}$); HRMS (FAB$^+$) (M$\text{−}$2CO), found 648.0250, C$_{30}$H$_{26}$Co$_2$O$_9$ requires 648.0241 (+1.3 ppm); m/z 620 (20%), 592 (100%) and 536 (27%).

(2R,6R) and (2S,6S)-Dicobalt octacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-((E)-prop-1-enyl)-2H-pyran-3,3(4H)-dicarboxylate (14) isolated in 82% as a dark red oil.

Rf (15% EtOAc/petrol) 0.77; IR $\nu_{\text{max}}$ (DCM)/cm$^{-1}$ 1082, 1266 (C-O), 1726, 1731 (C=O), 2021, 2051, 2090 (C≡O complex), 2954 (ArC-H) and 3058 (=CH); $\delta_H$(400 MHz; CDCl$_3$) 1.62 (3H, d, $J$ 6.4 Hz, CHC$_3$H$_3$), 1.79-2.02 (2H, m, CHC$_2$H$_2$), 2.13 (1H, dt, $J$ 4.8, 13.2 Hz, CHCH$_2$CHH), 2.55 (1H, ddd $J$ 2.8, 4.0, 13.2 Hz, CHCH$_2$CHH), 3.64 (3H, s, CO$_2$CH$_3$), 3.67 (3H, s, CO$_2$CH$_3$), 4.41 (1H, d, $J$ 6.4 Hz, OCHCH), 4.78 (1H, dd, $J$ 3.2, 11.2 Hz, CH$_2$CHO), 5.64 (1H, ddd, $J$ 0.8, 6.4, 15.2 Hz, CH=CHCH$_3$), 5.83 (1H, ddd, $J$ 1.6, 6.4, 15.2 Hz, CH=CHCH$_3$), 7.19-7.29 (3H, m, ArCH) and 7.46-7.53 (2H, m, ArCH); $\delta_C$(100 MHz; CDCl$_3$) 16.9 (CHC$_3$H$_3$), 28.8 (CHCH$_2$CH$_2$), 30.8 (CHCH$_2$CH$_2$), 51.0 (CO$_2$CH$_3$), 51.8 (CO$_2$CH$_3$), 57.2 (C(CO$_2$CH$_3$)$_2$), 77.0 (CH$_2$CHO), 81.3 (OCHCH), 88.9 (CoCCC$_3$), 95.5 (CoCCCo), 126.7 (ArCH), 126.9 (CH=CHCH$_3$), 127.3 (CH=CHCH$_3$), 127.7 (2ArCH), 128.9 (2ArCH), 136.8 (ArC), 168.2 (CO$_2$CH$_3$), 170.0 (CO$_2$CH$_3$) and 198.3 (CO$_{\text{complex}}$); HRMS (FAB$^+$) (M$\text{−}$2CO) found 571.9915, C$_{26}$H$_{24}$Co$_2$O$_8$ requires 571.99278 (−1.4 ppm); m/z 629 (4%), 572 (19%), 545 (14%), 517 (65%), 516 (100%), 488 (15%) and 460 (30%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-((1E,3E)-penta-1,3-dienyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (15) isolated in 51% as a dark red oil.

S11
Rf (15% EtOAc/petrol) 0.78; IR ν\text{max} (DCM)/cm⁻¹ 1083, 1262 (C-O), 2631 (C=O), 2020, 2089 (C≡O complex), 2953 (ArC-H), 3019 and 3057 (=CH); δH(400 MHz; CDCl₃) 1.75 (3H, d, J 6.8 Hz, CH₃), 1.98-2.10 (2H, m, CHCH₂), 2.19 (1H, dt, J 5.2, 13.2 Hz, CHCH₂CHH), 2.63 (1H, ddd, J 2.8, 4.0, 13.2 Hz, CHCH₂CHH), 3.72 (6H, s, OCH₃), 4.59 (1H, d, J 6.0 Hz, OCHCH), 4.87 (1H, dd, J 4.0, 10.8 Hz, CH₂CHO), 5.62 (1H, dd, J 6.8, 14.9 Hz, CH₂CH=CH), 5.92 (1H, dd, J 6.0, 15.6 Hz, OCHCH), 6.03-6.14 (1H, m, CH₂CH=CH), 7.27-7.36 (3H, m, ArC-H) and 7.52-7.59 (2H, m, ArCH); δC(100 MHz; CDCl₃) 18.2 (CH₂CH₃), 29.8 (CH₂CH₂), 31.7 (CHCH₂CH₂), 52.1 (CO₂CH₃), 52.6 (CO₂CH₃), 58.1 (C(CO₂CH₃)₂), 78.2 (CH₂CHO), 81.7 (OCHCH), 89.9 (CoCCCO), 96.5 (CoCCCO), 127.4 (OCHCH), 127.8 (ArCH), 128.8 (2ArCH), 129.7 (CH₂CH), 129.8 (2ArCH), 131.2 (CH₂CH=CH), 131.5 (CH₂CH=CHCH), 137.8 (ArC), 169.1 (CO₂CH₃), 180.0 (CO₂CH₃) and 199.4 (CO complex); HRMS (FAB⁺) (M−2CO), found 598.0071, C₂₆H₂₄Co₂O₉ requires 598.0084 (−2.1 ppm); m/z 570 (37%), 542 (100%), 514 (11%) and 486 (89%).

(2 R, 6 R) and (2 S, 6 S) - Dicobalt hexacarbonyl dimethyl dihydro-2-(4-methoxyphenyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (16) isolated in 85% as a dark red oil.

Rf (15% EtOAc/petrol) 0.61; IR ν\text{max} (DCM)/cm⁻¹ 1085, 1251 (C-O), 1731, 1736 (C=O), 2021, 2090 (C≡O complex) and 2954 (ArC-H); δH(400 MHz; CDCl₃) 2.01-2.11 (2H, m, CHCH₂), 2.28-2.38 (1H, m, CHCH₂CHH), 2.64 (1H, dt, J 3.2, 13.2 Hz, CHCH₂CHH), 3.49 (3H, s, CO₂CH₃), 3.61 (3H, s, CO₂CH₃), 3.72 (3H, s, ArOCH₃), 4.91-4.97 (1H, m, CH₂CHO), 5.14 (1H, s, OCHAr), 6.70-6.75 (2H, m, ArCH), 7.17-7.25 (3H, m, ArCH), 7.26-7.31 (2H, m, ArCH) and 7.48-7.53 (2H, m, ArCH); δC(100 MHz; CDCl₃) 29.0 (CHCH₂), 31.6 (CHCH₂CH₂), 50.7 (CO₂CH₃), 51.5 (CO₂CH₃), 54.0 (ArOCH₃), 58.0 (C(CO₂CH₃)₂), 78.2 (OCHAr), 81.6 (CH₂CHO), 88.9 (CoCCCO), 95.1 (CoCCCO), 111.4 (2ArCH), 126.7 (ArCH), 127.6 (2ArCH), 127.8 (2ArCH), 128.8 (2ArCH), 130.1 (ArC), 136.6 (ArC), 157.8 (ArC), 168.0 (CO₂CH₃), 170.2 (CO₂CH₃) and 198.4 (CO complex); HRMS (FAB⁺) (M−2CO), found 638.0047, C₂₈H₂₄O₁₀ requires 638.0033 (+2.2 ppm); m/z 610 (77%), 582 (75%), 554 (100%) and 526 (26%).

S12
(2R,6R) and (2S,6S)-Dicoalt hexamyl diborial dihydro-2-(4-phenoxyphenyl)-6-(2-phenylethynyl)-2H-pyrn-3,3(4H)-dicarboxylate (17) isolated in 65% as a dark red oil.

Rf (15% EtOAc/petrol) 0.66; IR ν max (DCM)/cm -1 1072, 1240, 1263 (C-O), 1730 (C=O), 2021, 2050, 2089 (C≡O complex), 2952 and 3059 (ArC-H);

δ H (400 MHz; CDCl 3 ) 2.09-2.21 (2H, m, CHCH 2 C H), 2.33-2.45 (1H, m, CHCH 2 C H), 2.72 (1H, dt, J 3.2, 13.6 Hz, CHCH 2 CH), 3.57, (3H, s, CO 2 C H), 3.70 (3H, s, CO 2 C H), 4.94 (1H, dd, J 4.0, 10.0 Hz, CH 2 CHO), 5.18 (1H, s, OCHAr), 6.79-6.86 (2H, ArCH), 6.90-6.96 (2H, ArCH), 6.97-7.06 (1H, m, ArCH), 7.18-7.36 (7H, m, ArCH) and 7.47-7.54 (2H, m, ArCH); δ C (100 MHz; CDCl 3 ) 30 (CH 2 CH), 32.7 (CHCH 2 C H), 51.7 (CO 2 C H), 52.6 (CO 2 C H), 59.0 (C(CO 2 C H) 2 ), 72.3 (OCHAr), 82.5 (CH 2 CHO), 90.0 (CoCCo), 96.0 (CoCCo), 117.3 (2ArCH), 119.1 (2ArCH), 123.2 (ArCH), 127.9 (ArCH), 128.8 (2ArCH), 128.9 (2ArCH), 129.7 (2ArCH), 129.9 (2ArCH), 133.8 (ArC), 137.7 (ArC), 156.6 (ArC), 157.2 (ArC), 168.9 (CO 2 C H), 171.2 (CO 2 C H) and 199.4 (CO complex); HRMS (FAB) (M+3CO), found 672.0253, C 32 H 26 Co 2 O 9 requires 672.0241 (+1.8 ppm); m/z 672 (21%), 644 (11%), 616 (3%) and 588 (100%).

(2R,6S) and (2S,6R)-Dicoalt hexamyl diborial dihydro-2-(furan-2-yl)-dihydro-6-(2-phenylethynyl)-2H-pyrn-3,3(4H)-dicarboxylate (18) isolated in 95% as a dark red crystal.

Rf (15% EtOAc/petrol) 0.62; IR ν max (DCM)/cm -1 1080, 1263 (C-O), 1734 (C=O), 2022, 2052, 2091 (C≡O complex) and 2953 (ArCH); δ H (400 MHz; CDCl 3 ) 1.94-2.06 (1H, m, CHCHH), 2.07-2.17

S13
(1H, m, CHCHH), 2.34 (1H, dt, J 4.4, 13.2 Hz, CHCH₂CHH), 2.73 (1H, ddd, J 2.8, 4.0, 13.2 Hz, CHCH₂CHH), 3.59 (3H, s, CO₂CH₃), 3.80 (3H, s, CO₂CH₃), 5.03 (1H, dd, J 2.8, 11.2 Hz, CH₂CHO), 5.34 (1H, s, OCH₃Ar), 6.33 (2H, d, J 1.2 Hz, ArCH₃), 7.27-7.36 (4H, m, ArCH₃) and 7.55-7.60 (2H, m, ArCH₃); δC (100 MHz; CDCl₃) 29.9 (CH₂CH₂), 31.8 (CHCH₂CH₂), 52.1 (CO₂CH₃), 52.9 (CO₂CH₃), 57.6 (C(CO₂CH₃)₂), 78.0 (OCH₃Ar), 78.9 (CH₂CHO), 89.9 (CoC₃Co), 95.6 (CoC₃Co), 106.5 (ArCH), 110.3 (ArCH), 127.9 (ArCH), 128.8 (2ArCH), 129.8 (2ArCH), 137.7 (ArC), 140.9 (ArCH), 152.2 (ArC), 168.5 (CO₂CH₃), 170.8 (CO₂CH₃) and 199.3 (CO_complex); HRMS (FAB+) (M−2CO), found 597.9734, C₂₅H₂₀Co₂O₁₀ requires 597.9720 (+2.2 ppm); m/z 570 (22%), 540 (100%) and 486 (42%); mp 119-120.

(2R,6S) and (2S,6R)-Dicobalt hexacarbonyl dimethyl dihydro-6-(2-phenylethynyl)-2-(thiophen-2-yl)-2H-pyran-3,3(4H)-dicarboxylate (19) isolated in 89% as a dark red solid.

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{CO}_2\text{Me} \\
\text{(OC)}_3\text{Co} & \quad \text{Co(OC)}_3
\end{align*}
\]

Rf (15% EtOAc/petrol) 0.66; IR ν_max (DCM)/cm⁻¹ 1077, 1265 (C=O), 1728 (C=O), 2024, 2052, 2091 (C=O_complex) and 2952 (ArC=H); δH (400 MHz; CDCl₃) 1.98-2.19 (2H, m, CHCH₂), 2.20-2.32 (1H, dt, J 4.0, 12.8 Hz, CHCH₂CHH), 2.60-2.70 (1H, broad d, J 12.8 Hz, CHCH₂CHH), 3.49 (3H, s, CO₂CH₃), 3.70 (3H, s, CO₂CH₃), 4.96 (1H, broad d, J 9.8 Hz, CH₂CHO), 5.50 (1H, s, OCH₃Ar), 6.83-6.98 (2H, m, ArCH), 7.12-7.31 (4H, m, ArCH) and 7.47-7.57 (2H, m, ArCH); δC (100 MHz; CDCl₃) 29.9 (CH₂CH₂), 32.3 (CHCH₂CH₂), 52.0 (CO₂CH₃), 52.7 (CO₂CH₃), 59.2 (C(CO₂CH₃)₂), 79.4 (OCH₃Ar), 79.8 (CH₂CHO), 90.2 (CoC₃Co), 95.5 (CoC₃Co), 124.6 (ArCH), 124.8 (ArCH), 125.8 (ArCH), 127.9 (ArCH), 128.8 (2ArCH), 129.9 (2ArCH), 137.6 (ArC), 142.0 (ArC), 168.6 (CO₂CH₃), 171.1 (CO₂CH₃) and 199.3 (CO_complex); HRMS (FAB+) (M−2CO), found 613.9482, C₂₅H₂₀Co₂O₉S requires 613.9492 (−1.6 ppm); m/z 614 (5%), 586 (77%), 558 (100%), 530 (9%), 502 (27%); mp 122-123.

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-(2,4-dimethoxyphenyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (20) isolated in 92% as a dark red oil.
RF (15% EtOAc/petrol) 0.30; IR $\nu_{max}$ (DCM)/cm$^{-1}$ 1045, 1085, 1158, 1208, 1255 (C=O), 1732, 1736 (C=O), 2019, 2050, 2089 (C=O), 2952 and 3000 (ArC-H); $\delta_H$(400 MHz; CDCl$_3$) 1.58-1.71 (1H, m, CHCH), 2.01-2.12 (1H, m, CHCH), 2.52-2.68 (2H, m, CHCH), 3.48 (3H, s, OC$_3$H$_3$), 3.58 (3H, s, OC$_3$H$_3$), 3.67 (3H, s, OC$_3$H$_3$), 3.73 (3H, s, OC$_3$H$_3$), 4.88 (1H, dd, $J$ 2.6, 11.2 Hz, CH$_2$CO), 5.13 (1H, s, OCH$_3$Ar), 6.27 (1H, d, $J$ 2.4 Hz, ArCH), 6.42 (1H, dd, $J$ 2.0, 8.4 Hz, ArCH), 7.20-7.28 (3H, m, ArCH), 7.51-7.57 (2H, m, ArCH) and 7.72 (1H, d, $J$ 8.4 Hz, ArCH); $\delta_C$(100 MHz; CDCl$_3$) 29.6 (CH$_2$CH), 30.9 (CHCH), 50.7 (OC$_3$H$_3$), 51.6 (OC$_3$H$_3$), 54.2 (CO$_2$CH$_3$), 54.4 (ArC=O), 76.4 (CH$_2$CO), 78.5 (OCH$_3$), 89.0 (CoCCo), 95.0 (CoCCo), 95.4 (ArCH), 118.3 (ArC), 126.7 (ArCH), 127.7 (2ArCH), 128.9 (2ArCH), 130.5 (ArCH), 157.5 (ArOMe), 159.0 (ArOMe), 168.3 (CO$_2$CH$_3$), 168.6 (CO$_2$CH$_3$) and 198.4 (CO$_3$H$_3$); HRMS (FAB$^+$) (M$-$3CO), found 640.0177, C$_{28}$H$_{26}$Co$_2$O$_{10}$ requires 640.0189 (2.0 ppm); m/z 612(100%), 584 (13%) and 556 (12%).

(2R,6R) and (2S,6S)-Dicobalt hexacarbonyl dimethyl dihydro-2-(3,4-dimethoxyphenyl)-6-(2-phenylethynyl)-2H-pyran-3,3(4H)-dicarboxylate (21) isolated in 92% as a dark red oil.

RF (15% EtOAc/petrol) 0.19; IR $\nu_{max}$ (DCM)/cm$^{-1}$ 1029, 1074, 1234, 1264 (C=O), 1731 (C=O), 2022, 2050, 2090 (C=O), 2953, 3002 and 3075 (ArC-H); $\delta_H$(400 MHz; CDCl$_3$) 2.03-2.11 (2H, m, CHCH), 2.28-2.37 (1H, m, CHCH), 2.64 (1H, dd, $J$ 3.2, 13.2 Hz, CHCH), 3.49 (3H, s, OCH$_3$), 3.62 (3H, s, OCH$_3$), 3.66 (3H, s, OCH$_3$), 3.80 (3H, s, OCH$_3$), 4.95 (1H, dd, $J$ 6.0, 8.0 Hz, CH$_2$CHO), 5.17 (1H, s, OCH$_3$), 6.68 (1H, d, $J$ 8.4 Hz, ArCH), 6.83 (1H, dd, $J$ 2.0, 8.4 Hz, ArCH), 7.03 (1H, d, $J$ 2.0 Hz, ArCH), 7.19-7.27 (3H, m, ArCH) and 7.48-7.55 (2H, m, ArCH); $\delta_C$(100 MHz; CDCl$_3$) 29.0 (CHCH), 37.7 (CHCH), 50.7 (CO$_2$CH$_3$), 51.6 (CO$_2$CH$_3$), 54.4 (ArOCH$_3$), 198.4 (CO$_3$H$_3$).
54.6 (ArOCH₃), 58.2 \((\text{C(O₂CH₃)} )₂\), 78.3 (OCHAr), 81.6 (CH₂CHO), 89.0 (CoC₃Co), 95.1 (CoCCCo), 108.4 (ArCH), 109.3 (ArCH), 118.4 (ArCH), 126.9 (ArCH), 127.8 (2ArCH), 128.7 (2ArCH), 130.5 (ArC), 136.6 (ArC), 146.8 (ArCOMe), 147.1 (ArCOMe), 168.1 (CO₂CH₃), 170.2 (CO₂CH₃) and 198.2 (CO complex); HRMS (FAB⁺) (M–3CO), found 640.0178, C₂₈H₂₆Co₂O₁₀ requires 640.0189 (–1.8 ppm); \(m/z\), 612 (43%), 584 (100%) and 556 (60%).
Proton and Carbon Spectra Section

Compound 2
Compound 3
Compound 4
Compound 5
Compound 6
Compound 7a
Compound 7b
Compound 8a
Compound 8b
Compound 9
Compound 10
Compound 11
Compound 12
Compound 13
Compound 14
Compound 15
Compound 18
Compound 19
Compound 20
Compound 21
ESIFIG1. Ellipsoid plot at 50% probability level for compound 8. Most H atoms omitted for clarity.

ESIFIG2. Ellipsoid plot at 50% probability level for compound 10·CH₂Cl₂. Minor disorder components and most H atoms omitted for clarity.
ESIFIG3. Ellipsoid plot at 50% probability level for compound 18. Most H atoms omitted for clarity.

ESIFIG4. Ellipsoid plot at 50% probability level for compound 19. Most H atoms omitted for clarity.