

# Supplementary Material (ESI) for Chemical Communications  
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### **Novel formation and use of a Nicholas carbocation in the synthesis of highly substituted furan ring systems**

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#### **General information**

All reactions were carried out in one of the following solvents which were dried and purified, or purchased in the following procedures.

Dichloromethane	For general use $\text{CH}_2\text{Cl}_2$ was distilled over boiling stones or $\text{CaH}_2$ for anhydrous reactions.
Dimethylsulfide	Purchased from Aldrich (99+%) and used without further purification.
<i>n</i> -Hexane	Purchased from Fischer Scientific (99+%), used without purification for general use.
Light petroleum	Distilled over $\text{CaCl}_2$ for general use, collecting the fraction distilling below $60^\circ\text{C}$ .
$\text{Co}_2(\text{CO})_8$ from Strem	(stabilised by 1-5% hexane), used without any further purification.

Anhydrous reactions were extensively flame-dried under an atmosphere of nitrogen. All metal carbonyl complexes were stored under a nitrogen atmosphere and kept at  $-18^\circ\text{C}$  in a freezer.

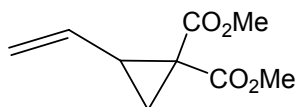
High resolution mass spectroscopy was carried out on a Jeol SX 102 machine, used for both electron ionisation (EI) and fast atom bombardment (FAB) ionisation techniques. For FAB spectroscopy a matrix of 1,3-nitrobenzylalcohol was used to dissolve the compounds under investigation, prior to ionisation. Nuclear magnetic resonance spectroscopy was acquired using either a Bruker AC 250 or Bruker DPX 400 instrument. The spectra were calibrated where possible to the signals of tetramethylsilane or the small quantity of  $\text{CHCl}_3$  present in  $\text{CDCl}_3$ , typically used as the standard solvent for these experiments. Where possible coupling constants ( $J$ ) are shown denoting their multiplicity as a singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) or broad signal (br) etc. The size of the coupling constants are given in Hertz (Hz). Elemental analysis was carried out using a Perkin Elmer CHN 2400 elemental analyser. Fourier transform Infra Red spectroscopy was recorded using a Paragon 1000 Perkin Elmer FT-IR spectrometer in the range of  $3500\text{-}600\text{cm}^{-1}$  following a standard background correction. Melting points of solid products was recorded using a Stuart Scientific SMP3 instrument.

Flash silica column chromatography was used as a standard purification procedure using Fluka Kiesel gel 60, 0.04-0.063 mm particle size silica. Thin layer chromatography was used where possible as a standard procedure for monitoring the course and rate of a given

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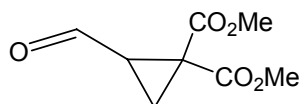
reaction. TLC plates used were Merck aluminium backed sheets with Kiesel gel 60 F<sub>254</sub> silica coating.

**2-Ethenylcyclopropane-1,1-dicarboxylic acid dimethyl ester<sup>1</sup>**



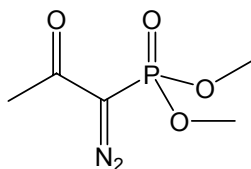
To a stirred solution of sodium methoxide, prepared from sodium (1.15 g, 50 mmol) and methanol (20 mL), was added dimethyl malonate (5.89 mL, 51.5 mmol) followed by a solution of (*E*)-1,4-dibromobutene (5.35 g, 25 mmol) in methanol (20 mL). The reaction mixture was refluxed for 2.5 h and then cooled to ambient temperature. The white precipitate was filtered (if present) and the filtrate reduced *in vacuo* to leave an oily residue, which was partitioned between diethyl ether (30 mL) and distilled water (30 mL). The diethyl ether layer was further washed with distilled water (2 x 30 mL), before drying over MgSO<sub>4</sub>, filtering and concentrating *in vacuo* to afford a pale yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the *title compound* as a colourless oil (6.71 g, 90%) (Found: M<sup>+</sup>, 184.0738. C<sub>9</sub>H<sub>12</sub>O<sub>4</sub> requires M, 184.0736);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2955 (sp<sup>3</sup> C-H), 1730 (C=O);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.58 (1H, dd, *J* 5, 9 Hz, CCHH), 1.72 (1H, dd, *J* 5, 7.5 Hz, CCHH), 2.57-2.59 (1H, m, CH<sub>2</sub>CHC), 3.74 (6H, s, (CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 5.13 (1H, d, *J* 10.5 Hz, CHCHH), 5.27 (1H, d, *J* 17.0 Hz, CHCHH), 5.41 (1H, m, CCHCHCH<sub>2</sub>);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 20.9 (CCH<sub>2</sub>), 31.8 (CCHCH), 36.1 (CCH), 52.9, 53.0 (OCH<sub>3</sub>), 119.0 (CCHCHCH<sub>2</sub>), 133.3 (CHCHCH<sub>2</sub>), 168.1, 170.3 (CO<sub>2</sub>CH<sub>3</sub>); *m/z* 184 (M<sup>+</sup>, 15%), 152 (67), 124 (64), 93 (50), 71 (66)

**2-Formyl-cyclopropane-1,1-dicarboxylic acid dimethyl ester<sup>2</sup>**



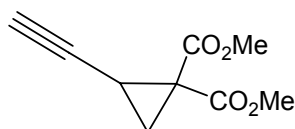
2-Ethenylcyclopropane-1,1-dicarboxylic acid dimethyl ester (4.3 g, 186.2 mmol) in DCM (35 mL) was added to a flame-dried 3-neck flask fitted with a stopper, cone adapter and gas inlet. Oxygen was bubbled into the reaction mixture for 15 min while cooling to -78°C. Ozone was then generated and bubbled through the reaction mixture at -78°C until a pale blue colour appeared, at which point oxygen was allowed to bubble through the reaction mixture and dimethylsulfide (10 mL) added, stirring for 12.0 h at room temperature. The reaction mixture was then concentrated *in vacuo* and the crude product partitioned between DCM (100 mL) and water (35 mL), washing the DCM fraction with water (2 x 35 mL) before drying, filtering and reducing *in vacuo* to give the *title compound* as a colourless oil (4.02 g, 91%);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2958 (sp<sup>3</sup> C-H), 1735, 1719 (C=O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 1.82 (1H, dd, *J* 5, 9 Hz, CHCHH), 2.08 (1H, dd, *J* 5, 7 Hz, CHCHH), 2.74-2.78 (1H, m, CH<sub>2</sub>CH), 3.77 (6H, s, C(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 9.36 (1H, d, *J* 4 Hz, CHO);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 20.0 (CHCH<sub>2</sub>), 35.1 (CHCH<sub>2</sub>), 37.9 (CCHCH<sub>2</sub>), 53.6, 53.7 (OCH<sub>3</sub>), 166.7, 168.7 (C(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 196.7 (CHO).

**Dimethyl-1-diazo-2-oxopropylphosphonate**<sup>3</sup>



To a cold suspension (0-5°C) of NaH (1.150 g, 28.9 mmol) in benzene (50 mL) and THF (8 mL) was added dimethyl 2-oxopropylphosphonate (4.4 g, 26.30 mmol) in benzene (20 mL) and the suspension stirred for 45 min. Tosyl azide (5.70 g, 28.90 mmol) in benzene (10 mL) was added and the reaction mixture stirred for 2 h, whilst warming to room temperature. The mixture was then filtered on a pad of celite and concentrated *in vacuo*, purifying by trituration of the two oils, collecting the *title compound* as a red/orange liquid (5.0 g, 96%);  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2125 (C=N<sub>2</sub>), 1670, 1664, 1654, 1648 (C=O);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.28 (3H, s, CCH<sub>3</sub>), 3.85, 3.88 (3H, s, OCH<sub>3</sub>);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 27.4 (CCH<sub>3</sub>), 53.9, 54.0 (OCH<sub>3</sub>), 190.2, 190.3 (C=O, C=N).

**2-Ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester**<sup>4</sup>



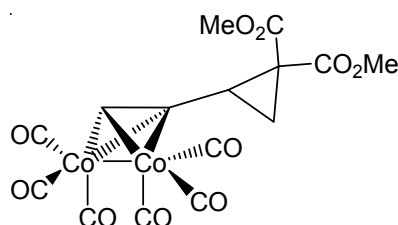
2-Formylcyclopropane-1,1-dicarboxylic acid dimethyl ester (4.4 g, 23.6 mmol) in dry methanol (35 mL) was placed under a nitrogen atmosphere and dimethyl-1-diazo-2-oxopropylphosphonate (9.5 g, 47.2 mmol) was added, followed by K<sub>2</sub>CO<sub>3</sub> (6.5 g, 47.20 mmol). The reaction mixture was stirred for 16 h at ambient temperature and then partitioned between diethyl ether (30 mL) and saturated NaHCO<sub>3</sub> (30 mL). The diethyl ether layer was further washed with distilled water (2 x 30 mL), before drying over MgSO<sub>4</sub> and concentrating *in vacuo* to afford a pale yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the *title compound* as a colourless oil (2.6 g, 60%) (Found: M<sup>+</sup>, 182.0576. C<sub>9</sub>H<sub>10</sub>O<sub>4</sub> requires

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M, 182.0579);  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2957 ( $\text{sp}^3$  C-H), 2124 ( $\text{C}\equiv\text{C}$ ), 1736 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.58 (1H, dd,  $J$  4.5, 9 Hz, CHCHH), 1.85 (1H, dd,  $J$  4.5, 7.5 Hz, CHCHH), 1.96 (1H, d,  $J$  2 Hz,  $\text{CH}_2\text{CH}$ ), 2.46 (1H, ddd,  $J$  2, 7.5, 9.5 Hz, CHCCH), 3.74, 3.80 (3H, s,  $\text{OCH}_3$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 22.3 ( $\text{CHCH}_2$ ), 24.2 ( $\text{CHCH}_2$ ), 36.2 ( $\text{CCHCH}_2$ ), 53.3, 53.5 ( $\text{OCH}_3$ ), 69.1 (CHCCH), 80.0 (CHCCH), 167.1, 169.3 ( $\text{CO}_2\text{CH}_3$ );  $m/z$  185 ( $\text{M}^+$ , 7%), 150 (16), 85 (44), 59 (42), 43 (100).

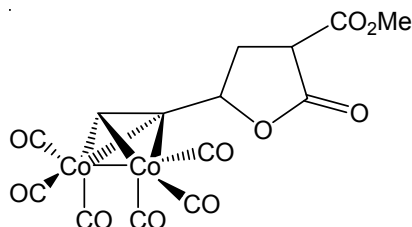
**Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester**

**(1)**



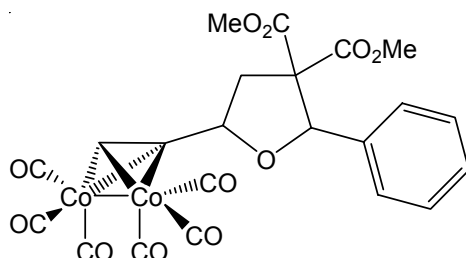
2-Ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.58 g, 3.2 mmol) was added to a RBF and placed under a nitrogen atmosphere, before dissolving in DCM (25 mL). Cobalt octacarbonyl (1.2 g, 3.5 mmol) was added and the reaction mixture stirred for 1.0 h. The reaction mixture was then filtered on a pad of celite and silica, before concentration *in vacuo* and purification of the residue by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a deep red solid (1.55 g, 85%) (Found: C, 38.3; H, 2.1%;  $\text{C}_{15}\text{H}_{10}\text{O}_{10}\text{Co}_2$  requires C, 38.5; H, 2.2%; Found:  $\text{M}^+-2\text{CO}$ , 411.9036.  $\text{C}_{13}\text{H}_{10}\text{O}_8\text{Co}_2$  (M-2CO) requires, 411.9040);  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2094, 2053, 2020 ( $\text{C}\equiv\text{O}$ ), 1736 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.77 (1H, dd,  $J$  4.5, 7.5 Hz, CHCHH), 1.90 (1H, dd,  $J$  4.5, 9 Hz, CHCHH), 3.34 (1H, ddd,  $J$  1, 7.5, 9 Hz,  $\text{CH}_2\text{CH}$ ), 3.77, 3.78 (6H, 2 x s, 2 x  $\text{OCH}_3$ ), 5.68 (1H, d,  $J$  1 Hz, CHCCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 27.0 ( $\text{CHCH}_2$ ), 31.6 ( $\text{CHCH}_2$ ), 41.5 ( $\text{CCH}_2$ ), 53.2, 53.4 ( $\text{OCH}_3$ ), 69.2 ( $\text{CH}_2\text{CH}$ ), 90.9 (CHCCH), 167.6, 169.5 ( $\text{CO}_2\text{CH}_3$ ), 199.5 ( $\text{Co}(\text{CO})_3$ );  $m/z$  412 ( $\text{M}^+-2\text{CO}$ , 9%), 384 (24), 356 (100), 328 (63), 300 (42).

**Dicobalt hexacarbonyl-(3-methoxycarbonyltetrahydrofuran-2-on-5-yl)-ethyne**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.075 g, 0.15 mmol) was added to a flame-dried RBF placed under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). After cooling to 0°C,  $\text{BF}_3 \cdot \text{OEt}_2$  (0.06 mL, 0.46 mmol) was added and the reaction mixture stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo* and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.043 g, 59%, 1:1 d.r.) (Found:  $\text{MH}^+$ , 454.8862.  $\text{C}_{14}\text{H}_8\text{O}_{10}\text{Co}_2$  requires  $\text{MH}$ , 454.8860);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2100, 2060, 2020 ( $\text{C}\equiv\text{O}$ ), 1736 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.24-2.31 (1H, m, CHCHH), 2.50-2.58 (1H, m, CHCHH), 2.91-2.98 (1H, m, CHCHH), 3.07-3.13 (1H, m, CHCHH), 3.74-3.78 (2H, m, 2 x  $\text{CH}_2\text{CH}$ ), 3.84, 3.84 (2 x 3H, s,  $\text{OCH}_3$ ), 5.63 (1H, ddd,  $J$  1, 6.5, 9 Hz,  $\text{OCHCH}_2$ ), 5.80-5.83 (1H, m,  $\text{OCHCH}_2$ ), 6.14 (1H, d,  $J$  1 Hz, CCH), 6.16 (1H, d,  $J$  1 Hz, CCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 34.6, 34.7 ( $\text{CHCH}_2$ ), 46.9, 47.5 ( $\text{CHCH}_2$ ), 53.2, 53.4 ( $\text{OCH}_3$ ), 72.1, 72.3 (CHCCH), 79.0, 80.0 ( $\text{OCHCH}_2$ ), 90.3, 90.8 (CHCCH), 167.7, 167.9 (OCO), 170.4 ( $\text{CO}_2\text{CH}_3$ ), 198.7 ( $\text{Co}(\text{CO})_3$ );  $m/z$  455 ( $\text{MH}^+$ , 20%), 399 (45), 371 (67), 343 (52).

**Dicobalt hexacarbonyl-5-ethynyl-2-phenyltetrahydrofuran-3,3-dicarboxylic acid**  
**dimethyl ester (2a)**

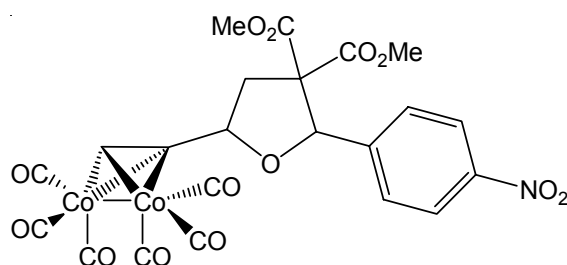


Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.045 g, 0.09 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). Benzaldehyde (0.02 mL, 0.19 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.04 mL, 0.28 mmol) were added and the reaction mixture stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i) 0.019 g, (ii) 0.019 g, 68%, 1:1 d.r.), (i) First eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 517.9454.  $\text{C}_{20}\text{H}_{16}\text{O}_9\text{Co}_2$  (M-2CO) requires, 517.9458);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2054, 2017 (C=O), 1739, 1734, 1730 (C=O);  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 2.25 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.18 (3H, s,  $\text{OCH}_3$ ), 3.34 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.78 (3H, s,  $\text{OCH}_3$ ), 5.76 (1H, app dt,  $J$  1, 7 Hz, CCHCH<sub>2</sub>), 5.81 (1H, s, OCHC), 6.10 (1H, d,  $J$  1 Hz, CHCCH), 7.25-7.35 (3H, m, ArCH), 7.43-7.46 (2H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 43.5 (CHCH<sub>2</sub>C), 52.7, 53.3 ( $\text{OCH}_3$ ), 66.7 (CHCH<sub>2</sub>C), 73.1 (CHCCH), 79.5 (OCHCH<sub>2</sub>), 83.9 (OCHC), 95.5 (CCH), 127.0, 128.3, 128.6 (ArCH), 137.8 (ArC), 169.6, 170.5 ( $\text{CO}_2\text{CH}_3$ ), 199.8 ( $\text{Co}(\text{CO})_3$ );  $m/z$  518 ( $\text{M}^+ - 2\text{CO}$ , 25%), 490 (35), 462 (100), 434 (17), 406 (33). (ii) Second eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 517.9454.  $\text{C}_{20}\text{H}_{16}\text{O}_9\text{Co}_2$  (M-2CO) requires, 517.9458);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2052, 2017 (C=O), 1739, 1734, 1730 (C=O);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.66 (1H, dd,  $J$  6.5, 13 Hz, CHCHH), 2.83 (1H, dd,  $J$  10, 13 Hz, CHCHH), 3.02, 3.75 (6H, 2 x s, 2 x  $\text{OCH}_3$ ), 5.00 (1H, ddd,  $J$  1, 6.5, 10 Hz, OCHCH<sub>2</sub>), 5.67 (1H, s, OCHC), 6.06 (1H, d,  $J$  1 Hz, CHCCH), 7.18-7.24 (3H, m, ArCH), 7.37-7.40 (2H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 41.8 (CHCH<sub>2</sub>C), 51.3, 52.0

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(OCH<sub>3</sub>), 65.0 (CHCH<sub>2</sub>C), 71.0 (CHCCH), 77.0 (OCHCH<sub>2</sub>), 83.4 (OCHC), 91.1 (CCH), 125.8, 126.8, 127.1 (ArCH), 135.8 (ArC), 168.0, 170.2 (CO<sub>2</sub>CH<sub>3</sub>), 199.3 (Co(CO)<sub>3</sub>); *m/z* 518 (M<sup>+</sup>-2CO, 11%), 490 (96), 462 (40), 434 (85), 406 (100).

**Dicobalt hexacarbonyl-5-ethynyl-2-(4-nitrophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (2c)**



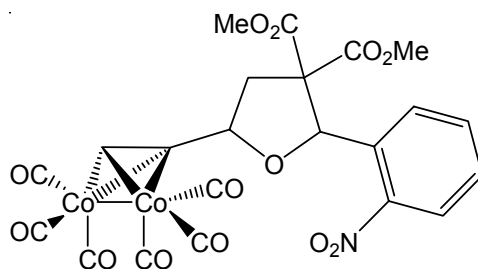
Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.045 g, 0.09 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). 4-Nitrobenzaldehyde (0.028 g, 0.18 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.04 mL, 0.28 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as a deep red solid and a deep red oil ((i) 0.021 g, (ii) 0.021 g, 71%, 1:1 d.r.), (i) First eluting diastereoisomer: m.pt. 124-126°C; (Found: C, 42.6; H, 2.3; N, 2.1%; C<sub>22</sub>H<sub>15</sub>NO<sub>13</sub>Co<sub>2</sub> requires C, 42.7; H, 2.4; N, 2.3%; Found: M<sup>+</sup>-2CO, 562.9306. C<sub>20</sub>H<sub>15</sub>NO<sub>11</sub>Co<sub>2</sub> (M-2CO) requires, 562.9309);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2953 (sp<sup>3</sup> C-H), 2095, 2057, 2017 (C≡O), 1740, 1734, 1730 (C=O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 2.27 (1H, dd, *J* 7.5, 13 Hz, CHCHH), 3.23 (3H, s, OCH<sub>3</sub>), 3.34 (1H, dd, *J* 7.5, 13 Hz, CHCHH), 3.81 (3H, s, OCH<sub>3</sub>), 5.78 (1H, app dt, *J* 1, 7.5 Hz, CCHCH<sub>2</sub>), 5.85 (1H, s, OCHC), 6.10 (1H, d, *J* 1 Hz, CHCCH), 7.69 (2H, d, *J* 8.5 Hz, ArCH), 8.18 (2H, d, *J* 8.5 Hz, ArCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 43.6 (CHCH<sub>2</sub>C), 52.9, 53.6 (OCH<sub>3</sub>), 66.8 (CHCH<sub>2</sub>C), 72.8 (CHCCH), 79.9 (OCHCH<sub>2</sub>), 82.8 (OCHC), 94.7 (CHCCH), 123.5, 128.0 (ArCH), 145.2, 148.1 (ArC), 169.0, 170.1 (CO<sub>2</sub>CH<sub>3</sub>), 199.6 (Co(CO)<sub>3</sub>); *m/z* 563 (M<sup>+</sup>, 25%), 535 (24), 507 (67), 451



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(13). (ii) Second eluting diastereoisomer (Found:  $M^+ - 2CO$ , 562.9320.  $C_{20}H_{15}NO_{11}Co_2$  (M-2CO) requires, 562.9309);  $\nu_{max}$  (film)/ $cm^{-1}$  2095, 2052, 2017 ( $C\equiv O$ ), 1734, 1706, 1700 ( $C=O$ ), 1521, 1346 ( $NO_2$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.82 (1H, dd,  $J$  7, 13.5 Hz, CHCHH), 2.88 (1H, dd,  $J$  10, 13.5 Hz, CHCHH), 3.16, 3.86 (6H, 2 x s, 2 x  $OCH_3$ ), 5.13 (1H, ddd,  $J$  1, 7, 10 Hz, CCHCH<sub>2</sub>), 5.78 (1H, s, OCHC), 6.16 (1H, d,  $J$  1 Hz, CHCCH), 7.69 (2H, d,  $J$  9 Hz, ArCH), 8.17 (2H, d,  $J$  9 Hz, ArCH);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 42.7 (CHCH<sub>2</sub>C), 52.4, 53.2 ( $OCH_3$ ), 66.1 (CHCH<sub>2</sub>C), 72.0 (CHCCH), 78.6 ( $OCHCH_2$ ), 83.2 ( $OCHC$ ), 91.4 (CHCCH), 123.0, 127.8 (2C, s, ArCH), 147.7, 151.1 (ArC), 168.6, 170.8 ( $CO_2CH_3$ ), 199.3 ( $Co(CO)_3$ );  $m/z$  563 ( $M^+ - 2CO$ , 10%), 535 (15), 507 (100), 451 (17).

**Dicobalt hexacarbonyl-5-ethynyl-2-(2-nitrophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (2d)**

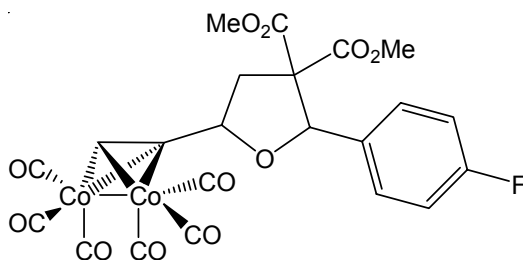


Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). 2-Nitrobenzaldehyde (0.032 g, 0.20 mmol) and  $BF_3 \cdot OEt_2$  (0.04 mL, 0.31 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in *n*-hexane-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i) 0.016 g, (ii) 0.008 g, 30%, 2:1 d.r.), (i) First eluting major diastereoisomer (Found:  $M^+ - CO$ , 590.9244.  $C_{22}H_{15}NO_{12}Co_2$  (M-CO) requires, 590.9258);  $\nu_{max}$  (film)/ $cm^{-1}$  2954 ( $sp^3$  C-H), 2096, 2054, 2025 ( $C\equiv O$ ), 1734 ( $C=O$ ), 1534, 1347 ( $NO_2$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.67 (1H, dd,  $J$  5.5, 13 Hz, CHCHH), 2.91 (1H, dd,  $J$  11, 13 Hz, CHCHH), 3.15, 3.86 (6H, 2 x s, 2 x  $OCH_3$ ), 5.20 (1H, ddd,  $J$  1, 5.5, 11 Hz,

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CCHCH<sub>2</sub>), 6.16 (1H, d, *J* 0.8 Hz, CHCCH), 6.44 (1H, s, OCHC), 7.45 (1H, m, ArCH), 7.58 (1H, m, ArCH), 7.75-7.83 (1H, m, ArCH), 7.94-7.97 (1H, m, ArCH); δ<sub>c</sub> (100 MHz; CDCl<sub>3</sub>) 43.9 (CHCH<sub>2</sub>C), 52.4, 53.3 (OCH<sub>3</sub>), 65.8 (CHCH<sub>2</sub>C), 72.1 (CHCCH), 78.4 (OCHCH<sub>2</sub>), 79.6 (OCHC), 91.1 (CHCCH), 124.3, 128.97, 129.01, 132.7 (ArCH), 148.5, 149.6 (ArC), 168.5, 170.8 (CO<sub>2</sub>CH<sub>3</sub>), 199.2 (Co(CO)<sub>3</sub>); *m/z* 591 (M<sup>+</sup>-CO, 2%), 563 (3), 535 (3), 507 (2), 451 (75). (ii) Second eluting minor diastereoisomer (Found: M<sup>+</sup>-CO, 590.9247. C<sub>20</sub>H<sub>15</sub>NO<sub>12</sub>Co<sub>2</sub> (M-CO) requires, 590.9258); ν<sub>max</sub> (film)/cm<sup>-1</sup> 2095, 2054, 2017 (C≡O), 1734, 1730 (C=O), 1528, 1346 (NO<sub>2</sub>); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>) 2.31 (1H, dd, *J* 7, 13 Hz, CHCHH), 3.27 (3H, s, OCH<sub>3</sub>), 3.35 (1H, dd, *J* 7, 13 Hz, CHCHH), 3.76 (3H, s, OCH<sub>3</sub>), 5.72 (1H, app dt, *J* 1, 7 Hz, CCHCH<sub>2</sub>), 6.10 (1H, d, *J* 1 Hz, CHCCH), 6.48 (1H, s, OCHC), 7.42-7.46 (1H, m, ArCH), 7.57 (1H, m, ArCH), 7.66-7.68 (1H, m, ArCH), 7.82-7.84 (1H, m, ArCH); δ<sub>c</sub> (100 MHz; CDCl<sub>3</sub>) 43.4 (CHCH<sub>2</sub>C), 52.5, 53.1 (OCH<sub>3</sub>), 66.7 (CHCH<sub>2</sub>C), 72.4 (CHCCH), 78.7 (OCHCH<sub>2</sub>), 79.7 (OCHC), not seen (CHCCH), 124.4, 128.6, 129.0, 132.1 (ArCH), 132.2, 149.2 (ArC), 168.7, 169.2 (CO<sub>2</sub>CH<sub>3</sub>), 199.2 (Co(CO)<sub>3</sub>); *m/z* 619 (M<sup>+</sup>, 8%), 591 (21), 563 (45), 535 (23) 451 (61).

**Dicobalt hexacarbonyl-5-ethynyl-2-(4-fluorophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (2e)**

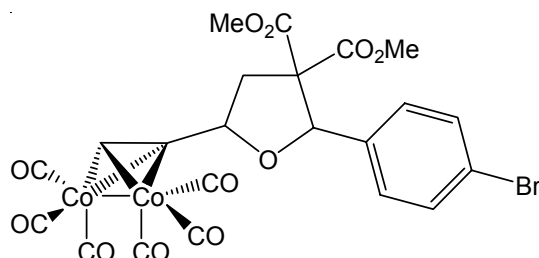


Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.025 g, 0.04 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (5 mL). 4-Fluorobenzaldehyde (0.01 mL, 0.08 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.02 mL, 0.12 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in

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petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i) 0.009, (ii) 0.016 g, 81%, 1:1.7 d.r.), (i) First eluting minor diastereoisomer (Found:  $M^+-2CO$ , 535.9374.  $C_{20}H_{15}FO_9Co_2$  (M-2CO) requires, 535.9364);  $\nu_{max}$  (film)/ $cm^{-1}$  2095, 2055, 2023 ( $C\equiv O$ ), 1740, 1734, 1730 ( $C=O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.17 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.09 (3H, s,  $OCH_3$ ), 3.25 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.71 (3H, s,  $OCH_3$ ), 5.63 (1H, s, OCHC), 5.67 (1H, app dt,  $J$  1, 7 Hz, CCHCH<sub>2</sub>), 6.06 (1H, d,  $J$  1 Hz, CHCCH), 6.89-6.95 (2H, m, ArCH), 7.36-7.39 (2H, m, ArCH);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 43.0 (CHCH<sub>2</sub>C), 52.4, 52.9 ( $OCH_3$ ), 66.1 (CHCH<sub>2</sub>C), 72.6 (CHCCH), 79.0 (OCHCH<sub>2</sub>), 82.8 (OCHC), 94.9 (CHCCH), 114.8 (2C, d,  $^2J_{C-F}$  21.0 Hz, ArCH), 128.3 (2C, d,  $^3J_{C-F}$  9.0 Hz, ArCH), 133.0 (1C, d,  $^4J_{C-F}$  3.0 Hz, ArC), 162.6 (1C, d,  $^1J_{C-F}$  245.0 Hz, ArC), 169.1, 170.0 ( $CO_2CH_3$ ), 199.3 ( $Co(CO)_3$ );  $m/z$  536 ( $M^+-2CO$ , 14%), 508 (15), 480 (100), 452 (25), 452 (25), 424 (28), 365 (20). (ii) Second eluting major diastereoisomer (Found:  $M^+-2CO$ , 535.9361.  $C_{20}H_{15}FO_9Co_2$  (M-2CO) requires, 535.9364);  $\nu_{max}$  (film)/ $cm^{-1}$  2096, 2054, 2026 ( $C\equiv O$ ), 1734 ( $C=O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.67 (1H, dd,  $J$  6.5, 13.5 Hz, CHCHH), 2.80 (1H, dd,  $J$  10, 13.5 Hz, CHCHH), 3.16, 3.75 (6H, 2 x s, 2 x  $OCH_3$ ), 4.99 (1H, ddd,  $J$  1, 6.5, 10 Hz, OCHCH<sub>2</sub>), 5.70 (1H, s, OCHC), 6.06 (1H, d,  $J$  1 Hz, CHCCH), 6.89-6.95 (2H, m, ArCH), 7.36-7.39 (2H, m, ArCH);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 42.7 (CHCH<sub>2</sub>C), 52.3, 53.0 ( $OCH_3$ ), 65.9 (CHCH<sub>2</sub>C), 72.0 (CHCCH), 78.0 (OCHCH<sub>2</sub>), 83.8 (OCHC), 91.9 (CHCCH), 114.7 (2C, d,  $^2J_{C-F}$  21.0 Hz, ArCH), 128.6 (2C, d,  $^3J_{C-F}$  8.0 Hz, ArCH), 132.6 (1C, d,  $^4J_{C-F}$  3.0 Hz, ArC), 162.6 (1C, d,  $^1J_{C-F}$  245.0 Hz, ArC), 169.0, 171.1 ( $CO_2CH_3$ ), 199.3 ( $Co(CO)_3$ );  $m/z$  536 ( $M^+-2CO$ , 31%), 508 (45), 480 (100), 452 (16), 424 (20).

**Dicobalt hexacarbonyl-5-ethynyl-2-(4-bromophenyl)tetrahydrofuran-3,3-**  
**dicarboxylic acid dimethyl ester (2f)**

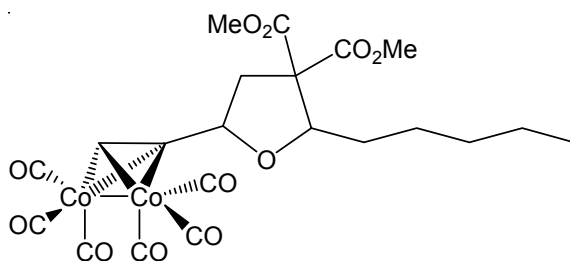


Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). 4-Bromobenzaldehyde (0.038 g, 0.20 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.04 mL, 0.29 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as a deep red oil (0.021 g, 0.021 g, 61%, 1:1 d.r.) (i) First eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 595.8568.  $\text{C}_{20}\text{H}_{15}^{79}\text{BrO}_9\text{Co}_2$  (M-2CO) requires, 595.8563);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2053, 2017 (C $\equiv$ O), 1740, 1734, 1730 (C=O), 1072, 1037 (C-O);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.23 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.25 (3H, s,  $\text{OCH}_3$ ), 3.31 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.78 (3H, s,  $\text{OCH}_3$ ), 5.71-5.75 (2H, m,  $\text{OCHCH}_2$ ,  $\text{OCHC}$ ), 6.09 (1H, d,  $J$  1 Hz, CHCCH), 7.34 (2H, d,  $J$  8 Hz, ArCH), 7.44 (2H, d,  $J$  8 Hz, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 43.1 (CHCH $_2$ C), 52.4, 52.9 ( $\text{OCH}_3$ ), 66.1 (CHCH $_2$ C), 72.5 (CHCCH), 79.1 (OCHCH $_2$ ), 82.9 (OCHC), 94.9 (CHCCH), 122.1 (ArC), 128.3, 131.0 (ArCH), 136.4 (ArC), 168.9, 169.9 ( $\text{CO}_2\text{CH}_3$ ), 199.2 ( $\text{Co}(\text{CO})_3$ );  $m/z$  598 ( $\text{M}^+ - 2\text{CO}$  ( $^{81}\text{Br}$ ), 22%), 595 (21), 569 (27), 567 (25), 541 (100), 539 (98), 485 (30), 483 (30). (ii) Second eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 595.8550.  $\text{C}_{20}\text{H}_{15}^{79}\text{BrO}_9\text{Co}_2$  (M-2CO) requires, 595.8563);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2095, 2054, 2023 (C $\equiv$ O), 1740, 1734, 1730 (C=O), 1066, 1035 (C-O);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.74 (1H, dd,  $J$  6.5, 13 Hz, CHCHH), 2.86 (1H, dd,  $J$  10, 13 Hz, CHCHH), 3.17, 3.83 (6H, 2 x s, 2 x  $\text{OCH}_3$ ), 5.07 (1H, ddd,  $J$  1, 6.5, 10 Hz, CCHCH $_2$ ), 5.67 (1H, s, OCHC), 6.12 (1H, d,  $J$  1

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Hz, CHCCH), 7.31 (2H, d,  $J$  8.5 Hz, ArCH), 7.43 (2H, d,  $J$  8.5 Hz, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 42.7 (CHCH<sub>2</sub>C), 52.4, 53.1 (OCH<sub>3</sub>), 65.9 (CHCH<sub>2</sub>C), 72.0 (CHCCH), 78.2, (OCHCH<sub>2</sub>), 83.8 (OCHC), 91.9 (CHCCH), 122.2 (ArC), 128.6, 131.0 (ArCH), 135.9 (ArC), 168.9, 171.0 (CO<sub>2</sub>CH<sub>3</sub>), 199.3 (Co(CO)<sub>3</sub>);  $m/z$  598 (M<sup>+</sup>-2CO (<sup>81</sup>Br), 5%), 569 (68), 567 (65), 513 (62), 511 (56), 485 (99), 483 (100).

**Dicobalt hexacarbonyl-5-ethynyl-2-pentyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (2g)**

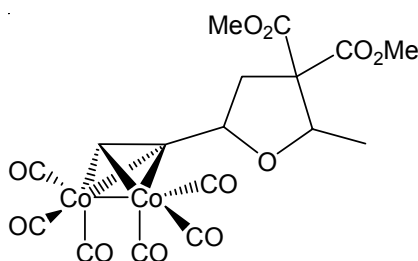


Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.060 g, 0.12 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). Hexanal (0.03 mL, 0.25 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.05 mL, 0.37 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.064 g, 83%, 1:1 d.r.) (Found: M<sup>+</sup>-2CO, 511.9938. C<sub>19</sub>H<sub>22</sub>O<sub>9</sub>Co<sub>2</sub> (M-2CO) requires, 511.9928);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2095, 2055, 2017 (C≡O), 1740, 1734, 1730 (C=O);  $\delta_H$  (400 MHz; CDCl<sub>3</sub>) 0.84-0.88 (6H, m, 2 x CHCH<sub>3</sub>), 1.26-1.36 (12H, m, 2 x CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.52-1.62 (4H, m, 2 x CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>), 2.08 (1H, dd,  $J$  7, 13 Hz, CHCHH), 2.60 (1H, dd,  $J$  10, 13 Hz, CHCHH), 2.72 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.16 (1H, dd,  $J$  7, 13 Hz, CHCHH), 3.74, 3.75, 3.78, 3.79 (12H, 4 x s, 4 x OCH<sub>3</sub>), 4.45-4.50 (2H, m, 2 x OCHCH<sub>2</sub>), 4.89 (1H, ddd,  $J$  1, 7, 10 Hz, OCHC), 5.45 (1H, dt,  $J$  1, 7 Hz, OCHC), 6.03 (1H, d,  $J$  1 Hz, CHCCH), 6.05 (1H, d,  $J$  1 Hz, CHCCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 14.0 (2 x CH<sub>2</sub>CH<sub>3</sub>), 22.5 (2 x CH<sub>2</sub>CH<sub>3</sub>), 26.4, 26.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.6, 31.65, 31.66, 31.8

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(CHCH<sub>2</sub>CH<sub>2</sub>), 42.5, 43.0 (CHCH<sub>2</sub>C), 52.4, 52.5, 52.8, 52.9 (OCH<sub>3</sub>), 63.7, 64.0 (CHCH<sub>2</sub>C), 71.6, 72.1 (CHCCH), 77.5, 78.1 (OCHCH<sub>2</sub>), 82.4, 82.9 (OCHC), 93.7, 96.3 (CHCCH), 169.82, 169.84, 169.9, 171.1 (CO<sub>2</sub>CH<sub>3</sub>), 199.4 (Co(CO)<sub>3</sub>); *m/z* 512 (M<sup>+</sup>-2CO, 17%), 584 (17), 456 (53).

**Dicobalt hexacarbonyl-5-ethynyl-2-methyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (2h)**

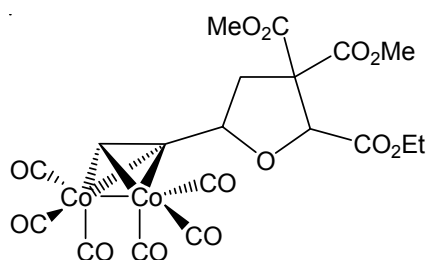


Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF, placed under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). Acetaldehyde (0.30 mL, 0.20 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.04 mL, 0.30 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.036 g, 65%, 1:1 d.r.) (Found: M<sup>+</sup>-2CO, 455.9306. C<sub>15</sub>H<sub>14</sub>O<sub>9</sub>Co<sub>2</sub> (M-2CO) requires, 455.9302);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2094, 2053, 2017 (C≡O), 1740, 1734, 1730 (C=O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 1.27 (3H, d, *J* 6.5 Hz, CHCH<sub>3</sub>), 1.31 (3H, d, *J* 6.5 Hz, CHCH<sub>3</sub>), 2.12 (1H, dd, *J* 7, 13 Hz, CHCHH), 2.65 (1H, dd, *J* 9.5, 13 Hz, CHCHH), 2.74 (1H, dd, *J* 7, 13 Hz, CHCHH), 3.17 (1H, dd, *J* 7, 13 Hz, CHCHH), 3.758, 3.761, 3.79, 3.80 (12H, 4 x s, 4 x OCH<sub>3</sub>), 4.64 (1H, q, *J* 6.5 Hz, OCHCH<sub>3</sub>), 4.66 (1H, q, *J* 6.5 Hz, OCHCH<sub>3</sub>), 4.93 (1H, ddd, *J* 1, 7, 9.5 Hz, CCHCH<sub>2</sub>), 5.45 (1H, dt, *J* 1.0, 7 Hz, CCHCH<sub>2</sub>), 6.05 (1H, d, *J* 1 Hz, CHCCH), 6.06 (1H, d, *J* 1.0 Hz, CHCCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 16.3, 17.0 (CHCH<sub>3</sub>), 42.1, 42.7 (CHCH<sub>2</sub>), 52.6, 52.7, 52.8, 53.0 (OCH<sub>3</sub>),

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63.8, 64.0 (CHCH<sub>2</sub>C), 72.0, 72.4 (CHCCH), 77.5, 77.8 (OCHCH<sub>2</sub>), 78.1, 78.9 (OCHC),  
93.5, 96.0 (CHCCH), 169.6, 169.69, 169.74, 171.1 (CO<sub>2</sub>CH<sub>3</sub>), 199.4 (Co(CO)<sub>3</sub>); *m/z* 456  
(M<sup>+</sup>-2CO, 100%), 428 (84), 400 (100), 372 (37), 344 (38).

**Dicobalt hexacarbonyl-5-ethynyltetrahydrofuran-2,3,3-tricarboxylic acid 2-ethyl  
ester 3,3-dimethyl ester (2i)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.052 g, 0.11 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). Ethyl glyoxylate (0.04 mL, 0.21 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.04 mL, 0.31 mmol) were added, the reaction mixture was heated to reflux and stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.052 g, 85%, 1.6:1 d.r.) (Found: M<sup>+</sup>-2CO, 513.9366. C<sub>17</sub>H<sub>16</sub>O<sub>11</sub>Co<sub>2</sub> (M-2CO) requires, 513.9357);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2096, 2054, 2017 (C≡O), 1751, 1740, 1734 (C=O); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.21 (3H, t, *J* 8.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.32 (1H, dd, *J* 7.5, 13 Hz, CHCHH), 3.24 (1H, dd, *J* 7.5, 13 Hz, CHCHH), 3.69, 3.75 (6H, 2 x s, 2 x OCH<sub>3</sub>), 4.08-4.15 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 5.15 (1H, s, OCHC), 5.58 – 5.68 (1H, m, CCHCH<sub>2</sub>), 6.07 (1H, d, *J* 1 Hz, CHCCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 14.0 (CH<sub>2</sub>CH<sub>3</sub>), 42.2 (CHCH<sub>2</sub>C), 53.3, 53.4 (OCH<sub>3</sub>), 61.5 (CH<sub>2</sub>CH<sub>3</sub>), 64.6 (CHCH<sub>2</sub>C), 72.7 (CHCCH), 79.8 (OCHCH<sub>2</sub>), 81.4 (OCHC), 93.3 (CHCCH), 168.3, 169.2, 169.5 (CO<sub>2</sub>R), 199.1 (Co(CO)<sub>3</sub>); (ii) Minor diastereoisomer  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.20 (3H, t, *J* 7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.67 (1H, dd, *J* 10,

# Supplementary Material (ESI) for Chemical Communications

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13 Hz, CHCHH), 2.84 (1H, dd,  $J$  6, 13 Hz, CHCHH), 3.66, 3.79, (6H, 2 x s, 2 x OCH<sub>3</sub>), 4.08-4.15 (2H, m, OCH<sub>2</sub>CH<sub>3</sub>), 5.03 (1H, s, OCHC), 5.11 (1H, ddd,  $J$  1, 6, 10 Hz, CCHCH<sub>2</sub>), 6.07 (1H, d,  $J$  1 Hz, CHCCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 13.9 (CH<sub>2</sub>CH<sub>3</sub>), 41.4 (CHCH<sub>2</sub>C), 53.1, 53.7 (OCH<sub>3</sub>), 61.5 (CH<sub>2</sub>CH<sub>3</sub>), 64.6 (CHCH<sub>2</sub>C), 72.4 (CHCCH), 80.0 (OCHCH<sub>2</sub>), 81.3 (OCHC), 92.1 (CHCCH), 167.8, 169.1, 169.2 (CO<sub>2</sub>R), 199.1 (Co(CO)<sub>3</sub>);  $m/z$  514 (M<sup>+</sup>-2CO, 10%), 486 (42), 458 (100), 430 (18), 402 (59).

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2. C. Chen, Y. Liao, Y.-Z. Huang, *Tetrahedron*, 1989, **45**, 3011-3020.
3. P. Callant, L. D'Haenens, M. Vandewalle, *Synth Commun*, 1984, **14**, 155.
4. This procedure is adapted from: S. Müller, B. Liepold, G.J. Roth, H.J. Bestmann, *Synlett*, 1996, 521-522.