Preparation of Highly Substituted Pyrrolidines via an Organometallic Dipole

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General information

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

Dichloromethane (DCM)	For general use CH_2Cl_2 was distilled over boiling stones, or over CaH_2 for anhydrous reactions.
Dimethyl sulfide	Purchased from Aldrich (99+%) and used without further purification.
n-Hexane	Purchased from Fischer Scientific (99+%), used without purification for general use.
Light petroleum	Distilled over $CaCl_2$ for general use, collecting the fraction distilling below 60°C.
$Co_2(CO)_8$	Purchased from Strem (stabilised by 1-5% hexane), used without any further purification.

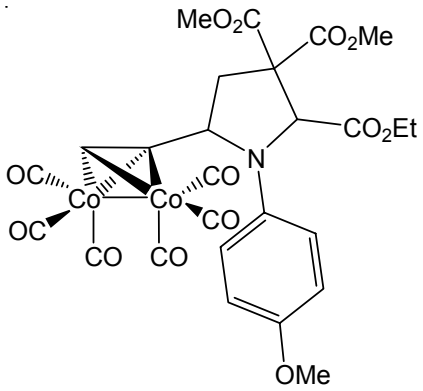
Glassware for anhydrous reactions was thoroughly flame-dried under an atmosphere of nitrogen.

All metal carbonyl complexes were stored under a nitrogen atmosphere and kept at -18°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 3-nitrobenzyl alcohol was used to dissolve the compounds under investigation, prior to ionisation. Nuclear magnetic resonance spectra were 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 $CHCl_3$ present in $CDCl_3$, typically used as the standard solvent for these experiments. Where possible coupling constants (*J* Hz) are shown for ^1H NMR signals, also denoting their multiplicity as a singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) or broad signal (br) etc. Combustion analysis was carried out using a Perkin Elmer CHN 2400 elemental analyser. Fourier transform Infrared spectroscopy was recorded using a Paragon 1000 Perkin Elmer FT-IR spectrometer in the range of 3500-600cm^{-1} following a standard background correction. Melting points of solid products was recorded using a Stuart Scientific SMP3 instrument.

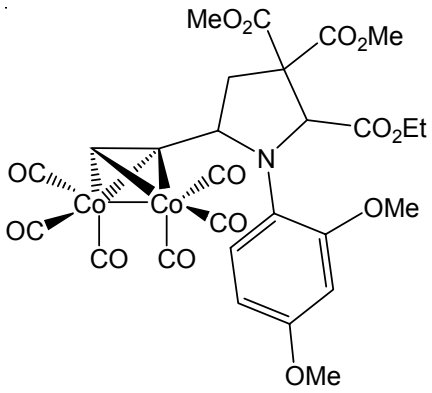
Flash column chromatography on silica was used as a standard purification procedure using Fluka Kieselgel 60, 0.04-0.063 mm particle size silica. Thin layer chromatography was used where possible as a standard procedure for monitoring the course and rate of a given reaction. TLC plates used were Merck aluminium backed sheets with Kieselgel 60 F_{254} silica coating.

Ethyl dicobalt hexacarbonyl-5-ethynyl-3,3-bis(methoxycarbonyl)-1-(4-methoxyphenyl)pyrrolidine-2-carboxylate (5a)



Dimethyl dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylate **1** (0.050 g, 0.10 mmol) was added to a flame-dried round-bottom flask under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). Ethyl (4-methoxyphenylimino)acetate (0.040 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, concentrated *in vacuo*, and the residue purified by flash column chromatography on silica eluting in light petroleum-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers **5a** as a deep red oil (0.063 g, 91%, 1:1 d.r.) (Found: M^+-2CO, 618.9928. $C_{26}H_{22}O_{13}Co_2N$ requires M-2CO, 618.9935); ν_{max} (film)/cm^{-1} 2092, 2053, 2023 (C≡O), 1751, 1743, 1740, 1734, 1730 (C=O); δ_H (400 MHz; $CDCl_3$) 1.02 (3H, t, *J* 6.8 Hz, CH_2CH_3), 1.31 (3H, t, *J* 7.2 Hz, CH_2CH_3), 2.82 (1H, dd, *J* 4.4, 14.0 Hz, CHCH*H*), 3.00 (1H, dd, *J* 6.2, 12.8 Hz, CHCH*H*), 3.28 (1H, dd, *J* 10.2, 12.8 Hz, CHC*H*H), 3.56 (1H, dd, *J* 9.4, 14.0 Hz, CHC*H*H), 3.72, 3.74, 3.76, 3.77, 3.78, 3.86 (each 3H, s, OCH_3), 3.92-3.96 (2H, m, CH_2CH_3), 4.20-4.23 (2H, m, CH_2CH_3), 4.73 (1H, s, NC*H*C), 4.87 (1H, dd, *J* 6.2, 10.2 Hz, NC*H*CH_2), 5.26 (1H, s, NC*H*C), 5.28 (1H, dd, *J* 4.4, 9.4 Hz, NC*H*CH_2), 5.75 (1H, d, *J* 0.9 Hz, CHCC*H*), 6.06 (1H, d, *J* 1.2 Hz, CHCC*H*), 6.81-6.95 (8H, m, ArC*H*); δ_c (100 MHz; $CDCl_3$) 14.0, 14.1 (CH_2CH_3), 39.6, 40.3 ($CHCH_2C$), 53.0, 53.3, 53.56, 53.63 (CO_2CH_3), 55.4, 55.5 ($ArOCH_3$), 58.7, 59.0 ($CHCH_2C$), 60.9, 61.5 (CH_2CH_3), 61.4, 61.8 (NCHC), 70.7, 71.6 (NCHCH$_2$), 75.5, 76.1 (CHCCH), 94.6, 96.2 (CHCCH), 114.0, 114.3, 116.0, 121.8 (ArCH), 137.3, 140.5, 153.2, 154.9 (ArC), 168.0, 168.6, 169.73, 169.74, 170.0, 170.7 (CO_2R), 199.5 ($Co(CO)_3$); *m/z* 619 (M^+-2CO, 8%), 591 (26), 563 (100), 535 (34), 507 (54).

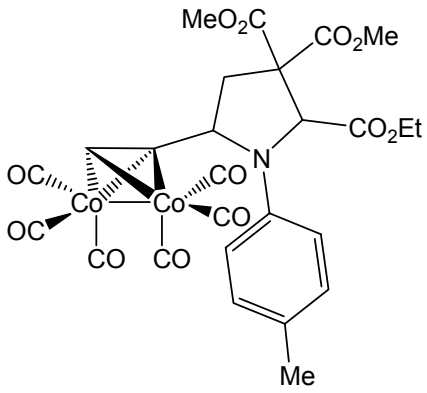
Ethyl dicobalt hexacarbonyl-5-ethynyl-3,3-bis(methoxycarbonyl)-1-(2,4-dimethoxyphenyl)pyrrolidine-2-carboxylate (5b)



Dimethyl dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylate **1** (0.025 g, 0.05 mmol) was added to a flame-dried round-bottom flask under an atmosphere of nitrogen and dissolved in dry DCM (6 mL). Ethyl (2,4-dimethoxyphenylimino)acetate (0.024 g, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (0.02 mL, 0.15 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, concentrated *in vacuo*, and the residue purified by flash column chromatography on silica eluting in light petroleum-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers **5b** as deep red oils ((i) 0.020 g, (ii) 0.010 g, 78%, 2:1 d.r.), (i) First eluting, major diastereoisomer (Found: M^+-3CO, 621.0099. $C_{27}H_{25}O_{14}Co_2N$ requires M-3CO, 621.0092); ν_{max} (film)/cm^{-1} 2953 (sp^3 C-H), 2092, 2052, 2023 (C≡O), 1740, 1734 (C=O); δ_H (250 MHz; $CDCl_3$) 1.01 (3H, t, *J* 7.1 Hz, CH_2CH_3), 2.83 (1H, dd, *J* 5.4, 13.6 Hz, CHCH*H*), 3.43 (1H, dd, *J* 9.4, 13.6 Hz, CHC*H*H), 3.72, 3.73, 3.79, 3.84 (each 3H, s, OCH_3), 3.93 (2H, q, *J* 7.1 Hz, CH_2CH_3), 5.33 (1H, dd, *J* 5.4, 9.4 Hz, NC*H*CH_2), 5.41 (1H, s, NC*H*C), 5.62 (1H, s, CHCC*H*), 6.38-6.42 (2H, m, ArC*H*), 6.90 (1H, d, *J* 8.3 Hz, ArC*H*); δ_c (100 MHz; $CDCl_3$) 14.0 (CH_2CH_3), 38.8 ($CHCH_2C$), 53.1, 53.3 (CO_2CH_3), 55.2, 55.4 ($ArOCH_3$), 59.0 (N*C*HCH_2), 60.5 (CH_2CH_3), 61.5 ($CHCH_2C$), 69.2 (*C*HCCH), 76.1 (N*C*HC), 96.3 (CH*C*CH), 99.4 (2C, s, Ar*C*H), 103.0 (Ar*C*H), 125.6, 155.0, 157.0 (Ar*C*), 169.1, 169.7, 170.0 (CO_2R), 199.3, 199.7 ($Co(CO)_3$); *m/z* 621 (M^+-3CO, 9%), 593 (100), 565 (8), 537 (52). (ii) Second eluting, minor diastereoisomer (Found: M^+-3CO, 621.0099. $C_{27}H_{25}O_{14}Co_2N$ requires M-3CO, 621.0092); ν_{max} (film)/cm^{-1} 2955 (sp^3 C-H), 2093, 2053, 2023 (C≡O), 1740, 1734 (C=O); δ_H (400 MHz; $CDCl_3$) 1.29 (3H, t, *J*

7.2 Hz, CH_2CH_3), 2.87 (1H, dd, *J* 5.9, 12.5 Hz, CHCH*H*), 3.01 (1H, dd, *J* 10.7, 12.5 Hz, CHC*H*H), 3.60, 3.73, 3.78, 3.79 (each 3H, s, OCH_3), 4.09-4.26 (2H, m, CH_2CH_3), 4.65 (1H, s, NC*H*C), 4.87 (1H, dd, *J* 5.9, 10.7 Hz, NC*H*CH_2), 5.86 (1H, d, *J* 0.9 Hz, CHCC*H*), 6.39-6.44 (2H, m, ArC*H*), 6.82-6.86 (1H, m, ArC*H*); δ_c (100 MHz; $CDCl_3$) 14.3 (CH_2CH_3), 38.9 ($CHCH_2C$), 53.0, 53.4 (CO_2CH_3), 54.7, 55.5 ($ArOCH_3$), 59.3 ($NCHCH_2$), 61.0 (CH_2CH_3), 62.4 ($CHCH_2C$), 71.5 (*C*HCCH), 75.1 (N*C*HC), 94.7 (CH*C*CH), 99.7, 103.3, 120.6 (Ar*C*H), 129.1, 153.7, 156.2 (Ar*C*), 168.0, 169.9, 171.6 (CO_2R), 199.4, 199.7 ($Co(CO)_3$); *m/z* 621 (M^+-3CO, 3%), 593 (100), 565 (3), 537 (15).

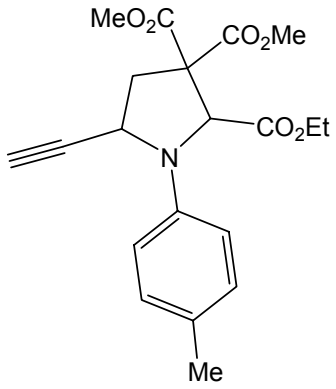
Ethyl dicobalt hexacarbonyl-5-ethynyl-3,3-bis(methoxycarbonyl)-1-(4-methylphenyl)pyrrolidine-2-carboxylate (5c)



Dimethyl dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylate **1** (0.050 g, 0.10 mmol) was added to a flame-dried round-bottom flask under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). Ethyl (4-methylphenylimino)acetate (0.041 g, 0.21 mmol) and $BF_3{\cdot}OEt_2$ (0.04 mL, 0.31 mmol) were added, the reaction mixture heated to reflux and stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash column chromatography on silica eluting in *n*-hexane-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers **5c** as a deep red oil (0.062 g, 89%, 1:1 d.r.) (Found: M^+ 658.9893. $C_{26}H_{23}O_{12}Co_2N$ requires M, 658.9884); ν_{max} (film)/cm^{-1} 2093, 2054, 2017 (C≡O), 1751, 1743, 1740, 1730 (C=O); δ_H (400 MHz; $CDCl_3$) 0.94 (3H, t, *J* 7.0 Hz, CH_2CH_3), 1.23 (3H, t, *J* 7.2 Hz, CH_2CH_3), 2.20 (6H, s, 2

x ArCH_3), 2.73 (1H, dd, *J* 4.0, 13.6 Hz, CHCH*H*), 2.94 (1H, dd, *J* 6.4, 12.9 Hz, CHCH*H*), 3.20 (1H, dd, *J* 10.0, 12.9 Hz, CHC*H*H), 3.50 (1H, dd, *J* 9.6, 13.6 Hz, CHC*H*H), 3.63, 3.66, 3.68, 3.78 (each 3H, s, OCH_3), 3.82-3.91 (2H, m, CH_2CH$_3$), 4.10-4.17 (2H, m, CH_2CH$_3$), 4.71 (1H, s, NC*H*C), 4.82 (1H, dd, *J* 6.4, 10.0 Hz, NC*H*CH$_2$), 5.24 (1H, dd, *J* 4.0, 9.6 Hz, NC*H*CH$_2$), 5.28 (1H, s, NC*H*C), 5.72 (1H, d, *J* 0.4 Hz, CHCC*H*), 6.01 (1H, d, *J* 0.4 Hz, CHCC*H*), 6.73-6.79 (4H, m, ArC*H*), 6.97-7.01 (4H, m, ArC*H*); δ_c (100 MHz; $CDCl_3$) 12.9, 13.0 (CH$_2$*C*H$_3$), 19.4, 19.6 (Ar*C*H$_3$), 38.7, 39.3 (CH*C*H$_2$C), 52.0, 52.3, 52.5, 52.6 (CO$_2$*C*H$_3$), 57.6, 57.8 (N*C*HCH$_2$), 60.0, 60.5 (*C*H$_2$CH$_3$), not seen (CHCH$_2$*C*), 69.2, 69.8 (N*C*HC), 74.7, 75.2 (*C*HCCH), 93.6, 95.2 (CH*C*CH), 113.6, 118.6 (Ar*C*H), 127.5, 129.8 (Ar*C*), 128.3, 128.5 (Ar*C*H), 140.6, 143.1 (Ar*C*), 167.0, 167.5, 168.6, 168.7, 168.9, 169.6 (*C*O$_2$R), 198.3 (Co(*C*O)$_3$); *m/z* 659 (M^+, 3%), 603 (3), 575 (14), 547 (13), 501 (3).

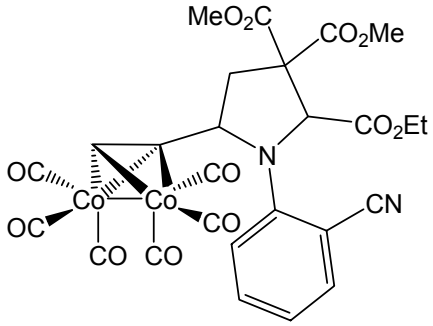
Ethyl 5-ethynyl-3,3-bis(methoxycarbonyl)-1-(4-methylphenyl)pyrrolidine-2-carboxylate (6)



Ethyl dicobalt hexacarbonyl-5-ethynyl-3,3-bis(methoxycarbonyl)-1-(4-methylphenyl)pyrrolidine-2-carboxylate **5c** (0.100 g, 0.15 mmol) in acetone (10 mL) was added to a round-bottom flask and cooled to -78°C. Triethylamine (0.10 mL) and ceric ammonium nitrate (0.416 g, 0.76 mmol) were added and the reaction mixture stirred for 18.0 h, whilst warming to ambient temperature. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash column chromatography on silica eluting in light petroleum-diethyl ether (4:1 v/v) to yield the two separable *title complex* diastereoisomers as colourless

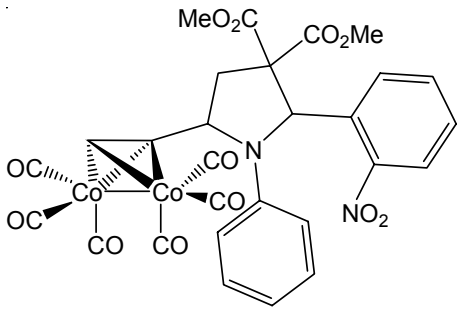
oils ((i) 0.016 g, (ii) 0.016 g, 57%, 1:1 d.r.), (i) First eluting diastereoisomer (Found: M^+, 373.1524. $C_{20}H_{23}NO_6$ requires M, 373.1525); ν_{max} (film)/cm^{-1} 3277 (sp C-H), 1741 (C=O), 1521, 802 (ArC-H); δ_H (400 MHz; $CDCl_3$) 1.11 (3H, t, *J* 7.0 Hz, CH_2CH_3), 2.17 (3H, s, $ArCH_3$), 2.20 (1H, d, *J* 1.6 Hz, CC*H*), 2.81 (1H, d, *J* 13.2 Hz, CHCH*H*), 3.16 (1H, dd, *J* 9.2, 13.2 Hz, CHC*H*H), 3.69, 3.72 (3H, s, OCH_3), 3.91-4.41 (2H, m, CH_2CH_3), 4.55-4.58 (1H, m, $NCHCH_2$), 5.17 (1H, s, NC*H*C), 6.58 (2H, d, *J* 8.4 Hz, ArC*H*), 6.98 (2H, d, *J* 8.4 Hz, ArC*H*); δ_c (100 MHz; $CDCl_3$) 14.1 (CH_2CH_3), 20.3 ($ArCH_3$), 38.0 ($CHCH_2C$), 48.2 ($NCHCH_2$), 53.3, 53.4 (CO_2CH_3), 61.6 (OCH_2CH_3), 62.5 ($CHCH_2C$), 65.2 (N*C*HC), 71.9 (*C*HCCH), 82.8 (CH*C*CH), 113.3 (Ar*C*H), 127.5 (Ar*C*), 129.7 (Ar*C*H), 141.7 (Ar*C*), 167.7, 168.9, 170.5 (CO_2R); *m/z* 373 (M^+, 18%), 354 (6), 314 (7), 301 (22), 300 (100), 241 (14). (ii) Second eluting diastereoisomer ν_{max} (film)/cm^{-1} 2923 (sp^3 C-H), 1734, 1718 (C=O), 1517 (ArC-H); δ_H (400 MHz; $CDCl_3$) 1.20 (3H, t, *J* 7.1 Hz, CH_2CH_3), 2.33 (4H, s, CC*H*, $ArCH_3$), 3.04 (1H, d, *J* 17.2 Hz, CHCH*H*), 3.58 (1H, d, *J* 17.2 Hz, CHC*H*H), 3.78, 3.85 (3H, s, OCH_3), 4.08-4.18 (3H, m, $NCHCH_2$, CH_2CH_3), 5.31 (1H, s, NC*H*C), 7.18 (2H, d, *J* 8.3 Hz, ArC*H*), 7.30 (2H, d, *J* 8.3 Hz, ArC*H*); δ_c (100 MHz; $CDCl_3$) 14.0 (CH_2CH_3), 21.0 ($ArCH_3$), 38.0 ($NCHCH_2$), 42.8 ($CHCH_2C$), 53.6, 54.0 (CO_2CH_3), 57.4 ($CHCH_2C$), 62.3 (N*C*HC), 66.6 (OCH_2CH_3), 79.2 (*C*HCCH), 88.6 (CH*C*CH), 123.6 (2C, s, Ar*C*H), 129.8 (2C, s, Ar*C*H), 132.5, 136.7 (Ar*C*), 167.5, 168.5, 170.1 (CO_2R).

Ethyl dicobalt hexacarbonyl-1-(2-cyanophenyl)-5-ethynyl-3,3-bis(methoxycarbonyl)pyrrolidine-2-carboxylate (5d)



Dimethyl dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylate **1** (0.070 g, 0.14 mmol) was added to a flame-dried round-bottom flask under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). Ethyl (2-cyanophenylimino)acetate (0.059 g, 0.29 mmol) and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.43 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, concentrated *in vacuo*, and the residue purified by flash column chromatography on silica eluting in light petroleum-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers **5d** as a deep red oil (0.050 g, 52%, 3:1 d.r.) (Found: M^+-3CO, 585.9829. $C_{26}H_{20}O_{12}Co_2N_2$ requires M-3CO, 585.9833); ν_{max} (film)/cm^{-1} 2955 (sp^3 C-H), 2213 (C≡N), 2094, 2055, 2023 (C≡O), 1740, 1734, 1730 (C=O); Assigned from combined spectrum (i) Major diastereoisomer δ_H (250 MHz; $CDCl_3$) 1.31 (3H, t, *J* 8.0 Hz, CH_2CH_3), 2.92-3.00 (1H, m, CHCH*H*), 3.08 (1H, dd, *J* 10.0, 12.8 Hz, CHC*H*H), 3.77, 3.78 (each 3H, s, OCH_3), 4.15-4.31 (2H, m, CH_2CH_3), 5.09 (1H, d, *J* 0.9 Hz, NC*H*C), 5.30 (1H, dd, *J* 6.9, 10.0 Hz, NC*H*CH_2), 6.11 (1H, d, *J* 0.9 Hz, CHCC*H*), 6.70-6.76 (1H, m, ArC*H*), 6.94-6.99 (1H, m, ArC*H*), 7.29-7.62 (2H, m, ArC*H*); δ_c (100 MHz; $CDCl_3$) 14.0 (CH_2CH_3), 39.9 ($CHCH_2C$), 53.2, 53.78 (CO_2CH_3), 58.4 (N*C*HCH_2), 62.2 (CH_2CH_3), 62.5 ($CHCH_2C$), 71.0 (*C*HCCH), 75.7 (N*C*HC), 100.5 (CH*C*CH), 117.6 (Ar*C*H), 119.0 (C*C*N), 120.6, 133.3, 135.6 (Ar*C*H), 148.5, 149.7 (Ar*C*), 166.9, 169.2, 169.9 (CO_2R), 199.1, 199.3 ($Co(CO)_3$). (ii) Minor diastereoisomer δ_H (250 MHz; $CDCl_3$) 0.87 (3H, t, *J* 6.0 Hz, CH_2CH_3), 2.32-2.44 (1H, m, CHCH*H*), 2.52-2.62 (1H, m, CHC*H*H), 3.79, 3.88 (each 3H, s, OCH_3), 4.15-4.31 (2H, m, CH_2CH_3), 4.86-4.95 (1H, m, NC*H*CH_2), 5.66 (1H, d, *J* 0.9 Hz, NC*H*C), 6.02 (1H, d, *J* 0.9 Hz, CHCC*H*), 6.70-6.76 (1H, m, ArC*H*), 6.94-6.99 (1H, m, ArC*H*), 7.29-7.62 (2H, m, ArC*H*); δ_c (100 MHz; $CDCl_3$) 13.8 (CH_2CH_3), 36.5 ($CHCH_2C$), 53.3, 53.83 (CO_2CH_3), 59.1 (N*C*HCH_2), 61.4 ($CHCH_2C$), 62.2 (CH_2CH_3), 70.6 (*C*HCCH), 73.1 (N*C*HC), 91.7 (CH*C*CH), 115.2 (Ar*C*H), 117.1 (C*C*N), 117.9, 132.3, 134.0 (Ar*C*H), 147.0, 148.2 (Ar*C*), 169.0, 169.2, 169.4 (CO_2R), 199.1, 199.3 ($Co(CO)_3$); *m/z* 586 (M^+-3CO, 15%), 558 (47), 530 (44), 502 (73).

Dimethyl dicobalt hexacarbonyl-5-ethynyl-2-(2-nitrophenyl)-1-phenylpyrrolidine-3,3-dicarboxylate (5e)



Dimethyl dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylate **1** (0.100 g, 0.21 mmol) was added to a flame-dried round-bottom flask under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). (2-Nitrobenzylidene)phenylamine (0.097 g, 0.42 mmol) and $BF_3{\cdot}OEt_2$ (0.08 mL, 0.63 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, concentrated *in vacuo*, and the residue purified by flash column chromatography on silica eluting in light petroleum-diethyl ether (5:1 v/v) to yield the two inseparable **(yes or no?)** *title complex* diastereoisomers **5e** as a deep red oil (0.056 g, 32%, 2:1 d.r.), (i) First eluting, major diastereoisomer (Found: M^+, 693.9697. $C_{28}H_{20}O_{12}Co_2N_2$ requires M, 693.9680); ν_{max} (film)/cm^{-1} 2953 (sp^3 C-H), 2093, 2054, 2023 (C≡O), 1740, 1734 (C=O), 1533, 1350 (NO_2), 1067, 1034 (C-O); δ_H (400 MHz; $CDCl_3$) 2.86 (1H, dd, *J* 5.8, 13.3 Hz, CHCH*H*), 3.10 (1H, dd, *J* 11.3, 13.3 Hz, CHC*H*H), 3.37, 3.79 (3H, s, OCH_3), 4.92 (1H, dd, *J* 5.8, 11.3 Hz, NC*H*CH_2), 6.24 (1H, d, *J* 0.9 Hz, CHCC*H*), 6.55 (1H, s, NC*H*C), 6.71-6.79 (2H, m, ArC*H*), 6.86-6.90 (1H, m, ArC*H*), 7.17-7.21 (2H, m, ArC*H*), 7.47-7.51 (1H, m, ArC*H*), 7.63-7.67 (1H, m, ArC*H*), 7.95-7.98 (1H, m, ArC*H*), 8.06-8.10 (1H, m, ArC*H*); δ_c (100 MHz; $CDCl_3$) 41.6 (CH*C*H_2C), 52.9, 53.6 ($CO_2C$$H_3$), 58.9 (N*C*H$CH_2$), 63.7 (CH$CH_2$*C*), 68.2 (*C*HCCH), 76.4 (N*C*HC), 92.8 (CH*C*CH), 116.7 (2C, s, Ar*C*H), 120.8, 125.0 (Ar*C*H), 128.8 (2C, s, Ar*C*H), 129.1, 131.2, 132.6 (Ar*C*H), 135.5, 146.9, 148.2 (Ar*C*), 167.4, 170.1 (CO_2CH_3), 199.1 (Co(CO)$_3$); *m/z* 694 (M^+, 8%), 638 (6), 610 (16), 609 (23), 582 (12), 581 (25), 554 (42), 553 (80) 525 (100). (ii) Second eluting, minor diastereoisomer (Found: M^+, 693.9666. $C_{28}H_{20}O_{12}Co_2N_2$ requires M, 693.9680); ν_{max} (film)/cm^{-1} 2092, 2053, 2019 (C≡O), 1744, 1740, 1734 (C=O), 1064, 1033 (C-O); δ_H

(400 MHz; $CDCl_3$) 2.64 (1H, dd, *J* 3.0, 14.3 Hz, CHCH*H*), 3.27 (3H, s, OCH_3), 3.60 (1H, dd, *J* 8.7, 14.3 Hz, CHC*H*H), 3.84 (3H, s, OCH_3), 5.74 (1H, d, *J* 0.8 Hz, CHCC*H*), 5.82 (1H, dd, *J* 3.0, 8.7 Hz, NC*H*CH_2), 6.69-6.73 (1H, m, ArC*H*), 6.85 (1H, s, NC*H*C), 6.87-6.89 (2H, m, ArC*H*), 7.09-7.15 (3H, m, ArC*H*), 7.29-7.37 (2H, m, ArC*H*), 7.78-7.80 (1H, m, ArC*H*); δ_c (100 MHz; $CDCl_3$) 40.0 (CH*C*H_2C), 53.3, peak absent (CO_2*C*H_3), 60.2 (N*C*HCH_2), 61.3 (N*C*HC), 64.9 (CHCH_2*C*), 75.6 (*C*HCCH), 92.8 (CH*C*CH), 118.0 (2C, s, Ar*C*H), 119.0, 124.7 (Ar*C*H), 128.70 (2C, s, Ar*C*H), 128.74, 129.1, 132.4 (Ar*C*H), 133.2, 142.9, 150.6 (Ar*C*), 168.5, 170.1 (*C*O_2CH_3), 199.1 (Co(*C*O)$_3$); *m/z* (M^+, 7%), 638 (5), 610 (13), 609 (34), 581 (17), 554 (41), 553 (85), 525 (100).