Electronic Supplementary Information for Dalton Transactions

Supporting information

The Effect of the Central Donor in Bis(benzimidazole)-based Cobalt Catalysts for the Selective *cis*-1,4-Polymerisation of Butadiene

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Experimental section

All manipulations of air and/or moisture sensitive compounds were performed under an atmosphere of N_2 using standard Schlenk techniques or by using a conventional nitrogen-filled glove-box. Air and moisture sensitive compounds were stored in a nitrogen filled glove-box at room temperature. All solvents were stored in glass ampoules under a nitrogen atmosphere. Toluene, pentane and heptane, were dried by passing them through a cylinder containing commercially available Q-5 reactant (13% w/w Cu(II)O on alumina) and activated alumina (pellets, 3mm) and stored over a potassium mirror. Diethyl ether was distilled under nitrogen, over sodium benzophenone ketyl and stored over potassium mirror. THF was distilled from potassium metal under an atmosphere of nitrogen, and stored over 4 Å molecular sieves. All solvents were thoroughly deoxygenated before use. Iminodiacetic acid required for the syntheses of **L1**, **L2**, **L5-L13** were commercially available and used as received, iminodiacetic esters required for the synthesis of **L3** and **L4** were synthesised according published procedure.[1] **L7**, **L9-L12**,[2] and **L8**,[3] were synthesised according to literature procedures. 1,3-Butadiene was purchased from Aldrich and used without further purification. MAO was purchased from Chemtura. Magnetic susceptibility measurements were obtained using Evans' NMR method.[4,5] Typically, 1-2 mg of complex was dissolved in a 90:10 v/v mixture of DMSO-d_6 and DCM in a 2 mL volumetric flask in a nitrogen filled glove-box. A portion of this solution was injected into a capillary which was then sealed and inserted into an NMR tube containing the same DMSO-d_6/DCM mixture. IR spectra were

recorded on a Perkin-Elmer spectrum 1760X FT-IR spectrometer using KBr discs. Polybutadiene samples were dissolved in $CDCl_3$ at ambient temperature in a 5 mm NMR tube. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400MHz spectrometer at ambient temperature. Samples soluble in chloroform were deposited on a KBr disk and the chloroform was evaporated to create a thin film. IR spectra were recorded on a Perkin-Elmer spectrum 1760X FT-IR spectrometer. Polybutadiene samples soluble in chloroform were analysed using Cirrus GPC/SEC software, connected to a Shodex RI-101 detector versus polystyrene standards (molecular weight 580-7,500,000). Samples were injected onto two linear 10 micron columns, using chloroform as eluant, at a flow rate of 1.0 $cm^3.min^{-1}$ at 35°C

_N_,_N_-bis(1_H_-benzimidazol-2-ylmethyl)-_N_-amine, L1

o-Phenylenediamine (10.0 g, 92.6 mmol) and iminodiacetic acid (6.15 g, 46.3 mmol) were stirred in ethyleneglycol (20 ml) at 180°C for 4 hours. The formed water by-product was distilled from the reaction mixture, which was then allowed to cool to room temperature. The product was triturated with water (100 ml), filtered, washed with water (4 x 20 ml), recrystallised from hot methanol-water mixture and finally dried at 60°C under vacuum. Yield = 11.50 g (90%) Anal. Calcd (%) for $C_{16}H_{15}N_5$ (277.32): C, 69.29; H, 5.45; N, 25.25. Found: C, 69.62; H, 5.45; N, 24.93. ^1H NMR (400MHz, DMSO-d_6, 298 K): δ 12.28 (br s, 2H, N*H*), 7.51 (m, 4H, Ar*H*), 7.13 (m, 4H, Ar*H*), 4.01 (s, 4H, N(CH_2)$_2$). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, 298 K): δ 153.8 (*C*q), 121.2 (Ar*C*H), 46.4 (NCH_2). CI-MS: (m/z): 274 [M-3H]$^+$. IR (KBr (s), cm^{-1}): 3053 (s), 2908 (s), 2779 (s), 1932 (w), 1892 (w), 1856 (w), 1770 (w), 1657 (s), 1622 (m), 1590 (w), 1534 (m), 1484 (m), 1437 (s), 1330 (m), 1310 (m), 1272 (s), 1222 (m), 1148 (w), 1111 (w), 1098 (w), 1019 (m), 999 (w), 966 (w), 932 (w), 897 (w), 875 (m), 843 (m), 767 (m), 744 (s), 655 (w), 618 (w).

_N_,_N_-bis(1_H_-benzimidazol-2-ylmethyl)-_N_-methylamine, L2

Employing an analogous procedure to that described for **L1**, using *o*-phenylenediamine (7.22 g, 66.8 mmol) and methyliminodiacetic acid (4.91 g, 33.4 mmol) in ethyleneglycol (20 ml). Yield = 8.14 g (84%). Anal. Calcd (%) for $C_{17}H_{17}N_5$ (291.35): C, 70.10; H, 5.84; N, 24.05. Found: C, 70.04; H, 5.77; N, 23.99.^1H NMR (400 MHz, DMSO-d_6, 298 K): δ 12.23 (br s, 2H, N*H*), 7.56-7.52 (m, 4H, Ar*H*), 7.18-7.13 (m, 4H, Ar*H*), 3.92 (s, 4H, N(CH_2)$_2$), 2.28 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, 298 K): δ 152.1 (*C*q), 121.4 (Ar*C*H), 54.7

(N*C*H$_2$), 42.1 (N*C*H$_3$). CI-MS (m/z): 292 [M+H]$^+$. IR (KBr (s), cm^{-1}): 3050 (s), 2970 (s), 2884 (s), 2841 (s), 1933 (w), 1892 (w), 1856 (w), 1774 (w), 1671 (w), 1621 (m), 1588 (w), 1526 (m), 1482 (m), 1455 (s), 1434 (s), 1415 (s), 1349 (m), 1309 (m), 1271 (s), 1244 (m), 1222 (m), 1193 (m), 1156(m), 1119 (w), 1067 (m), 1019 (m), 998 (w), 973 (w), 950 (w), 933 (w), 897 (w), 836 (m), 768 (m), 749 (s), 650 (w), 618 (w).

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-isopropylamine, L3**

Employing an analogous procedure to that described for **L1**, using *o*-phenylenediamine (3.66 g, 33.9 mmol) and diethyl 2,2'-(isopropylimino)diacetate **E1** (3.91 g, 16.9 mmol) without ethyleneglycol. Yield = 3.76 g (70%). Anal. Calcd (%) for $C_{19}H_{21}N_5$ (319.40): C, 71.47; H, 6.58; N, 21.94. Found: C, 71.57; H, 6.46; N, 21.81. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 12.29 (br s, 2H, N*H*), 7.56-7.58 (m, 4H, Ar*H*), 7.18-7.20 (m, 4H, Ar*H*), 4.01 (s, 4H, N(CH_2)$_2$), 2.91 (sept, 1H, $^3J_{HH}$ = 6.6Hz, C*H*(CH$_3$)$_2$), 1.06 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 298 K): δ 153.8 (*C*q), 137.4 (*C*q), 122.0 (Ar*C*H), 114.5 (Ar*C*H), 51.1 (N*C*H), 48.1 (N(*C*H)$_2$), 17.8 (*C*H$_3$). CI-MS (m/z): 320 [M+H]$^+$. IR (KBr (s), cm^{-1}): 3054 (s), 2965 (s), 1930 (w), 1888 (w), 1809 (w), 1770 (w), 1668 (m), 1621 (m), 1590 (m), 1528 (m), 1485 (m), 1455 (s), 1427 (s), 1389 (m), 1366 (m), 1345 (m), 1307 (m), 1272 (s), 1223 (m), 1167 (m), 1119 (w), 1103 (m), 1061 (m), 1019 (m), 998 (w), 928 (m), 884 (w), 849 (m), 796 (w), 767 (m), 748 (s) ,617 (w).

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-cyclohexylamine, L4**

Employing an analogous procedure to that described for **L1**, using *o*-phenylenediamine (5.71 g, 52.8 mmol) and diethyl 2,2'-(cyclohexylimino)diacetate (7.16 g, 26.4 mmol) without ethyleneglycol. Yield = 6.98 g (74%). Anal. Calcd (%) for $C_{22}H_{25}N_5$ (359.46): C, 73.53; H, 6.96; N, 19.49. Found: C, 73.02; H, 7.11; N, 19.30. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 12.35 (br s, 2H, N*H*), 7.53 (m, 4H, Ar*H*), 7.13 (m, 4H, Ar*H*), 4.01 (s, 4H, N(CH$_2$)$_2$), 0.99-1.86 (overlapped, 11H, CH$_2$ cyclohexyl). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 154.3 (*C*q), 121.4 (Ar*C*H), 60.0 (N*C*H), 48.9 (N(*C*H$_2$)$_2$), 28.3 (*C*H$_2$), 25.6 (*C*H$_2$), 25.4 (*C*H$_2$). CI-MS: (m/z): 360 [M+H]$^+$. IR (KBr (s), cm^{-1}): 3052 (m), 2931 (s), 2854 (s), 2784 (m), 1887 (w), 1770 (w), 1668 (w), 1621 (m), 1590 (w), 1538 (m), 1487 (w), 1440 (s), 1386 (m), 1336 (m), 1309 (m), 1272 (s), 1212 (w), 1194 (w), 1164 (w), 1146 (w), 1127 (w), 1114 (m), 1056 (w), 1021 (m), 999 (m), 973 (w), 946 (w), 923 (w), 892 (w), 870 (w), 835 (m), 767 (m), 743 (s), 667 (w), 620 (w).

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-benzylamine, L5**

Employing an analogous procedure to that described for **L1**, using *o*-phenylenediamine (6.73 g, 62.3 mmol) and benzyliminodiacetic acid (6.95 g, 31.1 mmol) in ethyleneglycol (20 ml). Yield = 9.10 g (80%). Anal. Calcd (%) for $C_{23}H_{21}N_5$ (367.44): C, 75.20; H, 5.72; N, 19.07. Found: C, 75.27; H, 5.64; N, 18.91. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 12.38 (br s, 2H, N*H*), 7.56 (br s, 4H, Ar*H*), 7.46 (d, 2H, $^3J_{HH}$ = 7.3 Hz, Ar*H*), 7.33 (t, 2H, $^3J_{HH}$ = 7.5 Hz, Ar*H*), 7.24 (t, 1H, $^3J_{HH}$ = 7.3 Hz, Ar*H*), 7.16 (br s, 4H, Ar*H*), 3.93 (s, 4H, N(CH_2)$_2$), 3.73 (s, 2H, NCH_2Ph). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 152.3 (*C*q), 138.4 (*C*q) 137.7 (Ar*C*H), 129.2 (Ar*C*H), 128.4 (Ar*C*H), 127.3 (Ar*C*H), 121.9 (ArC*H*), 121.2 (ArC*H*), 114.9 (Ar*C*H), 57.1 (N(*C*H$_2$)$_2$), 51.2 (N*C*H$_2$Ph). CI-MS: (m/z): 368 [M+H]$^+$. IR (KBr (s), cm^{-1}): 3048 (s), 3028 (s), 2944 (s), 2824 (s), 2798 (s), 1927 (w), 1888 (w), 1809 (w), 1769 (w), 1667 (w), 1620 (m), 1601 (w), 1586 (m), 1537 (s), 1495 (m), 1453 (s), 1437 (s), 1391 (m), 1357 (m), 1332 (m), 1307 (m), 1271 (s), 1221 (m), 1199 (m), 1161 (w), 1129 (m), 1115 (w), 1099 (s), 1072 (m), 1027 (s), 1011 (w), 998 (w), 982 (m), 968 (m), 951 (w), 923 (w), 893 (w), 858 (m), 845 (m), 767 (m), 735 (s), 697 (m), 654 (w), 618 (w).

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)aniline, L6**

Employing an analogous procedure to that described for **L1**, using *o*-phenylenediamine (2.16 g, 20.0 mmol) and phenyliminodiacetic acid (2.09 g, 10.0 mmol) in ethyleneglycol (10 ml). Yield = 2.95 g (84%). Anal. Calcd (%) for $C_{22}H_{19}N_5$ (353.41): C, 74.78; H, 5.38; N, 19.83. Found: C, 74.61; H, 5.27; N, 20.00. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 7.68 (m, 4H, Ar*H*), 7.13 (m, 4H, Ar*H*), 7.06 (t, 2H, $^3J_{HH}$ = 7.9 Hz, *m*eta-Ar*H*), 6.59 (m, 3H, *ortho*- + *para*-Ar*H*), 5.18 (s, 4H, (NCH_2)$_2$). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 154.2 (*C*q), 146.4 (*C*q), 137.3 (*C*q), 129.1 (Ar*C*H), 122.3 (Ar*C*H), 117.1 (*C*q), 114.7 (Ar*C*H), 111.7 (Ar*C*H), 50.3 (N*C*H$_2$). CI-MS: (m/z): 354 [M+H]$^+$. IR (KBr (s), cm^{-1}): 3052 (m), 2908 (m), 2747 (m), 2298 (w), 1601 (m), 1578 (w), 1560 (w), 1542 (w), 1528 (w), 1506 (s), 1446 (s), 1377 (m), 1352 (w), 1327 (m), 1272 (m), 1218 (m), 1184 (w), 1114 (w), 1061 (w), 1026 (m), 1000 (w), 990 (w), 947 (w), 837 (w), 768 (w), 742 (s), 689 (m), 657 (w), 617 (w).

***N*,*N*-bis(1-methyl-benzimidazol-2-ylmethyl)-*N*-methylamine, L13**

N,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine **L2** (3.85 g, 13.2 mmol) and potassium *tert*-butoxide (3.00 g, 26.8 mmol) were stirred in THF (20 ml) at room temperature for 30 min. Methyliodide (3.75 g, 26.4 mmol) was added and the reaction mixture stirred at room temperature overnight. Water was added to quench the reaction and the product extracted with DCM. The organic phase was dried on Na_2SO_4 and evaporated to dryness to afford a white solid. Recrystallisation from toluene/hexane mixture afforded **L13** as a white crystalline powder. Yield = 3.88 g (92%). Anal. Calcd (%) for $C_{19}H_{21}N_5$ (319.40): C, 71.47; H, 6.58; N, 21.94. Found: C, 71.38; H, 6.41; N, 21.89. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.75 (m, 2H, Ar*H*), 7.30-7.23 (m, 6H, Ar*H*), 3.92 (s, 4H, N(C*H*$_2$)$_2$), 3.67 (s, 6H, NC*H*$_3$), 2.42 (s, 3H, NC*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 151.2 (*C*q), 142.3 (*C*q), 136.1 (*C*q), 122.8 (Ar*C*H), 122.1 (Ar*C*H), 119.8 (Ar*C*H), 109.1 (Ar*C*H), 54.1 (*C*H$_2$), 43.4 (*C*H$_3$), 29.8 (*C*H$_3$). CI-MS: (m/z): 320 $[M-H]^+$. IR (KBr (s), cm^{-1}): 3049 (m), 2982 (m), 2950 (m), 2884 (m), 2852 (m), 2820 (m), 2791 (m), 1937 (w), 1895 (w), 1773 (w), 1677 (w), 1614 (m), 1515 (m), 1478 (s), 1442 (s), 1402 (s), 1352 (m), 1333 (s), 1289 (m), 1267 (w), 1244 (m), 1234 (m), 1199 (w), 1179 (w), 1152 (w), 1128 (m), 1100 (w), 1024 (s), 1003 (w), 986 (m), 938 (w), 910 (w), 862 (w), 852 (m), 771 (s), 757 (s), 749 (s), 728 (m), 673 (w), 656 (w).

_N_,_N_-bis(1_H_-benzimidazol-2-ylmethyl)amine]cobalt(II) dichloride, 1

Equimolar quantities of *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-amine **L1** (1.06 g, 3.83 mmol) and anhydrous $CoCl_2$ (0.498 g, 3.83 mmol) were stirred in 30 ml of THF at room temperature for 48 hours. The blue solid was filtered, washed twice with THF (2 x 20 ml), once with Et_2O (20 ml) and dried under vacuum overnight. Yield = 1.30 g (83%). Anal. Calcd (%) for $C_{16}H_{15}N_5Cl_2Co$ (407.16): C, 47.20; H, 3.71; N, 17.20. Found: C, 47.58; H, 3.23; N, 17.25. +FAB-MS (m/z): 371 $[M-Cl]^+$, 335 $[M-2Cl]^+$. IR (KBr (s), cm^{-1}): 3326 (s), 3286 (s), 3182 (s), 3071 (s), 2927 (m), 2784 (m), 1944 (w), 1911(w), 1794 (w), 1664 (m), 1622 (m), 1594 (m), 1542 (m), 1491 (m), 1471 (s), 1456 (s), 1426 (m), 1386 (m), 1369 (m), 1332 (s), 1275 (s), 1243 (m), 1225 (m), 1149 (w), 1114 (m), 1071 (m), 1047 (s), 1003 (m), 976 (w), 941 (w), 930 (w), 915 (m), 868 (m), 827 (m), 750 (s), 689 (m), 644 (w), 628 (m). μ_{eff} = 4.21 BM.

_N_,_N_-bis(1_H_-benzimidazol-2-ylmethyl)-_N_-methylamine]cobalt(II) dichloride, 2

Employing an analogous procedure to that described for 1, *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-methylamine **L2** (2.67 g, 9.17 mmol) was reacted with anhydrous $CoCl_2$ (1.19 g,

9.17 mmol) to afford **2** as a blue microcrystalline solid. Yield = 3.50 g (91%). Anal. Calcd (%) for $C_{17}H_{17}N_5Cl_2Co$ (421.18): C, 48.48; H, 4.07; N, 16.63. Found: C, 48.44; H, 4.13; N, 16.76. +FAB-MS (m/z): 385 $[M\text{-}Cl]^+$, 350 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3187 (m), 3126 (m), 3067 (m), 2977 (m), 2928 (m), 2360 (m), 2341 (m), 1791 (w), 1748 (w), 1716 (w), 1698 (w) 1683 (w), 1623 (m), 1595 (w), 1541 (m), 1490 (m), 1473 (s), 1455 (s), 1418 (w), 1388 (m), 1338 (m), 1312 (w), 1276 (m), 1224 (w), 1150 (w), 1131 (w), 1045 (m), 1030 (w), 1004 (w), 983 (w), 916 (w), 874 (w), 851 (w), 764 (s), 752 (s), 668 (w). μ_{eff} = 3.54 BM.

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-isopropylamine]cobalt(II) dichloride, 3**

Employing an analogous procedure to that described for **1**, *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-isopropylamine **L3** (0.500 g, 1.57 mmol) was reacted with anhydrous $CoCl_2$ (0.204 g, 1.57 mmol) to afford **3** as a blue microcrystalline solid. Yield = 0.606 g (86%). Anal. Calcd (%) for $C_{19}H_{21}N_5Cl_2Co$ (449.24): C, 50.80; H, 4.71; N, 15.59. Found: C, 50.66; H, 4.59; N, 15.73. +FAB-MS (m/z): 413 $[M\text{-}Cl]^+$, 377 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3185 (s), 3151 (s), 3066 (s), 2972 (s), 2931 (m), 1623 (m), 1595(m), 1541 (m), 1493 (m), 1472 (s), 1455 (s), 1434 (m), 1388 (m), 1336 (m), 1275 (m), 1219 (w), 1183 (w), 1163 (m), 1126 (m), 1097 (w), 1047 (m), 1005 (w), 981 (w), 942 (m), 914 (w), 889 (w), 853 (m), 799 (m), 748 (s), 631 (w). μ_{eff} = 4.16 BM.

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-cyclohexylamine]cobalt(II) dichloride, 4**

Employing an analogous procedure to that described for **1**, *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-cyclohexylamine **L4** (0.690 g, 1.92 mmol) was reacted with anhydrous $CoCl_2$ (0.250 g, 1.92 mmol) to afford **4** as a blue microcrystalline solid. Yield = 0.749 g (80%). Anal. Calcd (%) for $C_{22}H_{25}N_5Cl_2Co$ (489.31): C, 54.00; H, 5.15; N, 14.31. Found: C, 53.89; H, 5.15; N, 14.26. +FAB-MS (m/z): 453 $[M\text{-}Cl]^+$, 417 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3385 (s), 3193 (s), 2930 (s), 2855 (s), 1622 (m), 1595 (m), 1540 (m), 1491 (m), 1471 (s), 1455 (s), 1387 (m), 1337 (m), 1311 (w), 1274 (m), 1220 (w), 1160 (w), 1108 (m), 1048 (m), 1006 (m), 976 (w), 947 (w), 914 (w), 897 (w), 878 (w), 842 (w), 789 (w), 767 (m), 745 (s), 660 (w), 632 (w). μ_{eff} = 3.94 BM.

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-benzylamine]cobalt(II) dichloride, 5**

Employing an analogous procedure to that described for **1**, *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-benzylamine **L5** (1.41 g, 3.85 mmol) was reacted with anhydrous $CoCl_2$ (0.500

g, 3.85 mmol) to afford **5** as a blue microcrystalline solid. Yield = 1.58 g (83%). Anal. Calcd (%) for $C_{23}H_{21}N_5Cl_2Co$ (497.28): C, 55.55; H, 4.22; N, 14.08. Found: C, 55.26; H, 4.40; N, 13.70. +FAB-MS (m/z): 461 $[M\text{-}Cl]^+$, 425 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3380 (m), 3177 (s), 3146 (s), 3124 (s), 3067 (s), 3006 (m), 2976 (m), 2925 (m), 2878 (m), 2790 (m), 1916 (w), 1811 (w), 1622 (m), 1592 (m), 1542 (m), 1490 (m), 1473 (s), 1455 (s), 1436 (m), 1388 (m), 1337 (m), 1313 (w), 1276 (m), 1223 (m), 1212 (m), 1150 (w), 1119 (w), 1099 (w), 1076 (m), 1047 (s), 998 (m), 964 (m), 940 (w), 914 (w), 884 (m), 858 (m), 770 (s), 753 (s), 728 (m), 705 (s), 667 (w), 633 (w), 618 (m). μ_{eff} = 3.95 BM.

***N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-phenylamine]cobalt(II) dichloride, 6**

Employing an analogous procedure to that described for **1**, *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-phenylamine **L6** (0.414 g, 1.17 mmol) was reacted with anhydrous $CoCl_2$ (0.152 g, 1.17 mmol) to afford **6** as a turquoise blue microcrystalline solid. Yield = 0.468 g (83%). Anal. Calcd (%) for $C_{22}H_{19}N_5Cl_2Co$ (483.25): C, 54.66; H, 3.93; N, 14.49. Found: C, 54.58; H, 3.96; N, 14.58. +FAB-MS (m/z): 447 $[M\text{-}Cl]^+$, 411 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3375 (m), 3226 (m), 3065 (m), 2977 (m), 2877 (m), 1952 (w), 1790 (w), 1622 (m), 1597 (m), 1540 (w), 1498 (m), 1470 (m), 1449 (s), 1391 (m), 1359 (m), 1342 (m), 1317 (w), 1277 (m), 1209 (m), 1193 (m), 1148 (m), 1118 (w), 1051 (m), 1006 (w), 971 (w), 939 (w), 926 (m), 895 (w), 845 (m), 796 (w), 759 (s), 747 (s), 697 (m), 652 (w), 628 (w). μ_{eff} = 3.90 BM.

[*N*,*N*,*N*-tris(1*H*-benzimidazol-2-ylmethyl)]cobalt(II) dichloride, 7

Employing an analogous procedure to that described for **1**, *N*,*N*,*N*-tris(1*H*-benzimidazol-2-ylmethyl)amine **L7** (2.00 g, 4.91 mmol) was reacted with anhydrous $CoCl_2$ (0.638 g, 4.91 mmol) to afford **7** as pink microcrystalline solid. Yield = 2.39 g (91%). Anal. Calcd (%) for $C_{24}H_{21}N_7Cl_2Co$ (537.31): C, 53.65; H, 3.94; N, 18.25. Found: C, 53.70; H, 4.05; N, 18.13. +FAB-MS (m/z): 501 $[M\text{-}Cl]^+$, 465 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3370 (s), 3116 (s), 3060 (s), 2922 (s), 2773 (m), 1908 (w), 1791 (w), 1733 (w), 1623 (m), 1595 (m), 1540 (m), 1490 (m), 1473 (s), 1455 (s), 1389 (m), 1341 (m), 1314 (w), 1275 (m), 1222 (w), 1149 (w), 1128 (w), 1045 (m), 1003 (m), 966 (m), 939 (w), 916 (w), 887 (w), 849 (w), 747 (s), 657 (w), 632 (w). μ_{eff} = 4.10 BM.

[2,6-bis(1*H*-benzimidazol-2-yl)pyridine]cobalt(II) dichloride, 8

Employing an analogous procedure to that described for **1**, 2,6-bis(1*H*-benzimidazol-2-yl)pyridine **L8** (0.750 g, 2.41 mmol) was reacted with anhydrous $CoCl_2$ (0.313 g, 2.41 mmol) to afford **8** as green microcrystalline solid. Yield = 0.783 g (74%). Anal. Calcd (%) for $C_{19}H_{13}N_5Cl_2Co$ (441.18): C, 51.70; H, 2.94; N, 15.87. Found: C, 51.61; H, 3.01; N, 15.81. +FAB-MS (m/z): 405 $[M\text{-}Cl]^+$, 369 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3020 (s), 2968 (s), 2896 (s), 2771 (s), 1963 (w), 1907 (w), 1829 (w), 1647 (s), 1607 (s), 1573 (m), 1538 (w), 1495 (s), 1461 (s), 1432 (m), 1381 (s), 1320 (s), 1305 (m), 1237 (m), 1197 (w), 1151 (m), 1104 (m), 1058 (w), 1015 (m), 1003 (w), 994 (m), 970 (m), 936 (w), 909 (w), 848 (m), 818 (m), 765 (s), 751 (s), 686 (m), 657 (m), 630 (w). μ_{eff} = 3.82 BM.

[*N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-2-methylpropyl]cobalt(II) dichloride, 9

Employing an analogous procedure to that described for **1**, *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-2-methylpropyl **L9** (0.521 g, 1.79 mmol) was reacted with anhydrous $CoCl_2$ (0.233 g, 1.79 mmol) to afford **9** as a blue microcrystalline solid. Yield = 0.654 g (87%). Anal. Calcd (%) for $C_{18}H_{18}N_4Cl_2Co$ (420.20): C, 51.45; H, 4.32; N, 13.33. Found: C, 51.01; H, 4.19; N, 13.60. +FAB-MS (m/z): 384 $[M\text{-}Cl]^+$, 348 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3188 (s), 3149 (s), 3060 (m), 2966 (m), 2889 (m), 1907 (w), 1790 (w), 1747 (w), 1625 (m), 1598 (m), 1533 (m), 1506 (w), 1488 (m), 1456 (s), 1439 (s), 1380 (w), 1342 (m), 1317 (m), 1296 (w), 1278 (m), 1243 (w), 1211 (m), 1164 (w), 1124 (w), 1063 (m), 1049 (m), 1030 (m), 1006 (m), 932 (w), 913 (w), 883 (w), 850 (m), 811 (w), 765 (m), 742 (s), 667 (w), 630 (w). μ_{eff} = 3.91 BM.

[Bis(1*H*-benzimidazol-2-ylmethyl)ether]cobalt(II) dichloride, 10

Employing an analogous procedure to that described for **1**, bis(1*H*-benzimidazol-2-ylmethyl)ether **L10** (0.468 g, 1.68 mmol) was reacted with anhydrous $CoCl_2$ (0.218 g, 1.68 mmol) to afford **10** as a blue microcrystalline solid. Yield = 0.550 g (80%). Anal. Calcd (%) for $C_{16}H_{14}N_4OCl_2Co$ (408.15): C, 47.08; H, 3.46; N, 13.73. Found: C, 46.90; H, 3.50; N, 13.32. +FAB-MS (m/z): 372 $[M\text{-}Cl]^+$, 336 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3191 (s), 3068 (s), 2923 (m), 2788 (m), 1791 (w), 1623 (m), 1595 (m), 1541 (w), 1490 (m), 1473 (s), 1455 (s), 1387 (m), 1333 (m), 1312 (w), 1276 (s), 1216 (m), 1148 (m), 1111 (m), 1051 (m), 1004 (m), 942 (w), 912 (w), 845 (w), 747 (s), 645 (w), 625 (w). μ_{eff} = 4.21 BM.

[Bis(1*H*-benzimidazol-2-ylmethyl)thioether]cobalt(II) dichloride, 11

Employing an analogous procedure to that described for **1**, bis(1*H*-benzimidazol-2-ylmethyl)thioether **L11** (0.299 g, 1.02 mmol) was reacted with anhydrous $CoCl_2$ (0.132 g, 1.02 mmol) to afford **11** as a blue microcrystalline solid. Yield = 0.397 g (92%). Anal. Calcd (%) for $C_{16}H_{14}N_4SCl_2Co$ (424.21): C, 45.30; H, 3.33; N, 13.21. Found: C, 45.21; H, 3.29; N, 13.16. +FAB-MS (m/z): 388 $[M\text{-}Cl]^+$, 353 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3175 (s), 3142 (s), 3046 (m), 2976 (m), 2897 (m), 2769 (w), 2359 (w), 2341 (w), 1948 (w), 1909 (w), 1828 (w), 1791 (w), 1623 (m), 1596 (w), 1557 (w), 1530 (m), 1485 (m), 1452 (s), 1420 (m), 1369 (w), 1316 (m), 1277 (m), 1255 (w), 1241 (w), 1229 (w), 1218 (w), 1156 (m), 1131 (w), 1119 (w), 1047 (m), 1005 (m), 974 (w), 935 (w), 910 (m) , 889 (w), 852 (m), 804 (w), 769 (m), 749 (s), 706 (w), 668 (w), 645 (w), 624 (w). μ_{eff} = 3.55 BM.

[*N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-2,6-dimethylphenylamine]cobalt(II) dichloride, 12

Employing an analogous procedure to that described for **1**, *N*,*N*-bis(1*H*-benzimidazol-2-ylmethyl)-*N*-2,6-dimethylphenylamine **L12** (0.360 g, 0.94 mmol) was reacted with anhydrous $CoCl_2$ (0.123 g, 0.94 mmol) to afford **12** as a turquoise blue microcrystalline solid. Yield = 0.348 g (72%). Anal. Calcd (%) for $C_{24}H_{23}N_5Cl_2Co$ (511.31): C, 56.47; H, 4.50; N, 13.72. Found: C, 56.27; H, 4.63; N, 13.50. +FAB-MS (m/z): 475 $[M\text{-}Cl]^+$, 439 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3424 (m), 3170 (m), 3138 (m), 3099 (m), 3072 (m), 3032 (m), 2969 (s), 2910 (s), 2875 (s), 2777 (m), 1916 (w), 1623 (m), 1594 (m), 1538 (w), 1487 (m), 1467 (s), 1454 (s), 1414 (m), 1367 (w), 1346 (m), 1315 (w), 1279 (m), 1252 (w), 1225 (w), 1194 (m), 1160 (m), 1098 (w), 1051 (s), 1009 (w), 946 (w), 927 (w), 891 (m), 855 (m), 776 (m), 766 (m), 757 (s), 745 (s), 678 (w), 622 (w). μ_{eff} = 3.79 BM.

[*N*,*N*-bis(1-methyl-benzimidazol-2-ylmethyl)-2-methylamine]cobalt(II) dichloride, 13

Employing an analogous procedure to that described for **1**, *N*,*N*-bis(1-methylbenzimidazol-2-ylmethyl)-*N*-methylamine **L13** (0.245 g, 0.77 mmol) was reacted with anhydrous $CoCl_2$ (0.100 g, 0.77 mmol) to afford **13** as a blue microcrystalline solid. Yield = 0.261g (75%). Anal. Calcd (%) for $C_{19}H_{21}N_5Cl_2Co$ (449.24): C, 50.78; H, 4.68; N, 15.59. Found: C, 50.63; H, 4.52; N, 15.69. +FAB-MS (m/z): 413 $[M\text{-}Cl]^+$, 378 $[M\text{-}2Cl]^+$. IR (KBr (s), cm^{-1}): 3031 (m), 3038 (m), 3007 (m), 2949 (m), 2900 (m), 2802 (m), 2416 (w), 2350 (w), 2256 (w), 1955 (w), 1923 (w), 1842 (w), 1792 (w), 1748 (w), 1698 (w), 1615 (m), 1593 (w), 1498 (s), 1490 (s) 1457 (s), 1419 (m), 1412 (m), 1361 (m), 1333 (m), 1296 (m), 1244 (m), 1203 (w), 1151

(w), 1125 (m), 1038 (m), 1013 (m), 980 (m), 965 (w), 948 (w), 932 (m), 895 (m), 877 (m), 773 (m), 754 (s), 697 (w), 667 (w), 651 (w). μ_{eff} = 4.20 BM.

1,3-Butadiene polymerisation procedures

In a glove-box, a known quantity of pre-catalyst was transferred into a Schlenk. The pre-catalyst was activated by adding the desired amount of MAO and stirred for 15 minutes or until obtaining a clear solution. When required 1 ml of a PPh_3 solution (10 μmol/ml in toluene) was added and the mixture aged for 30 minutes. Toluene (20 ml) was added, and the Schlenk tube was purged with 1 bar of butadiene gas for no more than 5 seconds. The polymerisation was carried out for 10 minutes and were terminated by ceasing the 1,3-butadiene supply, venting off the excess 1,3-butadiene, followed by addition of acidified MeOH containing 0.01% of BHT as antioxidant. After filtration the polymer was washed with MeOH and dried under vacuum at 60 °C for 12 hours.

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Supporting Information — **X-Ray Crystallography**

VG0642 (**1**), VG0724 (**6**), VG0619 (**7**), VG0615 (**8**), VG0723 (**12**)

In all five structures the N–H hydrogen atoms were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å. Again in all five structures the methyl hydrogen atoms of the included dimethylformamide solvent molecules were added in idealised tetrahedral positions and then the groups were allowed to rotate about the associated N–C vectors to find the best fit with the electron density map (i.e. the SHELX HFIX/AFIX 137 command).

*The X-ray crystal structure of complex **1***

The included diethylether solvent molecule was found to be disordered across a C_2 axis. Two unique partial occupancy orientations were identified of ca. 37 and 13% occupancy (two further overlapping orientations are generated by the operation of the C_2 axis). The geometries of the two orientations were optimised and all of the atoms were refined isotropically with the thermal parameters of neighbouring atoms restrained to be similar.

The X-ray crystal structure of complex 7

The structure of **7** was found to contain two crystallographically independent complexes (I and II) as well as four included dimethylformamide solvent molecules and one included diethylether solvent molecule.

Three of the four dimethylformamide solvent molecules were found to be disordered. In each case two partial occupancy orientations were identified with occupancies of 91:9, 71:29 and 53:47 for the O(40), O(50) and O(60) based molecules respectively. In all three cases the geometries were optimised, and the non-hydrogen atoms of the major occupancy orientations were refined anisotropically, whilst those of the minor occupancy orientations were refined isotropically. The equivalent isotropic and isotropic thermal parameters of neighbouring equivalent atoms of the major and minor occupancy orientations respectively were restrained to be similar.

The included diethylether solvent molecule was found to be disordered across a centre of symmetry. Two unique partial occupancy orientations were identified of ca. 39 and 11% occupancy (two further overlapping orientations are generated by the operation of the inversion centre). The geometries of the two orientations were optimised and all of the atoms

were refined isotropically with the thermal parameters of neighbouring atoms restrained to be similar.

Fig. S1 The molecular structure of complex **1** (50% probability ellipsoids).

Fig. S2 The molecular structure of complex **6** (50% probability ellipsoids).

Fig. S3 The molecular structure of one (I) of the two crystallographically independent complexes present in the crystals of complex **7** (50% probability ellipsoids).

Fig. S4 The molecular structure of one (II) of the two crystallographically independent complexes present in the crystals of complex **7**.

Fig. S5 The molecular structure of one (II) of the two crystallographically independent complexes present in the crystals of complex **7** (50% probability ellipsoids).

Fig. S6 The molecular structure of complex **8** (50% probability ellipsoids).

Fig. S7 The molecular structure of complex **12** (50% probability ellipsoids).

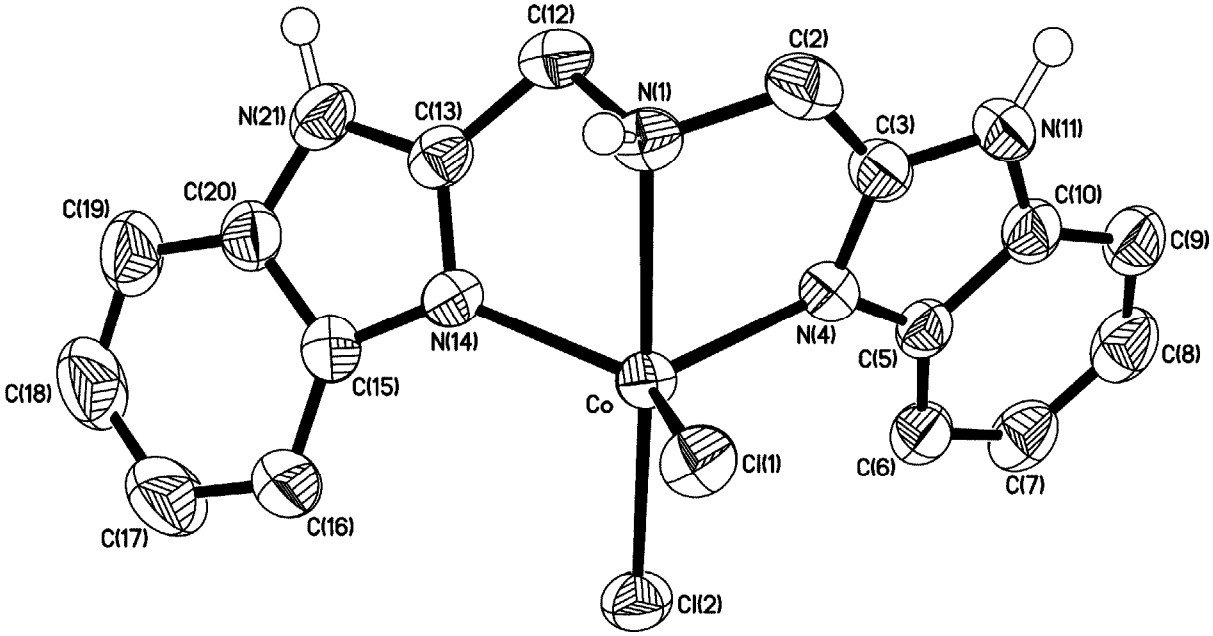


Fig. S1

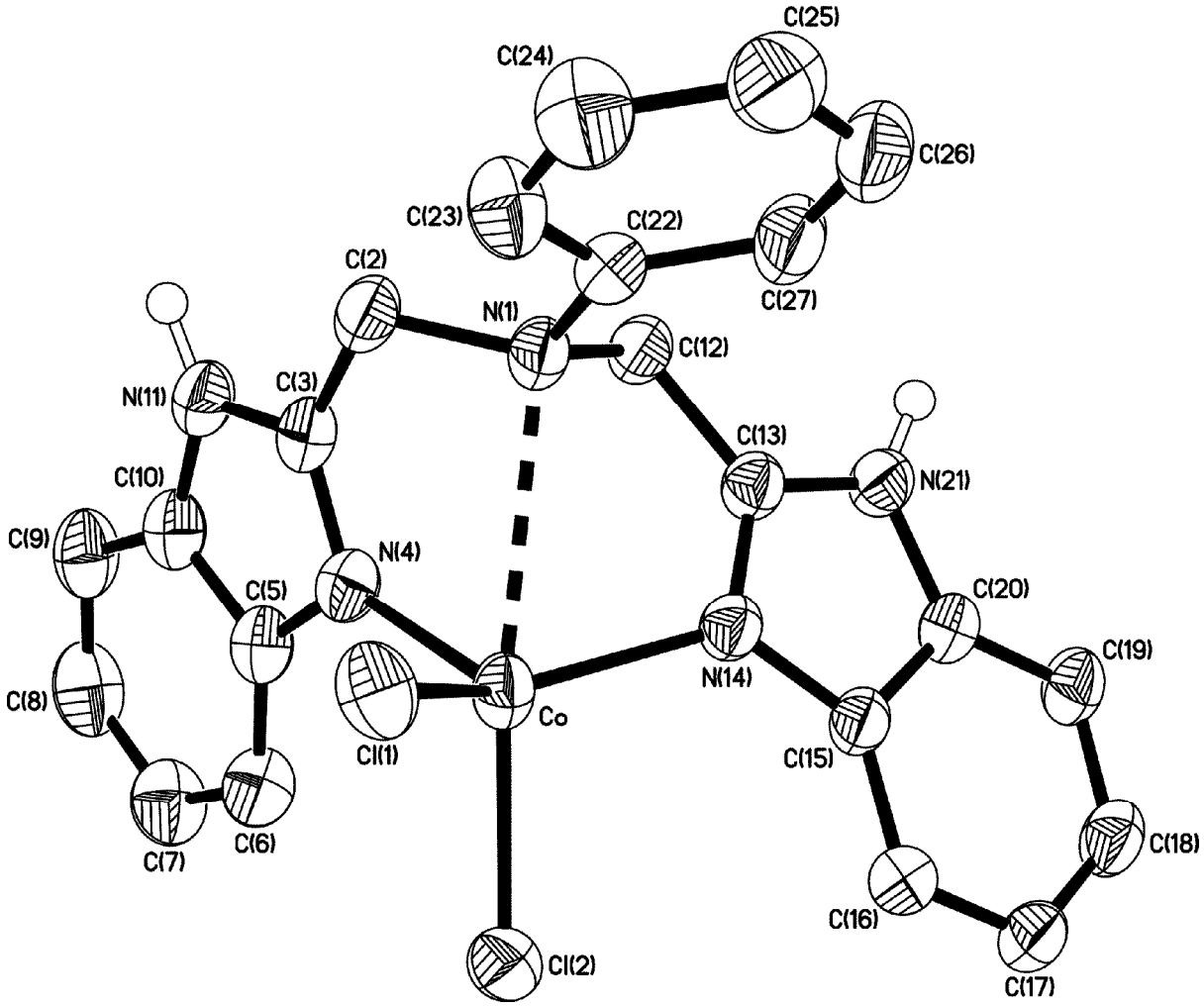


Fig. S2

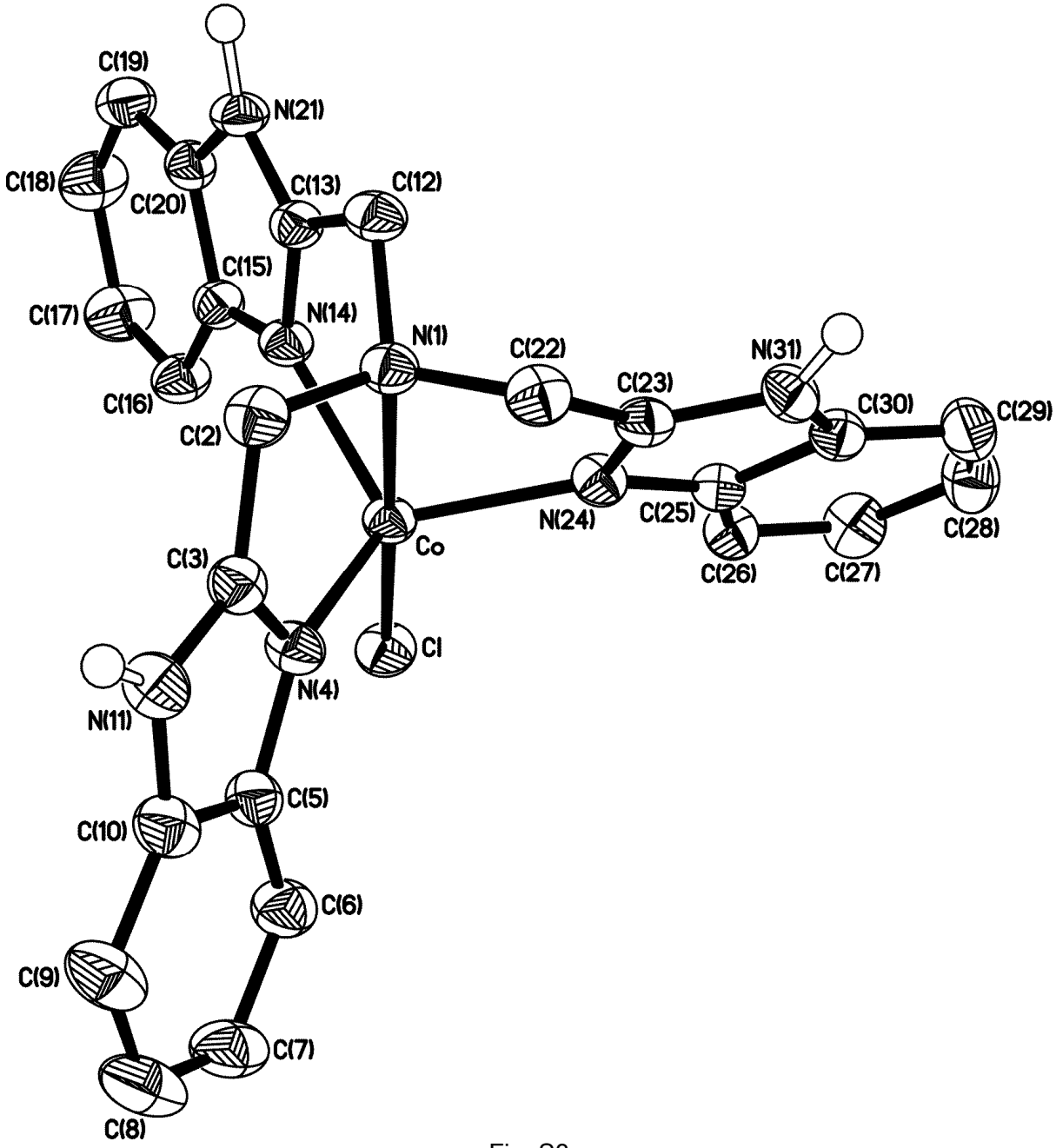


Fig. S3

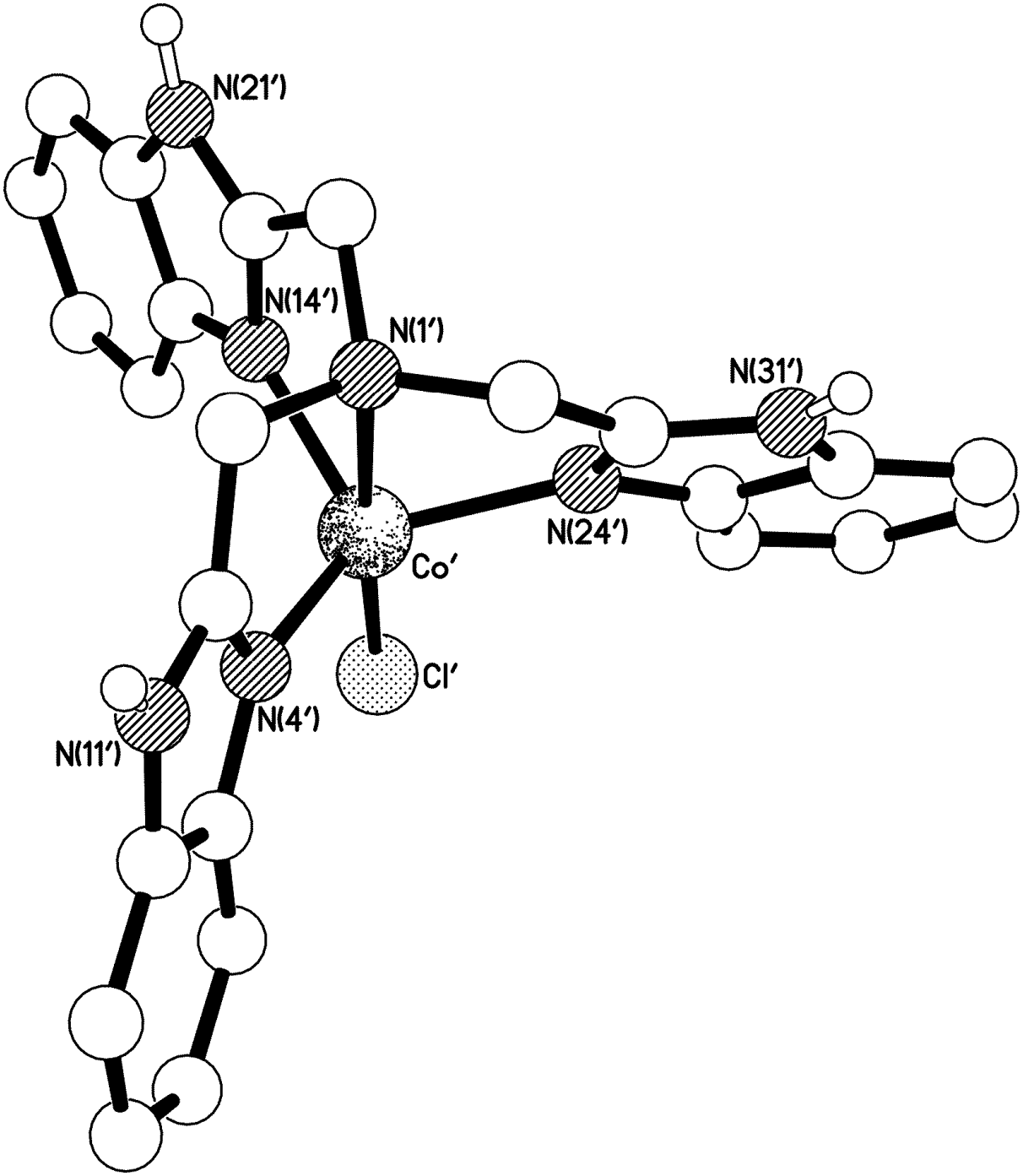


Fig. S4

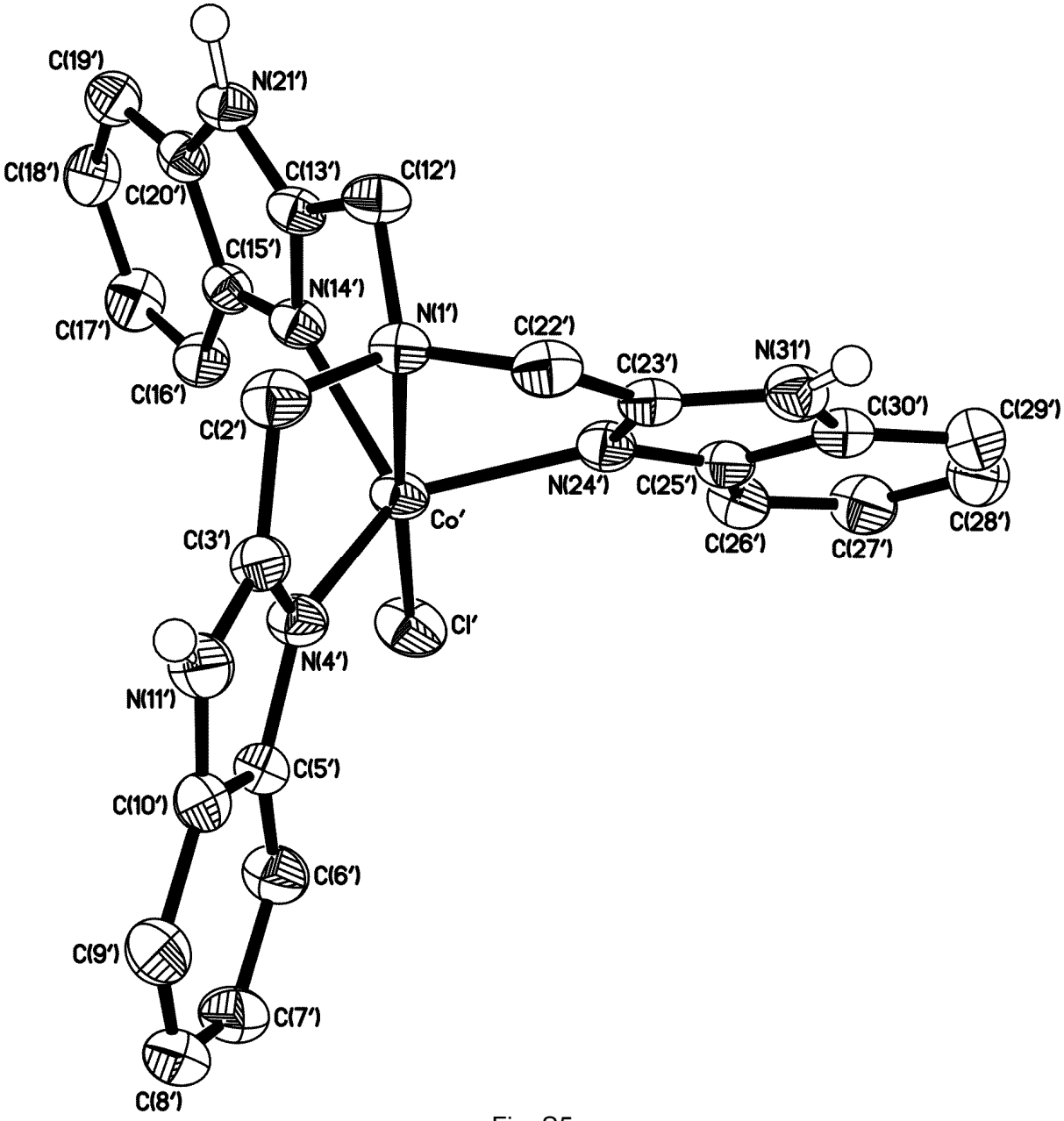


Fig. S5

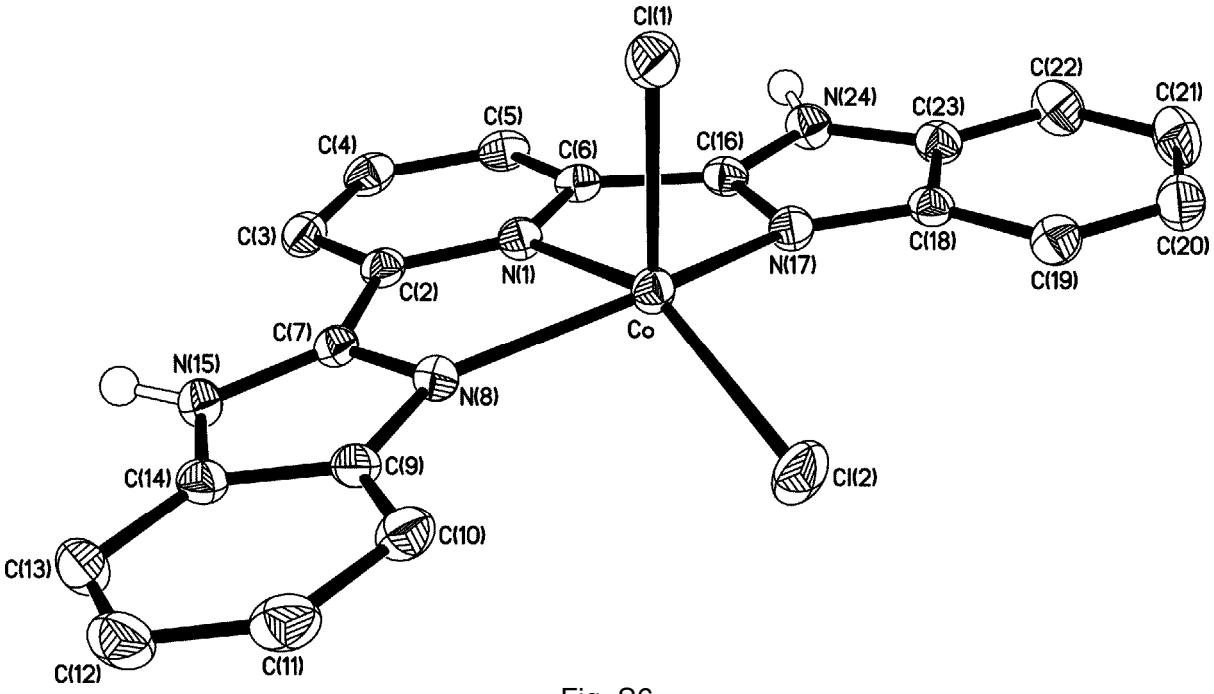


Fig. S6

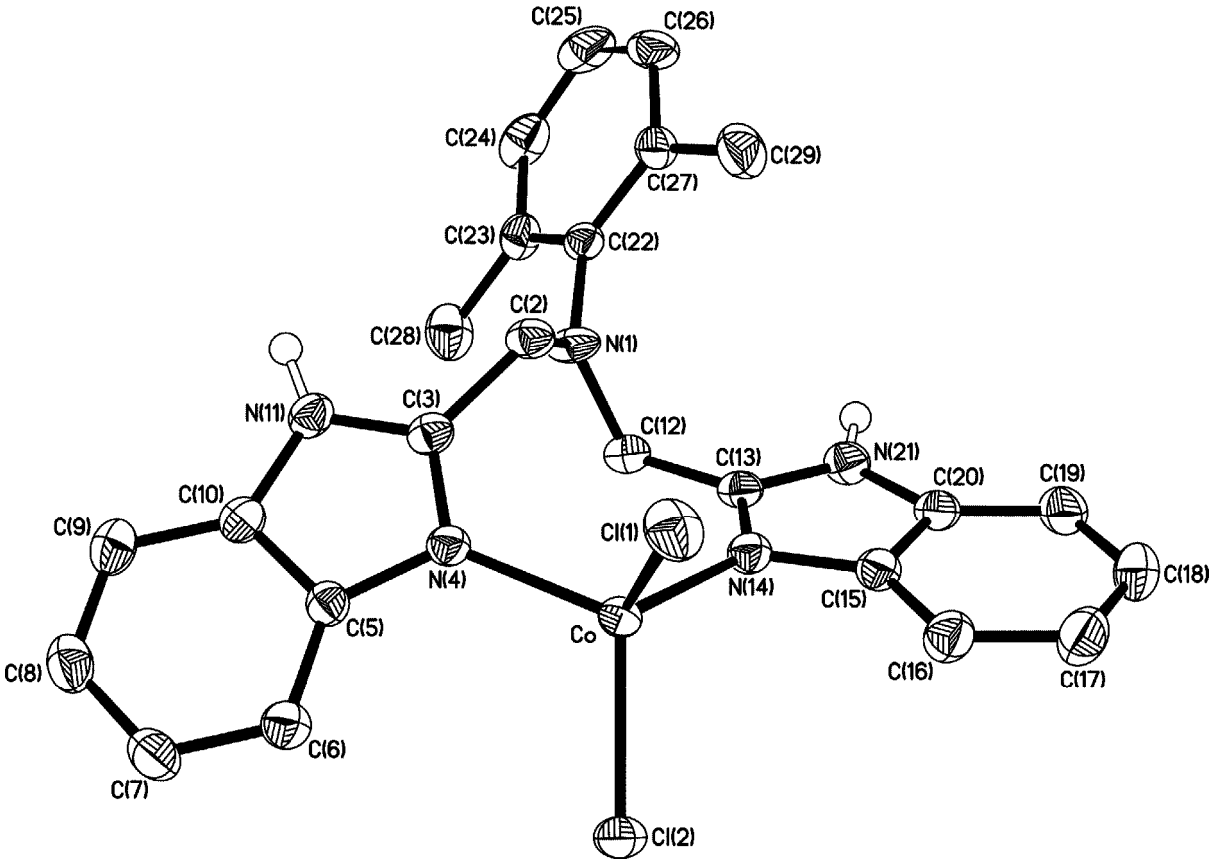
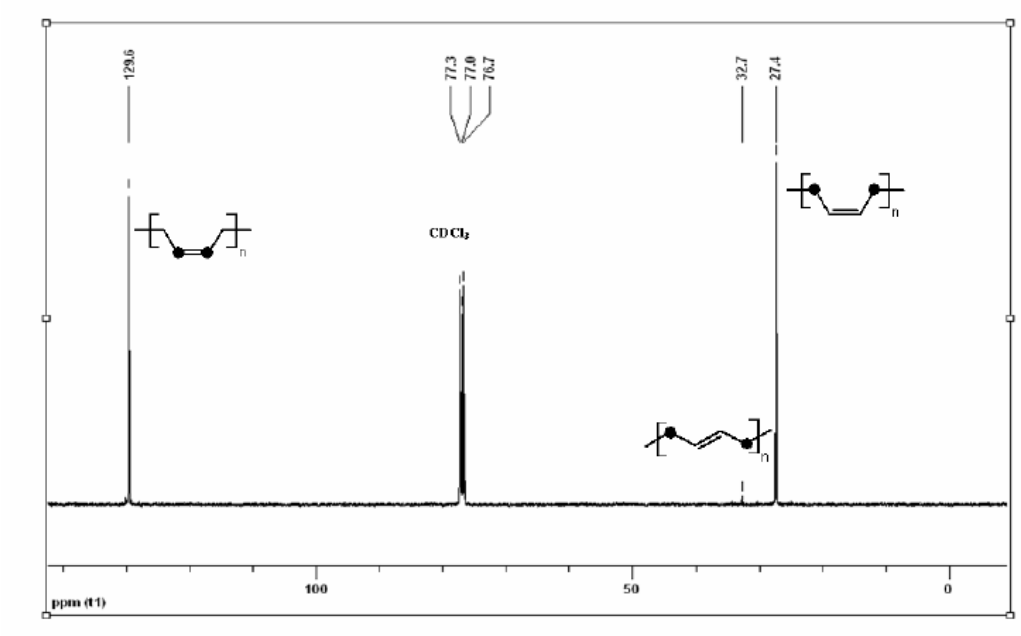
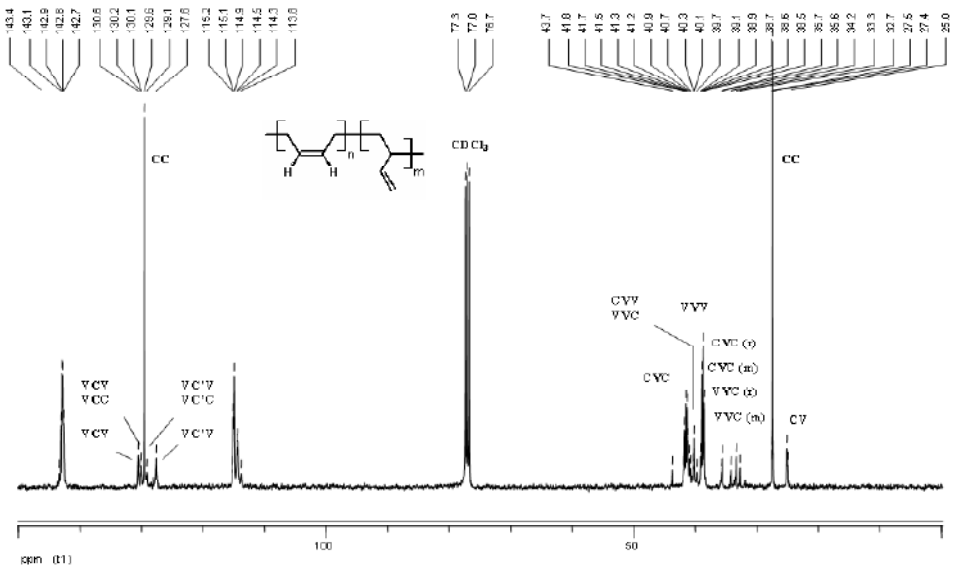


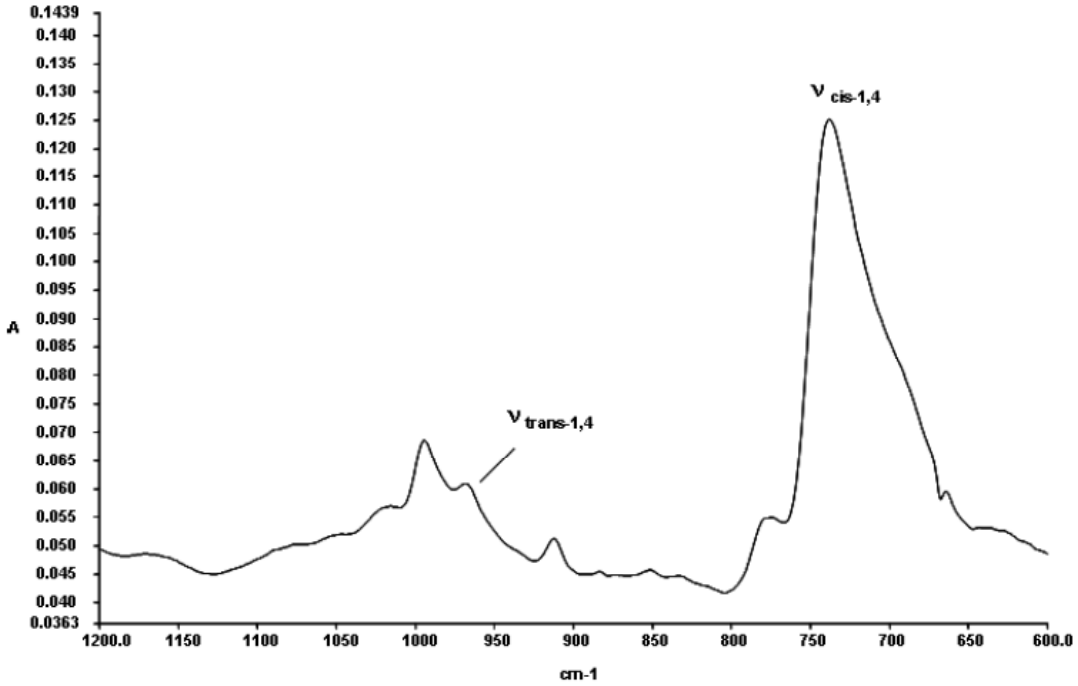
Fig. S7



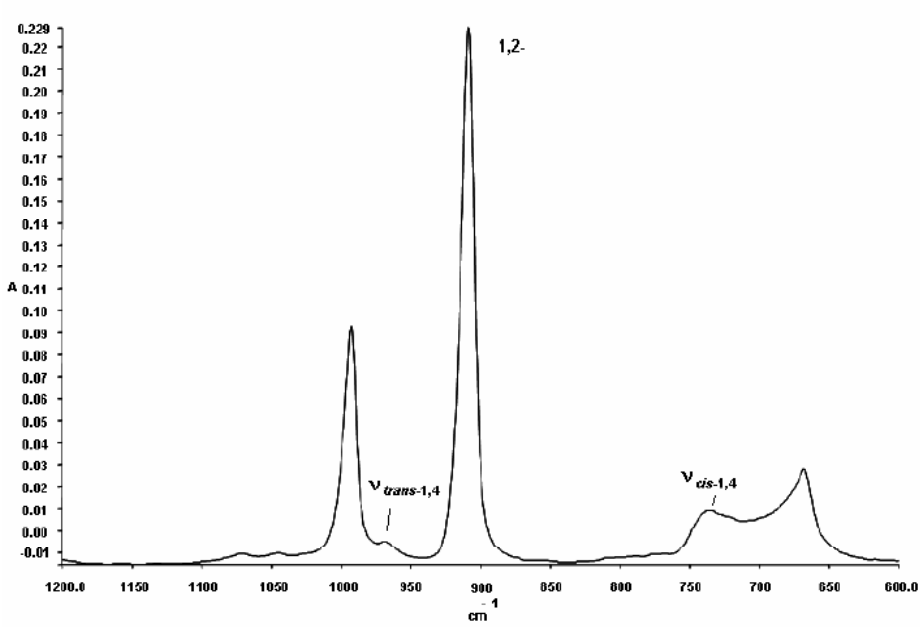
^{13}C NMR spectrum of polybutadiene obtained by catalyst **2**/MAO; polymer microstructure: *cis*-1,4- = 98 mol%, *trans*-1,4 = 2 mol%



^{13}C NMR spectrum of 1,2-polybutadiene-*co*-*cis*-1,4-polybutadiene obtained by catalyst **2**/MAO in the presence of PPh_3; Co/PPh_3 =1/1 mol/mol. Linkages distribution, mol%: 1,2- = 65, *cis*-1,4- = 31, *trans*-1,4- = 4 ; sequence abbreviations: C = *cis*-1,4, V = vinyl ; r = *rac*, m = *meso*



FT IR spectrum of polybutadiene obtained by catalyst **2**/MAO; polymer microstructure: *cis*-1,4- = 98 mol%, *trans*-1,4 = 2 mol%



FT IR spectrum of 1,2-polybutadiene-*co*-*cis*-1,4-polybutadiene obtained by catalyst **2**/MAO in the presence of PPh_3; Co/PPh_3 =1/1 mol/mol. Linkages distribution, mol%: 1,2- = 65, *cis*-1,4- = 31, *trans*-1,4- = 4.

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