Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Polymerization of phenylacetylene catalyzed by rhodium(I) complexes with N-functionalized N-heterocyclic carbene ligands

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Content

1.- General information.

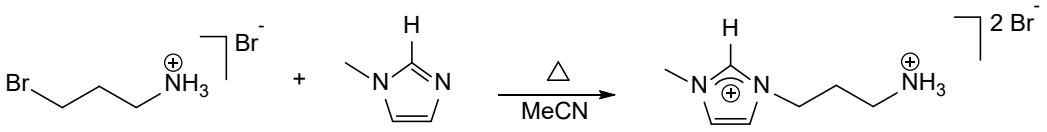
Synthesis. All experiments were carried out under an atmosphere of argon using Schlenk techniques or glovebox. Solvents were distilled immediately prior to use from the appropriate drying agents or obtained from a Solvent Purification System (Innovative Technologies). $CDCl_3$, CD_2Cl_2, C_6D_6, acetone-d_6 and THF-d_8 (Euriso-top) were dried using activated molecular sieves. The starting materials $[Rh(\mu\text{-}Cl)(diene)]_2$ (diene = cod,[1] nbd[2]) and $[Rh(\mu\text{-}OMe)(nbd)]_2$[3] were prepared following the reported methods. 1-Methylimidazole (MeImH) was purchased from Aldrich and purified by distillation under reduced pressure in a Kugelrohr apparatus. 1-tert-Butylimidazole (*t*-Bu-ImH) was prepared following the literature method.[4] The imidazolium salts $[MeImH(CH_2)_3NMe_2)]Cl{\cdot}HCl$,[5] [MeImH(quinolin-8-ylmethyl)]Br,[6] and [MeImH(pyridin-2-yl-mehyl)]Br[7] were prepared according to literature procedures. $[MeImH(CH_2)_3NH_2][PF_6]$ was prepared following the procedure described for the tetrafluroborate salt.[8] Phenylacetylene (Aldrich) was purified by vacuum distillation from CaH_2 and stored over molecular sieves.

Scientific Equipment. C, H and N analyses were carried out in a Perkin-Elmer 2400 Series II CHNS/O analyzer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 300 (300.1276 MHz and 75.4792 MHz) or Bruker Avance 400 (400.1625 MHz and 100.6127 MHz) spectrometers. NMR chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances. Coupling constants (*J*) are given in Hertz. Spectral assignments were achieved by combination of ^1H-^1H COSY, $^{13}C\{^1H\}$-APT and ^1H-^{13}C HSQC experiments. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formate as reference. MALDI-TOF mass spectra were obtained on a Bruker MICROFLEX spectrometer using DCTB, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, as matrix.[9] Conductivities were measured in *ca.* 5 10^{-4} M acetone solutions of the complexes using a Philips PW 9501/01 conductimeter.

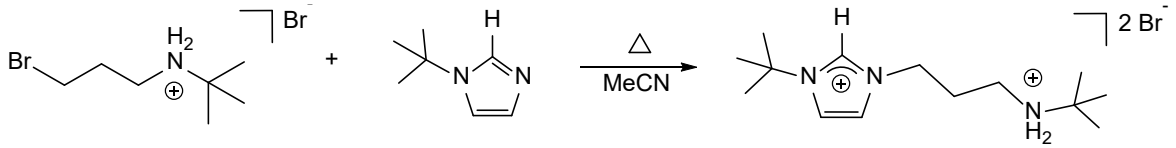
The absolute molecular weight averages (M_n and M_w), dispersity ($Đ$, M_w/M_n) and molecular weight distribution were determined by SEC-MALS at the Chromatography and Spectroscopy Service of the ISQCH. SEC-MALS analyses were carried out using a Waters 2695 instrument, equipped with three PL-Gel Mixed B LS columns fitted to a MALS detector (MiniDawn Treos, Wyatt) and a differential refractive index detector (Optilab Rex, Wyatt).

The polymer solutions in THF (≈ 2.0 mg/mL) were filtered through a 0.45 μm PTFE membrane filter before being injected in the GPC systems. To minimize sample degradation the analyses were carried out immediately after the dissolution of the polymer sample in THF.[10,11] Data analysis was performed with ASTRA Software from Wyatt. The samples were eluted at 25 ºC with THF at a flow rate of 1.0 mL/min. The reported dn/dc value of 0.2864 mL g^{-1} determined at 633 nm for atactic PPA[10] was used which resulted in calculated mass recoveries that were in reasonable agreement with the theoretical values.[12]

2.-Synthesis of N-functionalized imidazolium salts.



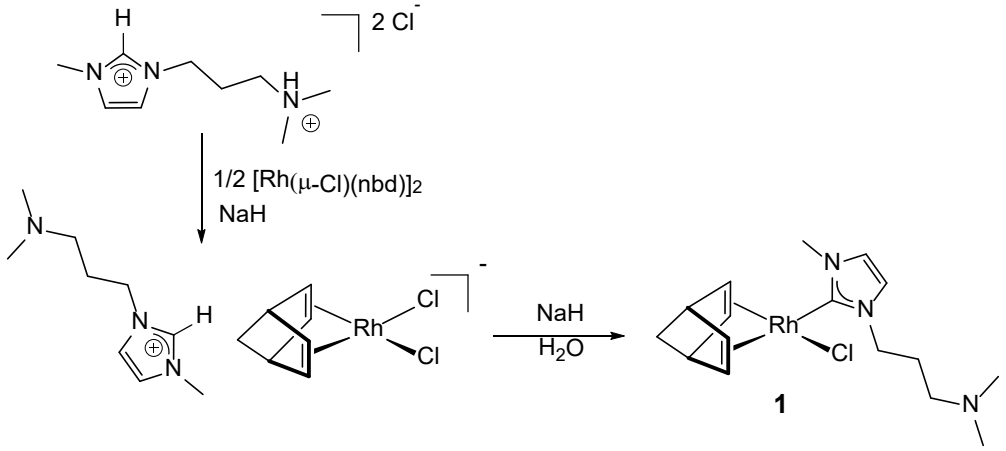
Synthesis of [MeImH(CH$_2$)$_3$NH$_2$]Br·HBr. A mixture of 1-methylimidazole (1.00 g, 12.18 mmol) and 3-bromopropan-1-amine hydrobromide (3.00 g, 13.43 mmol) was dissolved in anhydrous CH_3CN (20 mL) under argon and refluxed for 24 h. The white solid formed was filtered and extracted with MeOH (10 mL) under argon. The resulting solution was brought to dryness under vacuum to give a white solid which was washed with a CH_3CN/diethyl ether mixture (3 x 5 mL) and dried under vacuum. Yield: 82%. Anal. Calcd. for $C_7H_{15}N_3Br_2$: C, 27.93; H, 5.02; N, 13.96. Found: C, 27.72; H, 5.07; N, 13.93. MS (ESI+, $CHCl_3$, *m/z*, %): 140.1 ([M-H]$^+$, 100). ^{1}H NMR (298 K, D_2O): δ 8.81 (s, 1H, NC*H*N), 7.55 (s, 1H, CH), 7.47 (s, 1H, CH), 4.35 (t, 2H, $J_{H\text{-}H}$ = 7.2, NCH_2), 3.92 (s, 3H, NCH_3), 3.09 (m, 2H, NCH_2), 2.30 (m, 2H, CH_2), 2.13 (br, 3H, NH_3^+). ^{13}C{^{1}H} NMR (298 K, D_2O): δ 136.60 (N*C*HN), 124.0, 122.1 (CH), 55.3 (NCH_2), 46.1 (NCH_2), 35.8 (NCH_3), 27.4 (s, CH_2).



Synthesis of [*t*-BuImH(CH$_2$)$_3$NH-t-Bu]Br·HBr. 3-bromo-N-(t-butyl)propan-1-amine hydrobromide[13] (2.21 g, 8.06 mmol) was added to a solution of 1-*t*-butylimidazole (1.00 g, 8.06 mmol) in anhydrous acetonitrile (20 mL). The mixture was refluxed for 12 h to give a

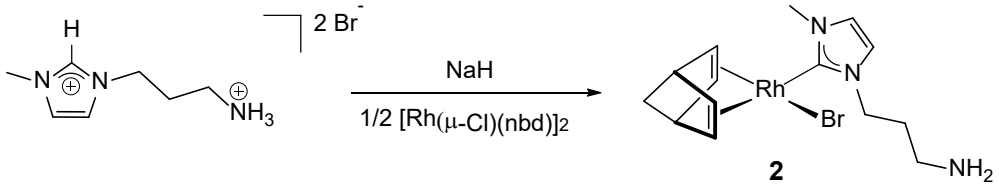
white suspension. The white solid was separated by decantation, washed with diethyl ether (3 x 5 mL) and dried under vacuum. Yield: 89%. Anal. Calcd. For $C_{14}H_{28}N_3Br_2$: C, 42.23; H, 7.09; N, 10.55. Found: C, 42.18; H, 7.03; N, 10.59. MS (ESI, CH_3OH, *m/z*, %): 237.2 ($[M-H]^+$, 100). ^1H NMR (298 K, CD_3OD): δ 9.31 (s, 1H, NC*H*N), 7.89 (s, 1H, CH), 7.79 (s, 1H, CH), 4.43 (t, 2H, J_{H-H} = 7.2, NCH_2), 3.13 (t, 2H, *J* = 7.2, NCH_2), 2.37 (q, 2H, *J* = 7.2, CH_2), 2.20 (br, 2H, NH_2^+), 1.70 (s, 9H, CH_3 *t*-$BuNH_2^+$), 1.42 (s, 9H, CH_3 *t*-Bu-Im). $^{13}C\{^1H\}$ NMR (298 K, CD_3OD): δ 143.0 (N*C*HN), 123.9, 121.7 (CH), 61.5 (C, *t*-$BuNH_2^+$), 58.6 (C Im-*t*-Bu), 47.8 (NCH_2), 39.6 (NCH_2), 29.8 (CH_3 *t*-$BuNH_2^+$), 28.6 (CH_2), 25.9 (CH_3 *t*-Bu-Im).

3.-Synthesis and characterization of Rh(MeIm∩Z) complexes.

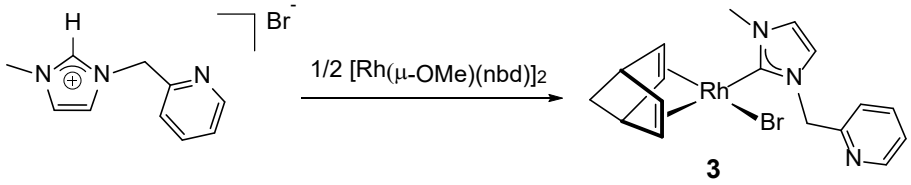


[RhCl(nbd){κ*C*-MeIm(CH₂)₃NMe₂}] (1). A suspension of $[MeImH(CH_2)_3NMe_2]Cl{\cdot}HCl$ (100 mg, 0.416 mmol), NaH (11.6 mg, 0.483 mmol) and $[Rh(\mu\text{-}Cl)(nbd)]_2$ (96 mg, 0.208 mmol) in THF (10 mL) was stirred for 12 h at room temperature to give a suspension of the ion-pair compound $[MeImH(CH_2)_3NMe_2][RhCl_2(nbd)]$. Then, NaH (27.9 mg, 1.163 mmol) and H_2O (0.3 mL) were added to give an orange suspension which was filtered and washed with THF (3 x 3 mL). The orange solution was evaporated under vacuum to give an orange residue which was washed with *n*-hexane (3 x 3 mL) and dried under vacuum. Yield: 73 %. Anal. Calcd. for $C_{16}H_{25}ClN_3Rh$: C, 48.32; H, 6.34; N, 10.56. Found: C, 48.20; H, 6.33; N, 10.56. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 362.1 ($[M-Cl]^+$, 100). ^1H NMR (298 K, CD_2Cl_2): δ 6.85 (s, 1H, CH), 6.80 (s, 1H, CH), 4.72 (br, 2H, =CH nbd), 4.45 (s, 2H, NCH_2), 4.02 (s, 3H, NCH_3), 3.79 (br, 2H, =CH nbd), 3.47 (s, 2H, CH nbd), 2.33 (m, 2H, NCH_2), 2.26 (s, 6H, NMe_2), 2.06 (m, *2*H, CH_2), 1.33 (ABq, J_{H-H} = 8.4, 2H, CH_2 nbd). $^{13}C\{^1H\}$ NMR (298 K,

CD_2Cl_2): δ 183.1 (d, $J_{C\text{-}Rh}$ = 58.4, C_{NCN}), 122.2 (CH), 121.5 (CH), 78.9 (d, $J_{C\text{-}Rh}$ = 5.8, =CH nbd), 63.8 (d, $J_{C\text{-}Rh}$ = 5.2, CH_2 nbd), 56.9 (NCH_2), 51.5 (d, $J_{C\text{-}Rh}$ = 2.7, =CH nbd), 49.0 (NCH_2), 48.2 (d, $J_{C\text{-}Rh}$ = 12.6, CH nbd), 45.8 (NMe_2), 38.1 (NCH_3), 29.8 (CH_2).

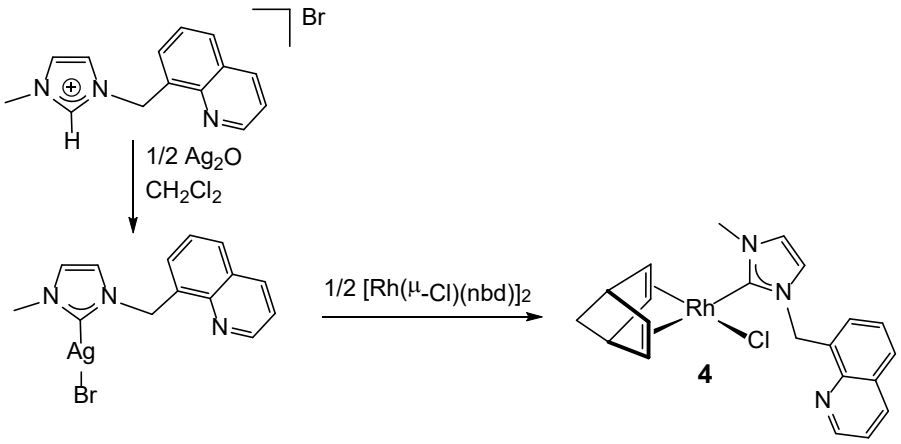


[RhBr(nbd){κ*C*-MeIm(CH_2)$_3$$NH_2$}] (2). A suspension of [MeImH(CH_2)$_3$$NH_2$]Br·HBr (100 mg, 0.332 mmol), NaH (17.5 mg, 0.731 mmol) and [Rh(μ-Cl)(nbd)]$_2$ (76.5 mg, 0.166 mmol) in THF (10 mL) was stirred for 24 h at room temperature to give a yellow suspension which was filtered and washed with THF (3 x 3 mL). The yellow solution was evaporated to dryness under vacuum to give a yellow solid which was washed with *n*-hexane (3 x 3 mL) and dried under vacuum. Yield: 46%. Anal. Calcd. for $C_{14}H_{21}BrN_3Rh$: C, 40.60; H, 5.11; N, 10.15. Found: C, 40.70; H, 5.16; N, 10.14. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 334.1 ([M-Br]$^+$, 100). ^{1}H NMR (298K, THF-d_8): δ 6.99 (d, 1H, $J_{H\text{-}H}$ = 1.7, CH), 6.93 (d, 1H, $J_{H\text{-}H}$ = 1.7, CH), 4.67 (br, 2H, =CH nbd), 3.92 (s, 3H, NCH_3), 3.82 (br, 2H, =CH nbd), 3.62 (br, 2H, CH nbd), 2.79 (br, 2H, NH_2), 2.41 (s, 2H, NCH_2), 2.14 (s, 2H, CH_2), 1.22 (s, 2H, NCH_2), 1.10 (m, 2H, CH_2 nbd). ^{13}C{^{1}H} NMR (298K, THF-d_8): δ 184.0 (C_{NCN}, $J_{C\text{-}Rh}$ = 58.1), 123.6 (CH), 121.3 (CH), 78.5 (=CH nbd), 62.2 (NCH_2), 53.9 (=CH nbd), 51.5 (CH nbd), 39.8 (NCH_2), 38.4 (NCH_3), 31.1 (CH_2).



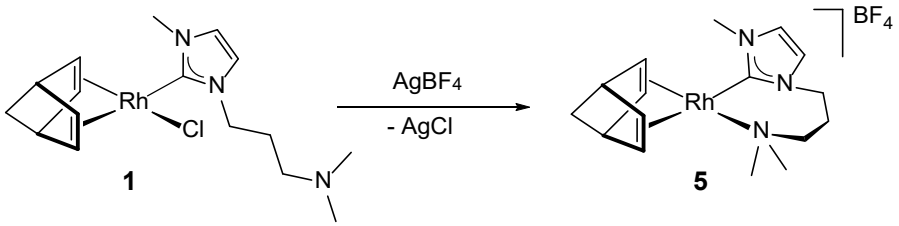
[RhBr(nbd){κ*C*-MeIm(pyridin-2-ylmethyl)}] (3). [Rh(μ-OMe)(nbd)]$_2$ (108 mg, 0.239 mmol) was added to a suspension of [MeImH(pyridin-2-ylmethyl)]Br (114.3 mg, 0.478 mmol) in THF (10 mL) and the mixture stirred for 15 h at room temperature to give an orange suspension. The suspension was filtered and washed with THF (3 x 3 mL) to give an orange solution which was brought to dryness under vacuum. The residue was washed with *n*-

hexane until obtaining a yellow solid which was dried under vacuum. Yield: 62 %. Anal. Calcd. for $C_{17}H_{19}BrN_3Rh$: C, 45.56; H, 4.27; N, 9.38. Found: C, 45.32; H, 4.17; N, 9.25. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 449.1 ($[M]^+$, 100). ^{1}H NMR (233 K, CD_2Cl_2): δ 8.41 (d, 1H, $J_{H\text{-}H}$ = 4.8, H_o py), 7.69 (m, 1H, H_p py), 7.46 (d, 1H, $J_{H\text{-}H}$ = 7.6, H_m py), 7.19 (m, 1H, H_m py), 7.06 (d, 1H, $J_{H\text{-}H}$ = 1.8, CH), 6.73 (d, 1H, $J_{H\text{-}H}$ = 1.8, CH), 5.36 (s, 2H, CH_2), 4.33 (br, 2H, =CH nbd), 3.92 (s, 3H, NCH_3), 3.55 (br, 2H, CH nbd), 2.69 (br, 2H, =CH nbd), 1.08 (ABq, 2H, $J_{H\text{-}H}$ = 7.35, CH_2 nbd). ^{13}C{^{1}H} NMR (233 K, CD_2Cl_2): δ 182.1 (d, $J_{C\text{-}Rh}$ = 53.8, C_{NCN}), 154.3 (C_i py), 154.1 (C_o py), 137.2 (C_p py), 124.0 (C_m py), 123.1 (C_m py), 121.4 (CH), 120.9 (CH), 76.2 (br, =CH nbd), 59.9 (CH_2 nbd), 56.1 (CH_2), 48.8 (CH nbd), 37.9 (NCH_3), 25.7 (br d, $J_{C\text{-}Rh}$ = 13.2, =CH nbd).

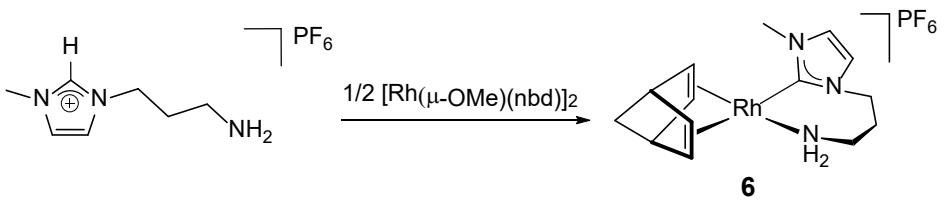


[RhCl(nbd){κ*C*-MeIm(quinolin-8-ylmethyl)}] (4). A mixture of [MeImH(quinolin-8-il-metil)]Br (71 mg, 0.233 mmol) and Ag_2O (28 mg, 0.121 mmol) was refluxed in CH_2Cl_2 (5 mL) for 1 h at room temperature and then filtered to remove the excess of Ag_2O. The resulting solution was added to a solution of [{Rh(μ-Cl)(nbd)}$_2$] (53.5 mg, 0.116 mmol) in THF (5 mL) and stirred for 30 min at room temperature to give a suspension that was filtered to remove the formed AgCl. The solution was evaporated to dryness under vacuum to give a yellow solid which was washed with *n*-hexane (3 x 3 mL) and dried under vacuum. Yield: 56%. Anal. Calcd. for $C_{21}H_{21}ClN_3Rh$: C, 55.58; H, 4.67; N, 9.26. Found: C, 55.62; H, 4.67; N, 9.28. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 418.1 ($[M\text{-}Cl]^+$, 100). ^{1}H NMR (298 K, $CDCl_3$): δ 8.97 (d, 1H, $J_{H2\text{-}H3}$ = 4.1, H_2), 8.20 (dd, 1H, $J_{H4\text{-}H3}$ = 8.3, $J_{H4\text{-}H2}$ = 1.6, H_4), 8.07 (d, 1H, $J_{H7\text{-}H6}$ = 7.0, H_7), 7.82 (d, 1H, $J_{H6\text{-}H5}$ = 8.2, H_6), 7.62 (t, 1H, $J_{H5\text{-}H6}$ = 7.57, H_5), 7.46 (dd, 1H, $J_{H3\text{-}H4}$ = 8.3, $J_{H3\text{-}H2}$ = 4.2, H_3), 6.92 (d, 1H, $J_{H\text{-}H}$ = 1.5, CH), 6.70 (d, 1H, $J_{H\text{-}H}$ = 1.5, CH), 5.32 (s,

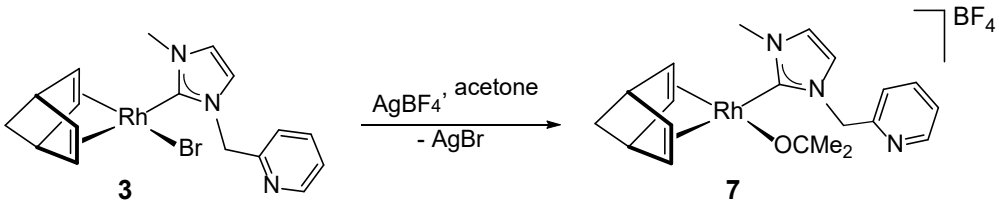
2H, CH_2), 4.87 (br, 2H, =CH nbd), 4.10 (s, 3H, NCH_3), 3.76 (br, 2H, =CH nbd), 3.44 (br, 2H, CH nbd), 1.33 (m, 2H, CH_2 nbd). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): δ 184.6 (C_{NCN}), 150.0 (C, C_2), 146.6 (C_{4a}), 136.6 (C_4), 135.3 (C_{8a}), 131.08 (C_8), 128.5 (C_5), 128.3 (CH, C_7), 126.9 (CH, C_6), 122.0 (CH) 121.6 (CH), 121.8 (CH, C_3), 78.9 (=CH nbd), 63.5 (CH_2 nbd), 51.2 (=CH nbd), 52.8 (CH_2), 48.0 (CH nbd), 38.1 (NCH_3).



[Rh(nbd){κ^2*C,N*-MeIm(CH$_2$)$_3$NMe$_2$)}]BF$_4$ (5). $AgBF_4$ (49.0 mg, 0.251 mmol) was added to a solution of [RhCl(nbd){κ*C*-MeIm$(CH_2)_3NMe_2$}] (**1**) (100 mg, 0.251 mmol) in a CH_3CN/acetone (1:1, 10 mL) mixture. After 6 h of stirring at 273 K the AgCl formed was separated by filtration. The resulting yellow solution was concentrated to ca. 1 mL and then layered with diethyl ether (10 mL) at room temperature to give a microcrystalline yellow solid which was filtered, washed with diethyl ether (3 x 2 mL), and dried in vacuo. Yield: 60%. Anal. Calcd. for $C_{16}H_{25}BF_4N_3Rh$: C, 42.79; H, 5.61; N, 9.36. Found: C, 42.65; H, 5.56; N, 9.24. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 362.1 ([M^+], 100). Λ_M (acetone, 5.0 x 10^{-4} M) = 68 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (298K, CD_2Cl_2): δ 6.94 (d, 1H, J_{H-H} = 1.9, CH), 6.89 (d, 1H, J_{H-H} = 1.9, CH), 5.67 (m, 1H, NCH_2), 4.75 (br, 1H, =CH nbd), 4.48 (br, 1H, =CH nbd), 4.27 (m, 1H, NCH_2), 4.04 (br, 1H, =CH nbd), 3.94 (m 3H, 1H =CH nbd and 2H CH nbd), 3.81 (s, 3H, NCH_3), 2.55 (m, 1H, NCH_2), 2.24 (s, 6H, NMe_2), 2.17 (m, 1H, CH_2), 1.84 (m, 2H, 1H, NCH_2 and 1H, CH_2), 1.45 (ABq, 2H, J_{H-H} = 8.7, CH_2 nbd). $^{13}C\{^1H\}$ NMR (298K, CD_2Cl_2): δ 179.2 (C_{NCN}), 124.1, 122.1 (CH), 83.9 (br, =CH nbd), 79.4 (d, J_{C-Rh} = 6.1, =CH nbd), 65.6 (d, J_{C-Rh} = 5.5, CH_2 nbd), 62.9 (NCH_2), 57.0 (br, =CH, nbd), 55.8 (br, =CH nbd), 52.8 (CH nbd), 49.3 (NMe_2), 47.8 (NCH_2), 37.5 (NCH_3), 26.5 (CH_2).

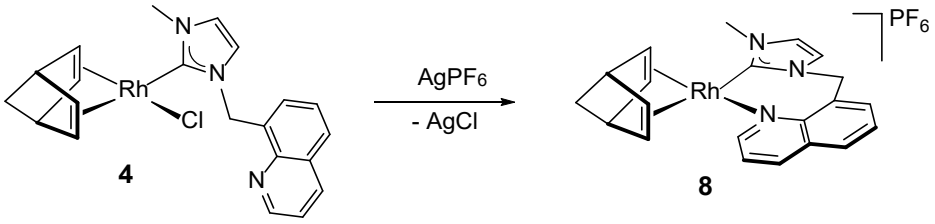


[Rh(nbd){κ^2*C,N*-MeIm(CH$_2$)$_3$NH$_2$}]PF$_6$ (6). [MeImH(CH$_2$)$_3$NH$_2$]PF$_6$ (100 mg, 0.351 mmol) and [Rh(μ-OMe)(nbd)]$_2$ (79.2 mg, 0.175 mmol) were reacted in methanol (8 mL) for 36 h. The resulting yellow solution was filtered and then brought to dryness under vacuum. The yellow residue was extracted with THF (3 x 3 mL) and the solution evaporated to dryness. The yellow solid was washed with diethyl ether (3 x 2 mL) and dried under vacuum. Yield: 56%. Anal. Calcd. for $C_{14}H_{21}F_6N_3PRh$: C, 35.09; H, 4.42; N, 8.77. Found: C, 35.16; H, 4.20; N, 8.76. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 334.1 ([M^+], 100). Λ_M (methanol, 5.0 x 10^{-4} M) = 72 $\Omega^{-1}cm^2mol^{-1}$. ^{1}H NMR (233K, THF-d_8): δ 7.13 (d, 1H, J_{H-H} = 1.7, CH), 7.10 (d, 1H, J_{H-H} = 1.7, CH), 4.99, 4.74, 4.13, 4.03 (br, 1:1:1:1, 4H, =CH nbd), 3.96 (s, 3H, NCH_3), 3.85, 3.73 (br, 1:1, 2H, CH nbd), 3.17-3.04 (br, 2H, NH_2), 2.50-2.33 (m, 2H, CH_2N), 2.60-2.17 (m, 2H, CH_2), 1.29 (ABq, 2H, J_{H-H} = 8.5, CH_2 nbd), 1.18 (s, 2H, NCH_2). ^{13}C{^{1}H} NMR (233K, THF-d_8) δ 185.0 (C_{NCN}, J_{C-Rh} = 54.1), 124.2, 121.7 (CH), 78.8 (J_{C-Rh} = 14.4, =CH nbd), 64.8 (NCH_2), 62.7 (CH_2), 52.6 (CH, nbd), 51.9 (CH nbd), 50.16, 49.6 (=CH nbd), 39.6 (CH_2), 38.4 (NCH_3), 33.63 (CH_2N).

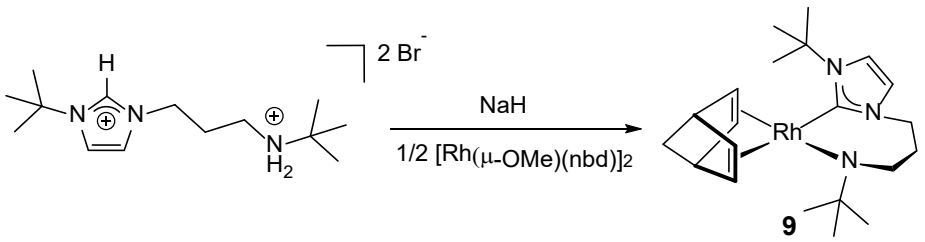


[Rh(nbd){κ*C*-MeIm(pyridin-2-ylmethyl)}(OCMe$_2$)]BF$_4$ (7). $AgBF_4$ (33.5 mg, 0.172 mmol) was added to a solution of [RhBr(nbd){κ*C*-MeIm(pyridin-2-ylmethyl)] (**3**) (77.2 mg, 0.172 mmol) in acetone (10 mL). The suspension was stirred for 2 h at room temperature and then filtered. The resulting orange solution was concentrated to ca. 1 mL and treated with diethyl ether (3 mL) to give an orange solid which was filtered, washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 52%. Satisfactory elemental analysis could not be obtained. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 368.1 ([M - $OCMe_2$]$^+$, 100). Λ_M (acetone, 5.0 x 10^{-4} M) = 63 $\Omega^{-1}cm^2mol^{-1}$. ^{1}H NMR (298K, acetone-d_6): δ 8.41 (d, 1H, J_{H-H} = 5.4, H_o py), 8.06 (td, 1H, J_{H-H} = 7.7, J_{H-H} = 1.6, H_p py), 7.87 (d, 1H, J_{H-H} = 7.8, H_m), 7.56 (m, 1H, H_m py), 7.42 (d, 1H, J_{H-H} = 1.8, CH), 7.14 (d, 1H, J_{H-H} = 1.8, CH), 5.73 (s, 2H, CH_2), 4.93 (br, 2H, =CH nbd), 4.70 (br, 2H, =CH nbd), 4.04 (br, 2H, CH nbd), 3.72 (s, 3H, NCH_3), 1.49 (m, 2H,

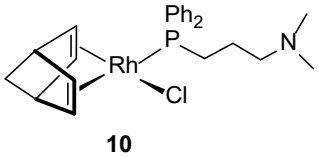
CH_2 nbd). $^{13}C\{^1H\}$ NMR (298K, acetone-d_6): δ 174.7 (C_{NCN}), 154.3 (C_i py), 152.5 (C_o py), 140.9 (C_p py), 126.1 (C_m py), 125.8 (C_m py), 123.7 (CH), 122.2 (CH), 80.4 (d, $J_{C\text{-}Rh}$ = 6.0, =CH nbd), 65.4 (d, $J_{C\text{-}Rh}$ = 5.3, CH_2 nbd), 60.0 (d, $J_{C\text{-}Rh}$= 10.7, =CH nbd), 55.5 (CH_2), 53.6 (CH nbd), 37.3 (NCH_3).



[Rh(nbd){κ²*C,N*-MeIm(quinolin-8-ylmethyl)}]PF_6 (8). $AgPF_6$ (44.6 mg, 0.176 mmol) was added to a solution of [RhCl(nbd){κ*C*-MeImCH_2(quinolin-8-ylmethyl)}] (**4**) (80 mg, 0.176 mmol) in CH_2Cl_2 (10 mL). The suspension was stirred for 1 h at room temperature and then filtered. The resulting yellow solution was evaporated to dryness to give a yellow solid which washed with *n*-hexane (3 x 3 mL) and dried under vacuum. Yield: 43%. Good quality single crystals for X-diffraction were obtained by slow diffusion of *n*-hexane into a solution of the complex in dichloromethane. Anal. Calcd. for $C_{21}H_{21}F_6N_3PRh$: C, 44.78; H, 3.76; N, 7.46. Found: C, 44.67; H, 3.52; N, 7.52. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 418.1 ([M^+], 100). Λ_M (acetone, 5.0 x 10^{-4} M) = 89 $\Omega^{-1}cm^2mol^{-1}$. ^1H NMR (253 K, CD_2Cl_2): δ 8.81 (d, 1H, $J_{H2\text{-}H3}$ = 4.7, H_2), 8.33 (dd, 1H, $J_{H4\text{-}H3}$ = 8.2, $J_{H4\text{-}H2}$ = 1.3, H_4), 8.18 (d, 1H, $J_{H\text{-}H}$ = 14.5, NCH_2), 7.97 (m, 2H, H_6 and H_7), 7.66 (t, 1H, $J_{H5\text{-}H6}$ = 7.0, H_5), 7.54 (dd, 1H, $J_{H3\text{-}H4}$ = 8.2, $J_{H3\text{-}H2}$ = 4.7, H_3), 7.03 (d, 1H, $J_{H\text{-}H}$ = 1.7, CH), 6.68 (d, 1H, $J_{H\text{-}H}$ = 1.7, CH), 5.33 (d, 1H, $J_{H\text{-}H}$ = 14.5, NCH_2), 4.88 (br, 1H, =CH nbd), 4.63 (br, 1H, =CH nbd), 4.44 (br, 1H, =CH nbd), 4.09 (br, 2H, CH nbd), 4.00 (br, 1H, =CH nbd), 3.68 (s, 3H, NCH_3), 1.50 (m, 2H, CH_2 nbd). $^{13}C\{^1H\}$ NMR (253 K, CD_2Cl_2): δ 176.3 (d, $J_{C\text{-}Rh}$ = 58.2, C_{NCN}), 152.1 (C_2), 145.9 (C_{4a}), 140.1 (C_4), 134.0 (C_8), 131.5 (C_7), 131.3 (C_{8a}), 130.8 (C_5), 127.36 (C_6), 123.0 (CH) 121.6 (C_3), 119.7 (CH), 82.9 (d, $J_{C\text{-}Rh}$ = 5.7, =CH nbd), 82.1 (d, $J_{C\text{-}Rh}$ = 6.0, =CH nbd), 64.9 (d, $J_{C\text{-}Rh}$ = 5.2, CH_2 nbd), 60.6 (d, $J_{C\text{-}Rh}$ = 12.1, =CH nbd), 53.0 (d, $J_{C\text{-}Rh}$ = 2.7, =CH nbd), 52.8 (NCH_2), 52.6 (CH nbd), 51.1 (CH nbd), 50.8 (d, $J_{C\text{-}Rh}$ = 11.7, CH nbd), 36.7 (NCH_3).

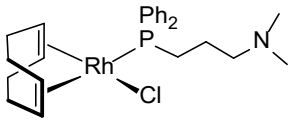


[Rh(nbd){κ²*C,N*-*t*-BuIm(CH₂)₃N-*t*-Bu}] (9). A suspension of [*t*-BuImH(CH₂)₃NH-*t*-Bu]Br·HBr (85.2 mg, 0.214 mmol), NaH (10.8 mg, 0.450 mmol) and [Rh(μ-OMe)(nbd)]₂ (48.4 mg, 0.107 mmol) in THF (10 mL) was stirred for 24 h at room temperature. The solution was passed through a 0.45 micron Teflon filter and the brought to dryness under vacuum. The yellow residue was washed with *n*-hexane (3 x 3 mL) and then dried under vacuum. Yield: 53%. Anal. Calcd. For $C_{21}H_{34}N_3Rh$: C, 58.46; H, 7.94; N, 9.74. Found: C, 58.97; H, 7.52; N, 9.12. MS (ESI+, THF, *m/z*, %): 432.2 ($[M+H]^+$, 100). ^{1}H NMR (298 K, C_6D_6): 6.51 (d, 1H, J_{H-H} = 1.8, CH), 6.49 (d, 1H, J_{H-H} = 1.8, CH), 5.70 (m, 1H, NCH_2), 5.13 (br, 1H, =CH nbd), 4.82 (br, 1H, =CH nbd), 4.30 (m, 1H, NCH_2), 3.65 (br, 1H, CH nbd), 3.49 (br, 1H, CH nbd), 3.41 (br, 1H, =CH nbd), 3.26 (br, 1H, =CH nbd), 2.65 (m, 1H, CH_2N), 2.50 (m, 1H, CH_2N), 2.19 (m, 1H, CH_2), 1.92 (m, 1H, CH_2), 1.75 (s, 9H, CH_3, *t*-Bu-Im), 1.11 (m, 11H, 9H CH_3 *t*-Bu and 2H CH_2 nbd). ^{13}C{^{1}H} NMR (298 K, C_6D_6): δ 183.4 (d, J_{C-Rh} = 56.4, C_{NCN}), 120.0 (CH), 119.4 (CH), 73.6 (d, J_{C-Rh} = 6.5, =CH nbd), 70.0 (d, J_{C-Rh} = 6.5, =CH nbd), 62.6 (CH_2 nbd), 57.6 (C Im-*t*-Bu), 50.7 (d, J_{C-Rh} = 3.0, CH nbd), 50.6 (NCH_2), 50.6 (CH nbd), 50.2 (CN-*t*-Bu), 48.0 (d, J_{C-Rh} = 12.7, =CH nbd), 46.6 (d, J_{C-Rh} = 12.2, =CH nbd), 39.6 (NCH_2), 32.5 (CH_2), 31.9 (*t*-Bu-Im), 29.2 (*t*-Bu).



[RhCl(nbd){κ*P*-Ph₂P(CH₂)₃NMe₂}] (10). A solution of [Rh(μ-Cl)(nbd)]₂ (100 mg, 0.217 mmol) in THF (5 mL) was slowly added to a stirred solution of $Ph_2P(CH_2)_3NMe_2$ (118 mg, 0.434 mmol) in THF (3 mL) at 273 K to give an orange solution which was stirred for 30 min. Removal of the solvent under vacuum gave the compound as an orange-yellow solid that was washed with cold n-hexane (3 x 3 mL) and dried in vacuo. Yield: 70%. Anal. Calcd.

for $C_{24}H_{30}ClNPRh$: C, 57.44; H, 6.03; N, 2.79. Found: C, 57.63; H, 6.21; N, 2.68. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 466.1 ($[M\text{-}Cl]^+$, 100). ^1H NMR (233 K, CD_2Cl_2): δ 7.69-7.41 (m, 10H, Ph), 5.21 (br, 2H, =CH nbd), 3.46 (br, 2H, CH nbd), 3.06 (br, 2H, =CH nbd), 2.35 (m, 4H, CH_2N y CH_2P), 2.17 (s, 6H, NMe_2), 1.71 (m, 2H, CH_2), 1.34 (s, 2H, CH_2 nbd). $^{31}P\{^1H\}$ NMR (233 K, CD_2Cl_2): δ 24.89 (d, $J_{P\text{-}Rh}$ = 162.7). $^{13}C\{^1H\}$ NMR (233 K, CD_2Cl_2): δ 133.3 (d, $J_{C\text{–}P}$ = 10.9, C_o), 131.3 d, $J_{C\text{–}P}$ = 40.6, C_i), 130.2 (C_p), 128.5 (d, $J_{C\text{–}P}$ = 9.4, C_m), 86.1 (dd, $J_{C\text{-}Rh}$ = 12.5, $J_{C\text{-}P}$ = 2.9, =CH nbd), 62.3 (d, $J_{C\text{–}P}$ = 4.1, CH_2 nbd), 60.7 (CH_2N), 49.9 (NMe_2), 55.1 (d, $J_{C\text{-}Rh}$ = 9.1, =CH nbd), 51.2 (CH nbd), 23.3 (d, $J_{C\text{-}P}$ = 23.6, CH_2P), 21.8 (CH_2).



12

[RhCl(cod){κ*P*-$Ph_2P(CH_2)_3NMe_2$}] (12). [Rh(μ-Cl)(cod)]$_2$ (100 mg, 0.203 mmol) and $Ph_2P(CH_2)_3NMe_2$ (110 mg, 0.406 mmol) were reacted in THF at 273 K as described above to give an orange solution. The solvent was removed under vacuum and the orange oily residue triturated with cold n-hexane to give an orange-yellow solid that was washed with cold n-hexane (3 x 3 mL) and dried in vacuo. Yield: 66 %. Anal. Calcd. for $C_{25}H_{34}ClNPRh$: C, 57.98; H, 6.62; N, 2.70. Found: C, 57.65; H, 6.17; N, 2.77. MS (MALDI-Tof, CH_2Cl_2, *m/z*, %): 482.1 ($[M\text{-}Cl]^+$, 100). ^1H NMR (253 K, CD_2Cl_2): δ 7.63-7.36 (m, 10H, Ph), 5.36 (br, 2H, =CH cod), 3.00 (br, 2H, =CH cod), 2.47-2.27 (m, 8H; 4H CH_2 cod, 2H CH_2P and 2H CH_2N), 2.16 (s, 6H, NMe_2), 2.02 (m, 4H, CH_2 cod), 1.88 (m, 2H, CH_2). $^{31}P\{^1H\}$ NMR (253 K, CD_2Cl_2): δ 26.30 (d, $J_{P\text{-}Rh}$ = 148.9). $^{13}C\{^1H\}$ NMR (253 K, CD_2Cl_2): δ 133.8 (d, $J_{C\text{-}P}$ = 10.4, C_o), 132.9 (d, $J_{C\text{-}P}$ = 40.2, C_i), 130.3 (d, $J_{C\text{-}P}$ = 2.0, C_p), 128.4 (d, $J_{C\text{-}P}$ = 9.3, C_m), 104.9 (dd, $J_{C\text{-}Rh}$ = 12.2, $J_{C\text{-}P}$ = 6.9, =CH cod), 70.3 (d, $J_{C\text{-}Rh}$ = 13.9, =CH cod), 60.8 (d, $J_{C\text{-}P}$ = 15.3, CH_2N), 45.6 (NMe_2), 33.2 (CH_2 cod), 29.0 (CH_2 cod), 25.3 (d, $J_{C\text{-}P}$ = 26.7, CH_2P), 24.8 (CH_2).

4.-Crystal structure determination.

Crystal structure determination of 8. Single crystals of **8** suitable for the X-ray diffraction studies were grown by slow diffusion of hexane into a dichloromethane solution of the compound. X-ray diffraction data were collected at 100(2) K on the diffractometers Bruker SMART APEX CCD with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) using ω rotations. Intensities were integrated and corrected for absorption effects with SAINT–PLUS[14] and SADABS[15] programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXS-97[16] and refined by full matrix least-squares on F^2 with SHELXL-2014,[17] under WinGX. [18]

Crystal data and structure refinement for 8. $[C_{21}H_{21}N_3Rh]PF_6 \cdot CH_2Cl_2$, $M = 648.21$ g mol^{-1}, $P2_1/c$, $a = 12.804(7)$ Å, $b = 13.813(8)$ Å, $c = 13.807(8)$ Å, $\beta = 95.465(8)°$, $V = 2431(2)$ Å^3, $Z = 4$, $D_{calc} = 1.771$ g cm^{-3}, $\mu = 1.052$ mm^{-1}, $F(000) = 1296$, orange prism, 0.294 x 0.211 x 0.165 mm^3, $\theta_{min}/\theta_{max}$ 1.60/29.65°, $-17 \le h \le 17$, $-18 \le k \le 19$, $-18 \le l \le 18$, reflections collected/independent 26422/6344 [R(int) = 0.0268], absorption correction: semi-empirical from equivalents, max./min. transmission 0.8410/0.7257, data/restraints/parameters 6344/2/398, GOF(F^2) = 1.069, $R_1 = 0.0305$ [$I > 2\sigma(I)$], $wR_2 = 0.0812$ (all data), largest diff. peak/hole 0.732/–0.409 e·Å^{-3}. CCDC deposit number: 1986054.

5.- Selected NMR spectra of Rh(MeIm∩Z) complexes and precursors.

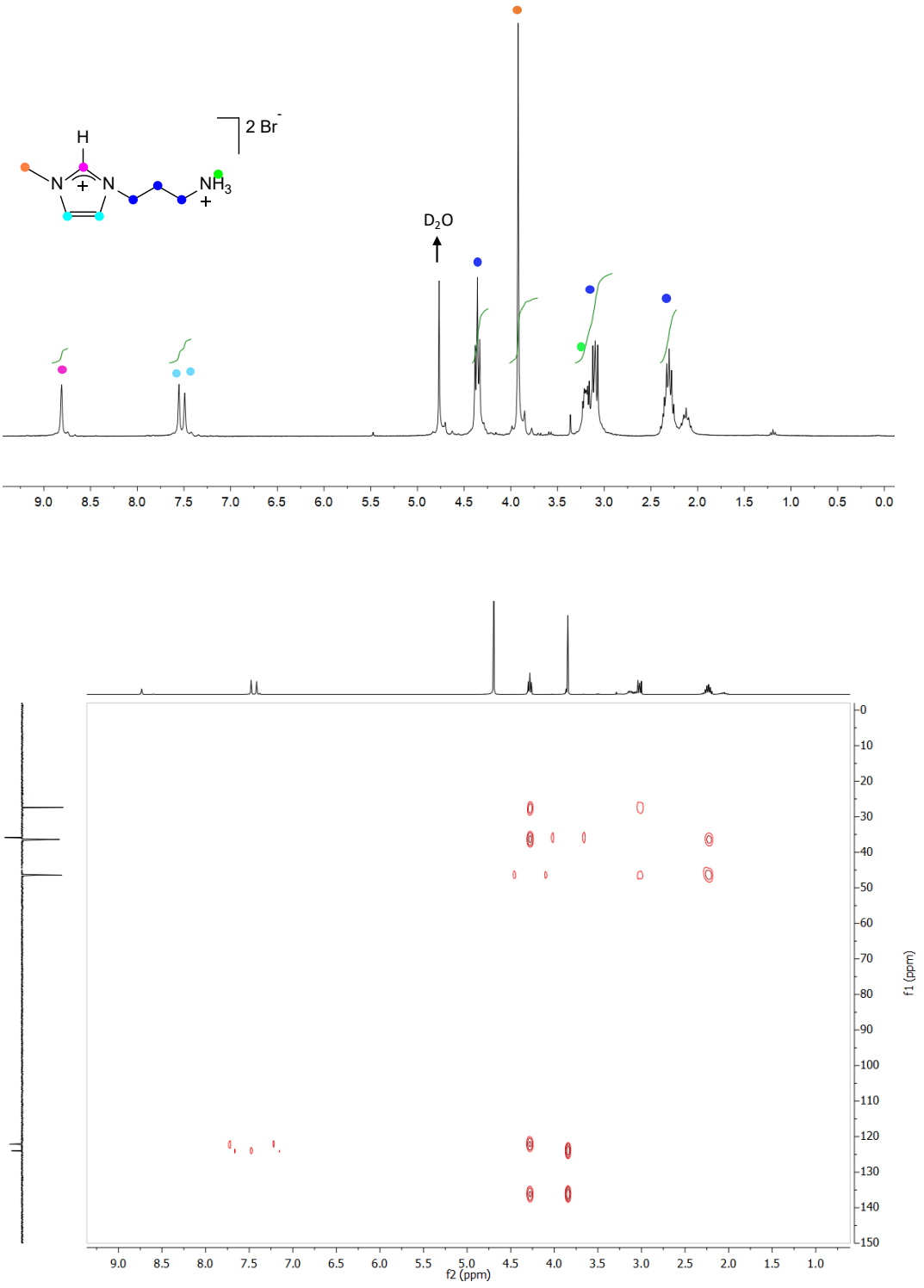


Figure S1. ^{1}H and $^{1}H/^{13}C\{^{1}H\}$-HMBC NMR spectra of $[MeIm(CH_2)_3NH_2]Br{\cdot}HBr$ in D_2O at 298K.

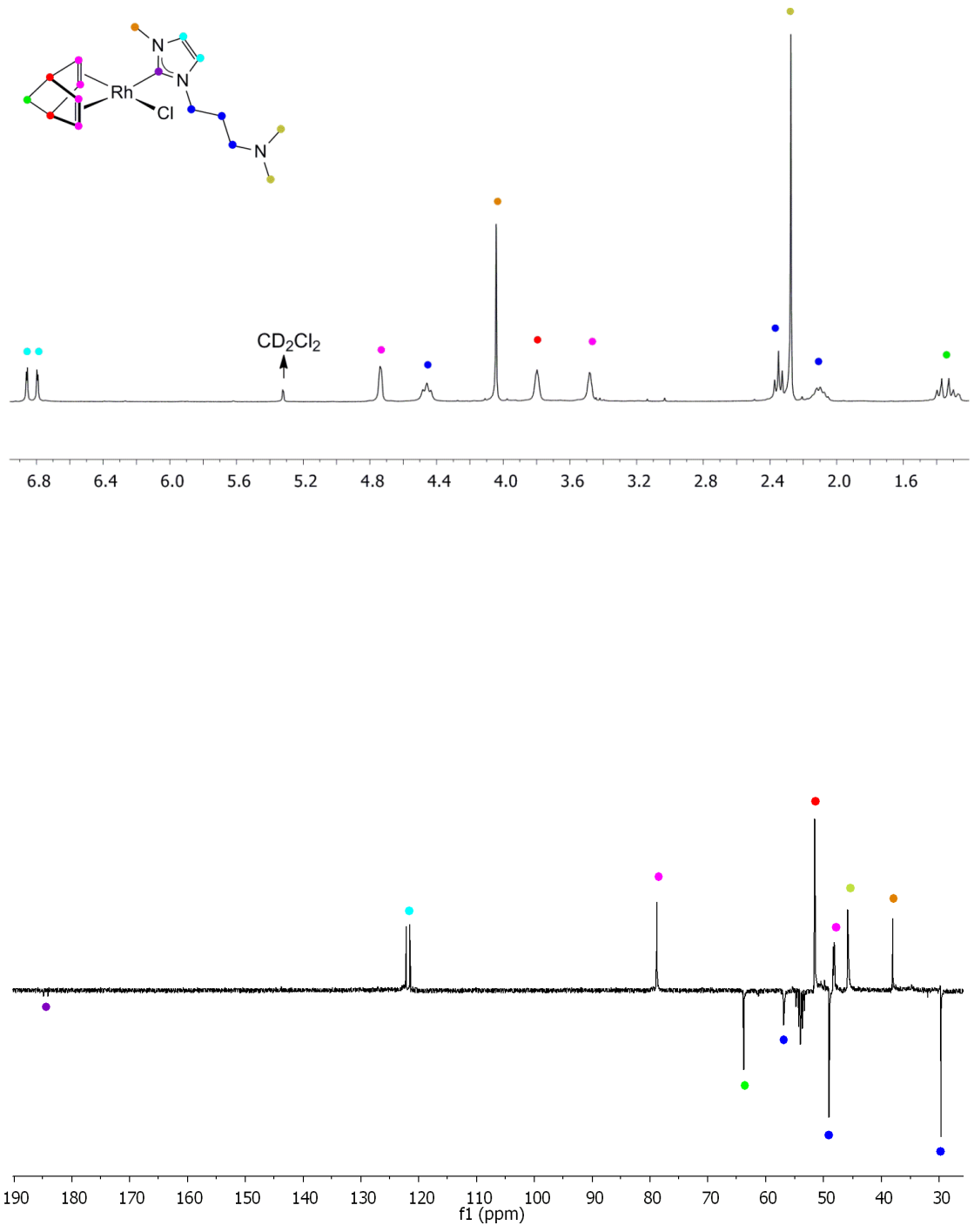


Figure S2. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of [RhCl(nbd){κ*C*-MeIm$(CH_2)_3NMe_2$}] (**1**) in CD_2Cl_2 at 298K.

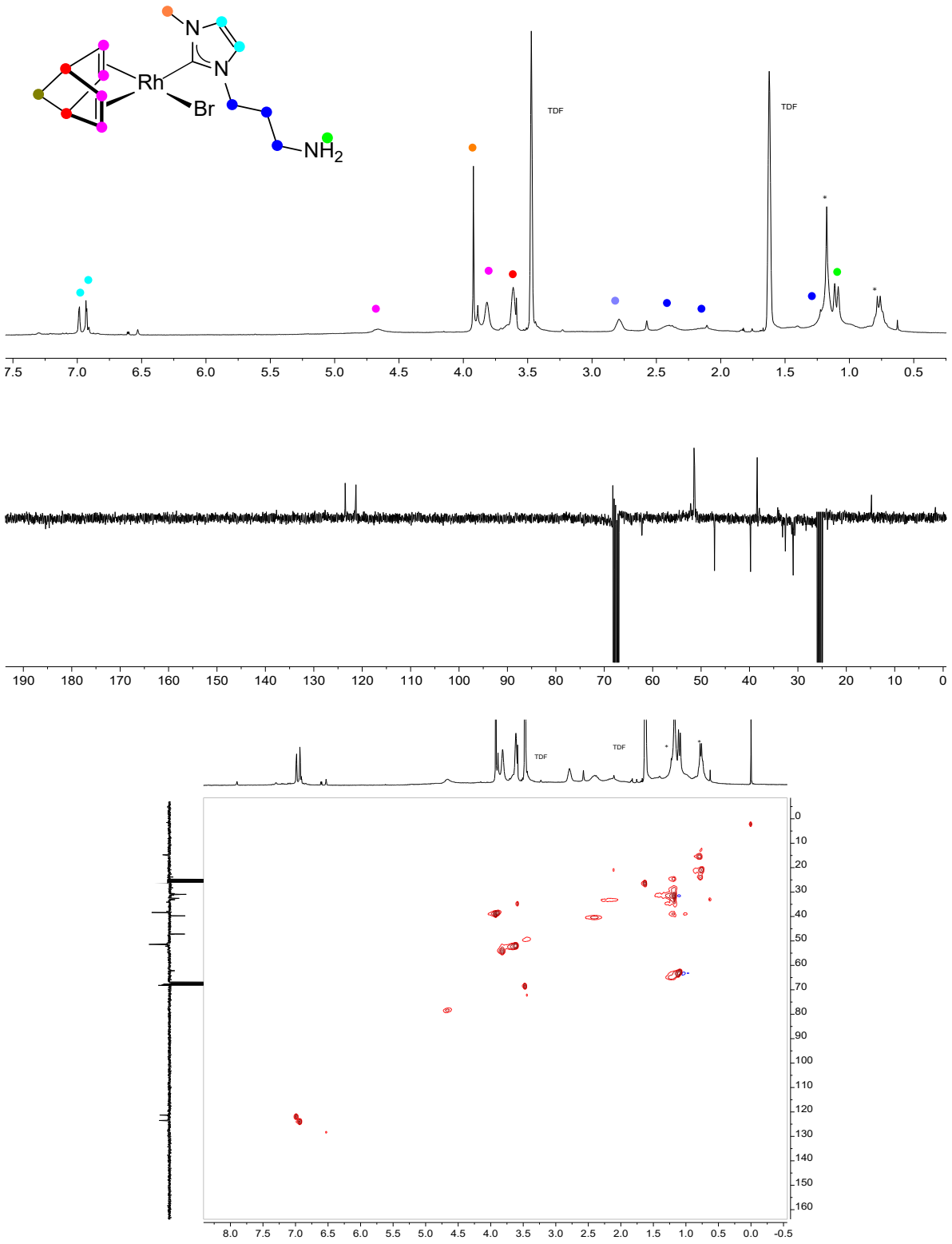


Figure S3. ^{1}H, ^{13}C{^{1}H} and ^{13}C-^{1}H HSQC NMR spectra of [RhBr(nbd){κ*C*-MeIm$(CH_2)_3NH_2$}] (**2**) in THF-d_8 (TDF) at 298K. Residuals solvents (∗ hexane).

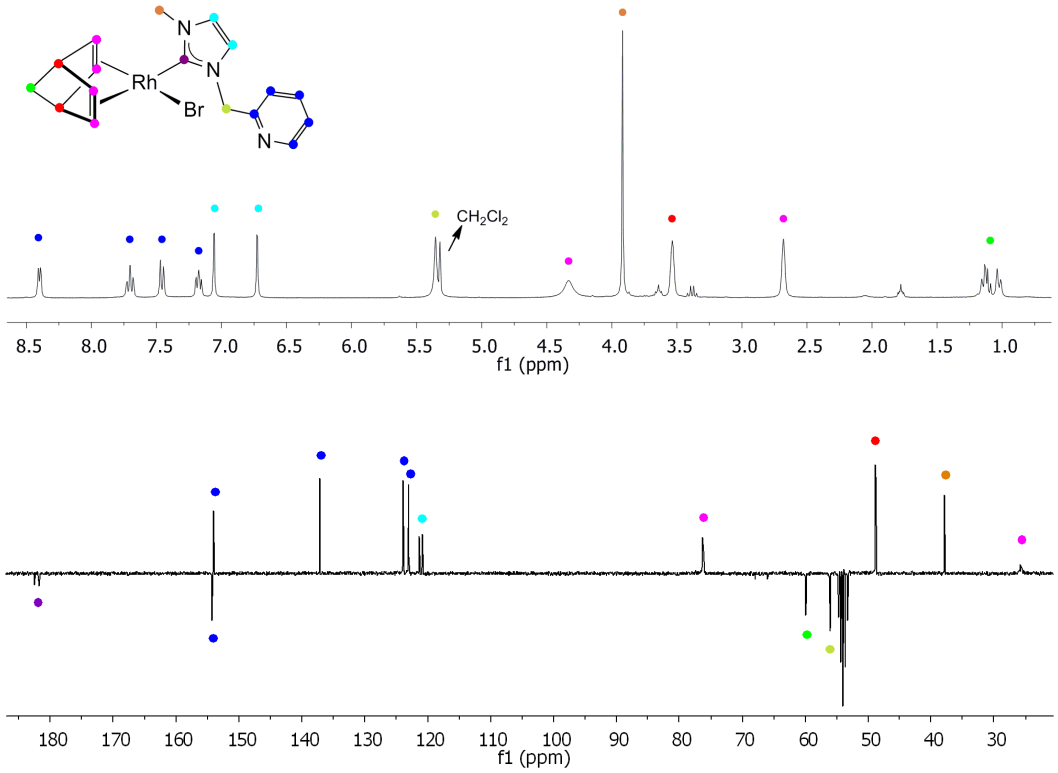


Figure S4. ^{1}H and $^{13}C\{^{1}H\}$-apt NMR spectra of [RhBr(nbd){κ*C*-MeIm(piridin-2-yl-methyl)}] (**3**) in CD_2Cl_2 at 233K.

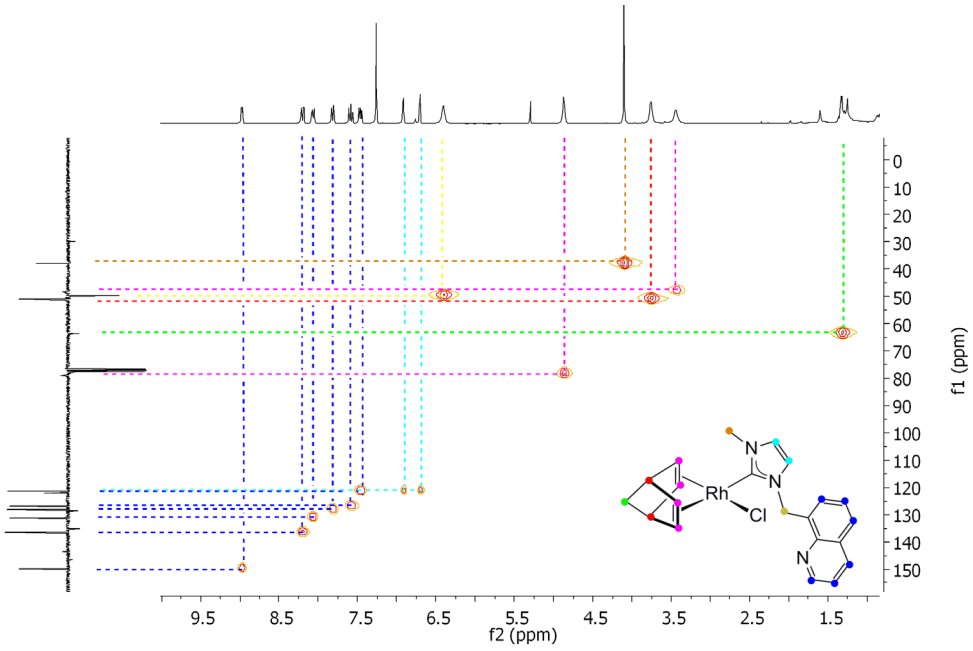


Figure S5. ^{1}H-^{13}C HSQC spectrum of [RhCl(nbd){κ*C*-MeIm(quinolin-8-yl-methyl)}] (**4**) in $CDCl_3$ at 298 K.

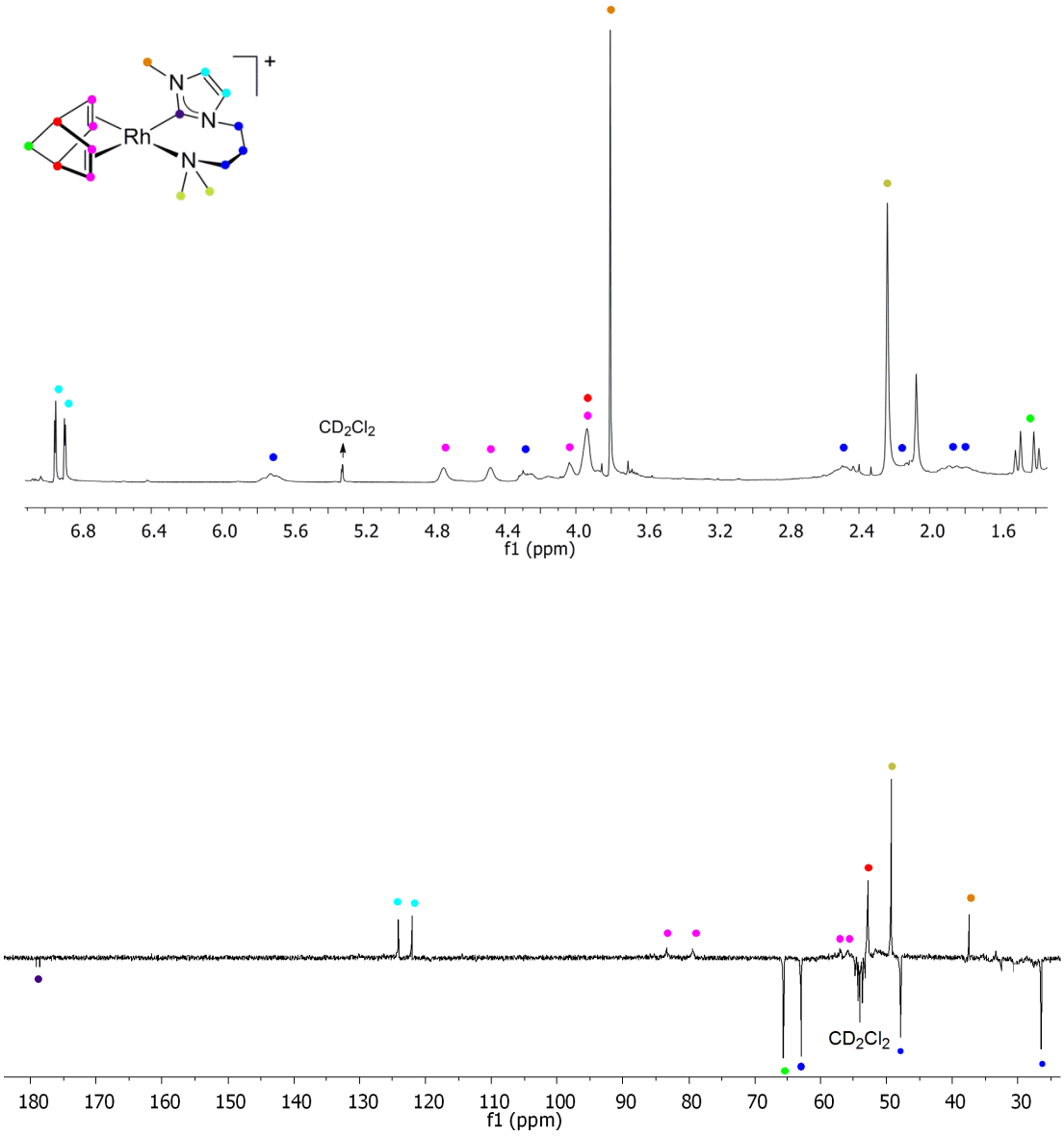


Figure S6. ^{1}H and $^{13}C\{^{1}H\}$-apt NMR spectra of [Rh(nbd){κ^{2}*C*,*N*-MeIm(CH$_2$)$_3$NMe$_2$)}][BF$_4$] (**5**) in CD_2Cl_2 at 298K.

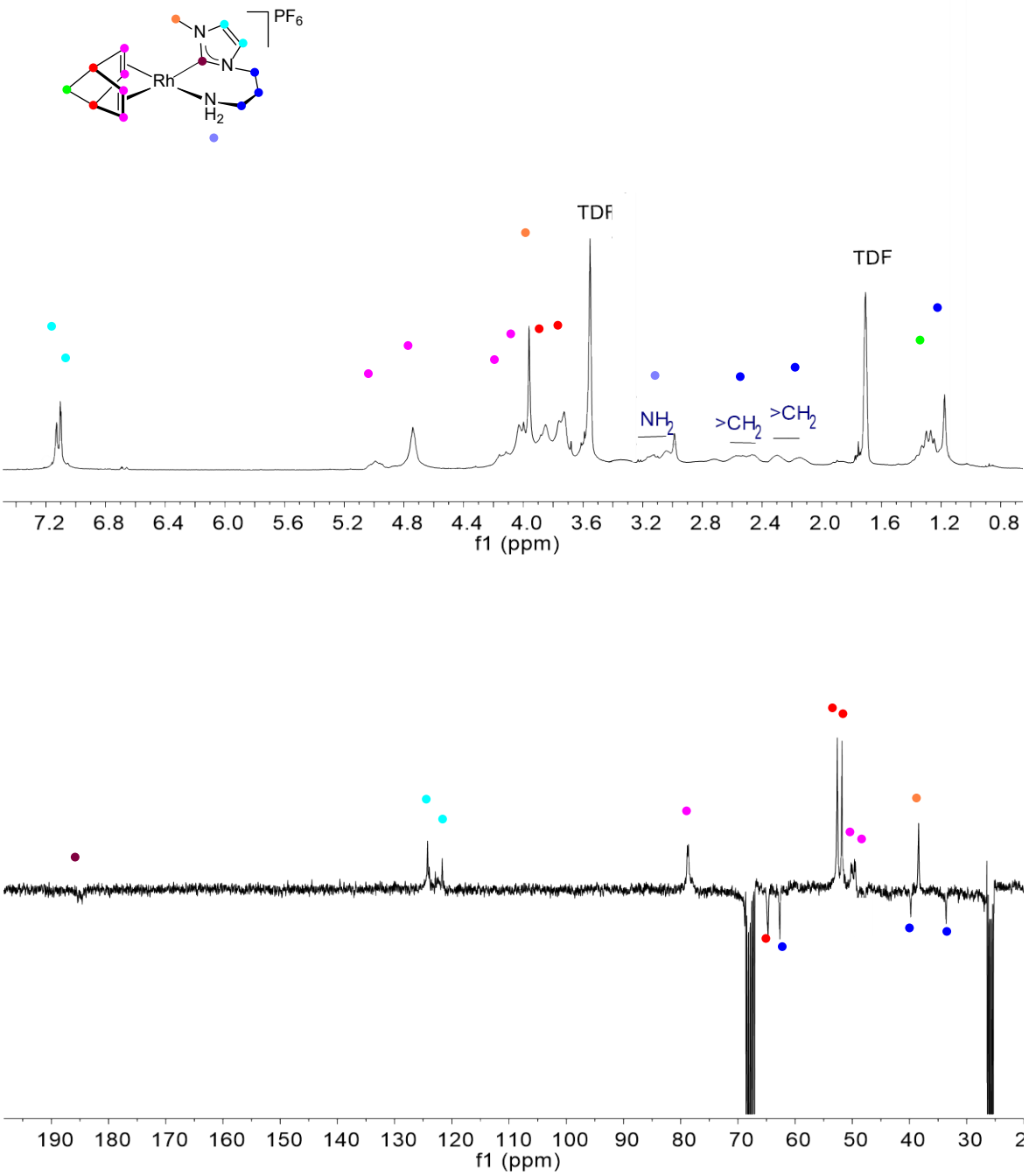


Figure S7. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of [Rh(nbd){κ^{2}*C,N*-MeIm$(CH_2)_3NH_2$}] [PF_6] (**6**) in THF-d_8 at 233K.

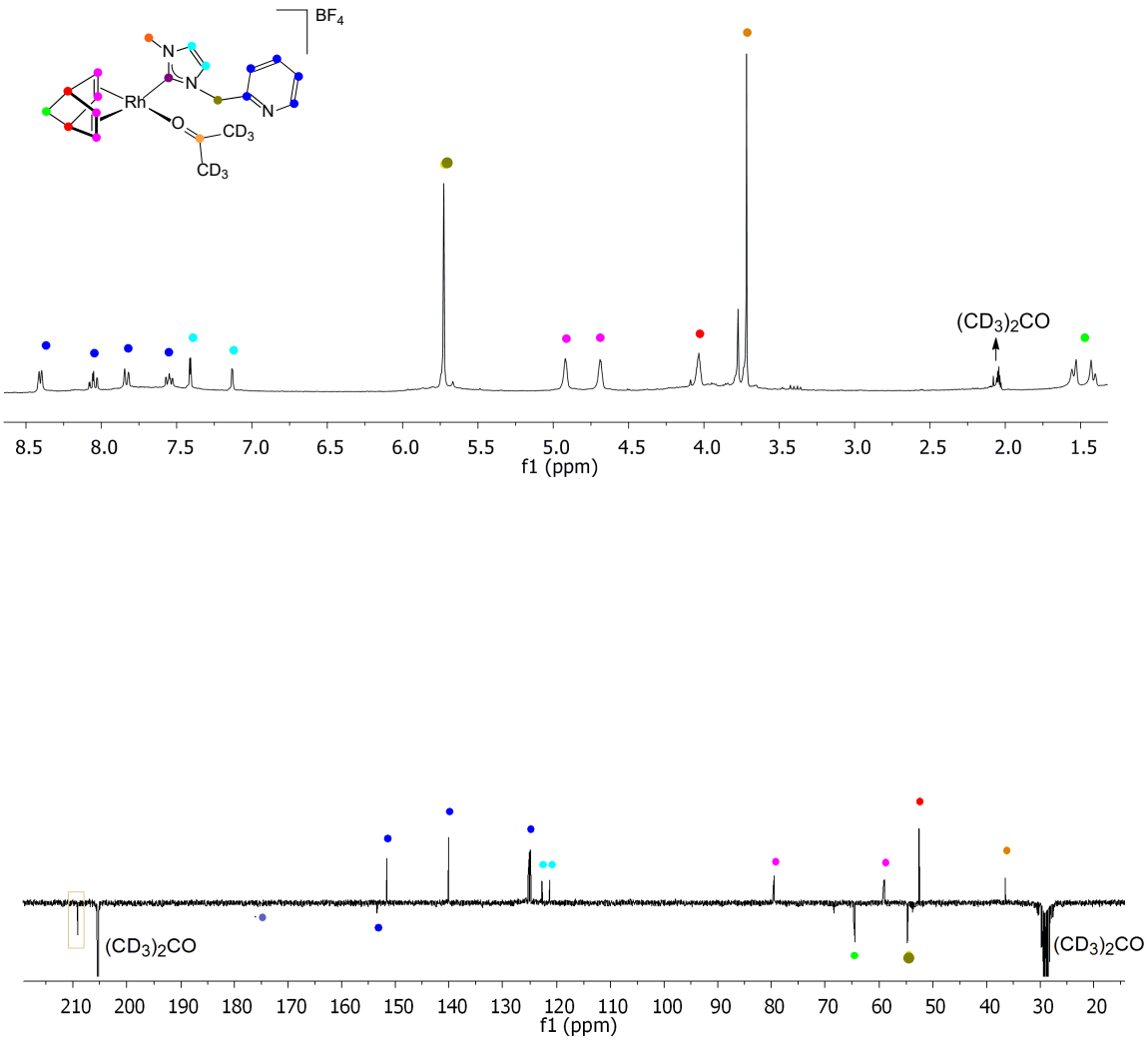


Figure S8. ^{1}H and $^{13}C\{^{1}H\}$-apt NMR spectra of [Rh(nbd){κ*C*-MeIm(pyridin-2-ylmethyl)}(O=$(CD_3)_2$)][BF_4] (**7**) in acetone-d_6 at 298K.

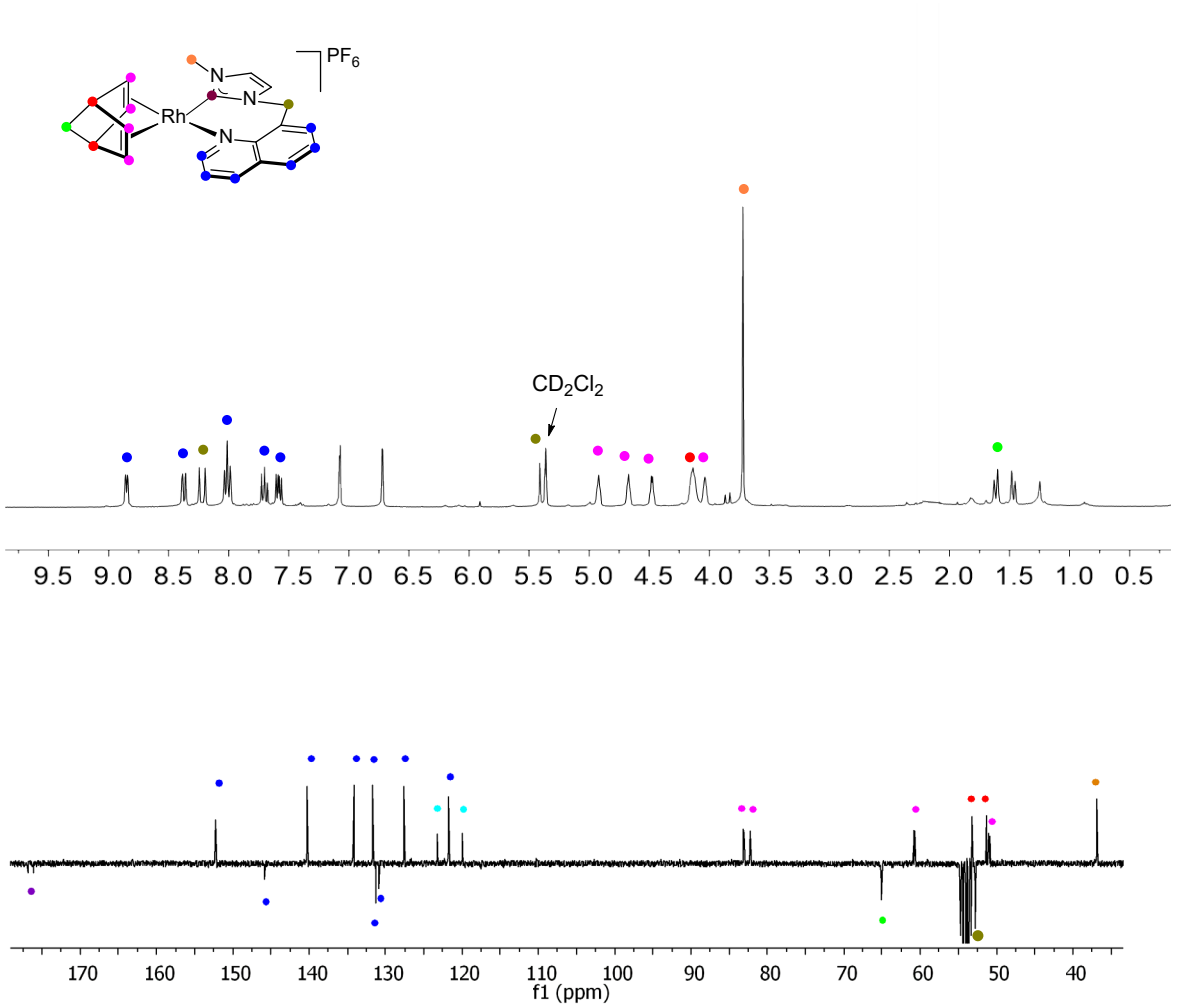


Figure S9. ^{1}H and $^{13}C\{^{1}H\}$-apt NMR spectra of [Rh(nbd){κ^{2}*C,N*-MeIm(quinolin-8-yl-methyl)}][PF_6] (**8**) in CD_2Cl_2 at 253K.

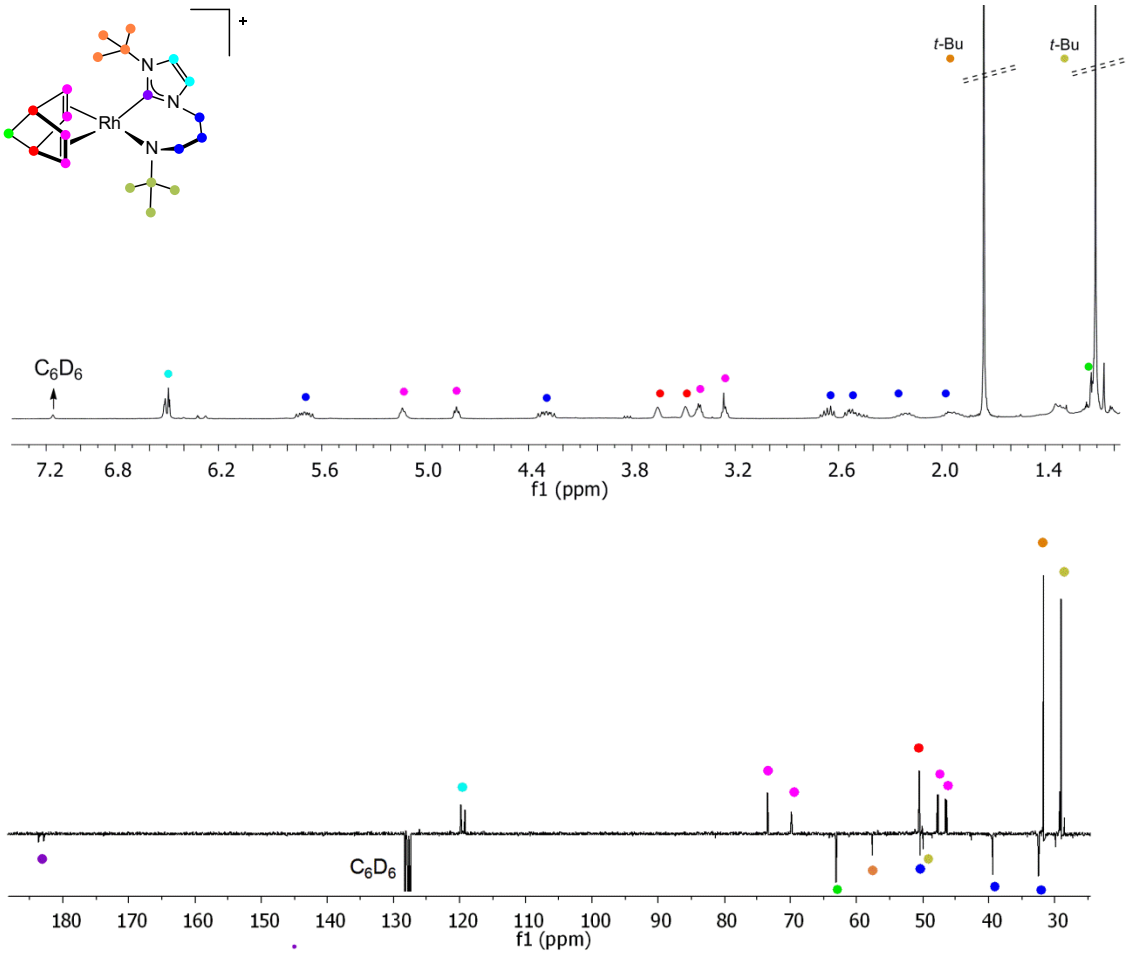


Figure S10. ^{1}H and $^{13}C\{^{1}H\}$-apt NMR spectra of [Rh(nbd){κ^{2}*C,N*-*t*-BuIm(CH$_2$)$_3$N-*t*-Bu}] (**9**) in C_6D_6 at 298K.

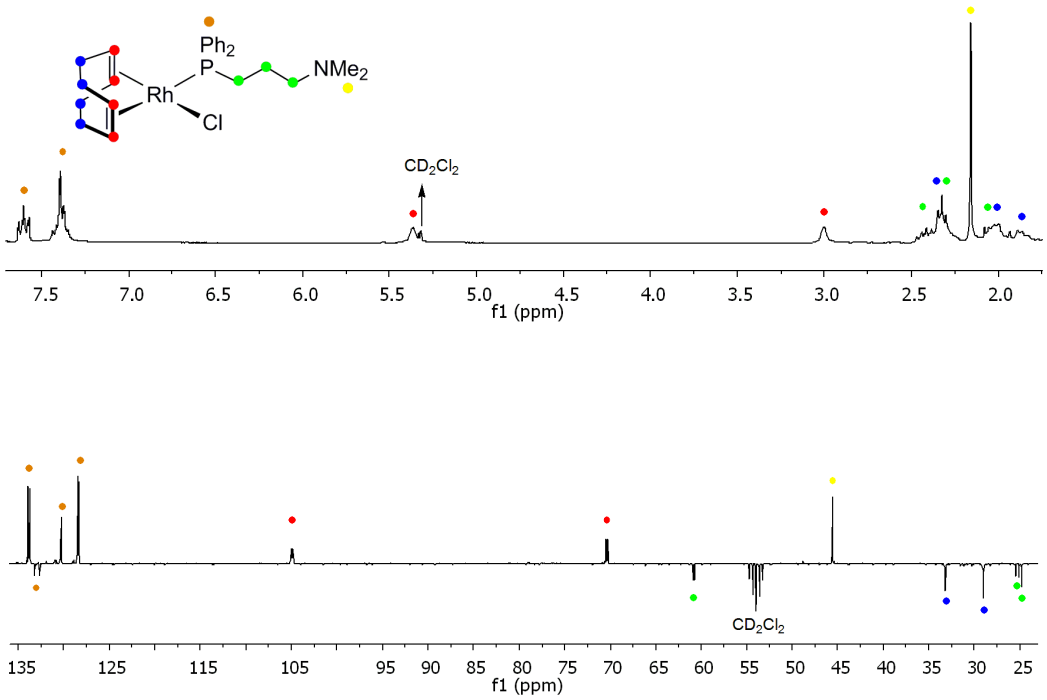


Figure S11. ^{1}H and $^{13}C\{^{1}H\}$-apt NMR spectra of [RhCl(cod){κ*P*-$Ph_2P(CH_2)_3NMe_2$}] (**12**) in CD_2Cl_2 at 253 K.

6.- Phenylacetylene polymerization reactions.

The polymerization reactions were carried out in round bottom flasks with efficient stirring. A typical polymerization procedure is as follows: phenylacetylene (70 μL, 0.64 mmol) was added to a THF solution (2.5 mL) of the catalysts (6.4 μmol) and the mixture stirred at 293 K in the absence of light. The consumption of monomer was monitored by GC using n-octane as internal standard. The polymer solutions were transferred into vigorously stirred cold methanol (25 mL, 273 K) using a cannula under argon. The polymers were filtered and washed with methanol and dried under vacuum to constant weight. The polymers were obtained as yellow-orange solids in good yields according to the conversion values.

7.- Polyphenylacetylene characterization.

Representative ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR of two PPA samples recorded in CD_2Cl_2 and THF-d_8 are shown in Figures S12-S14.

NMR data of cis-transoidal PPA: ^{1}H NMR (CD_2Cl_2): δ 6.98 (m, *o*-H and *p*-H, Ph), 6.69 (m, *m*-H, Ph), 5.86 (s, =CH). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 143.5 and 140.1 (C_q), 132.4 (=CH), 128.4 and 128.2 (*o*- and *m*-Ph), 127.3 (*p*-Ph).

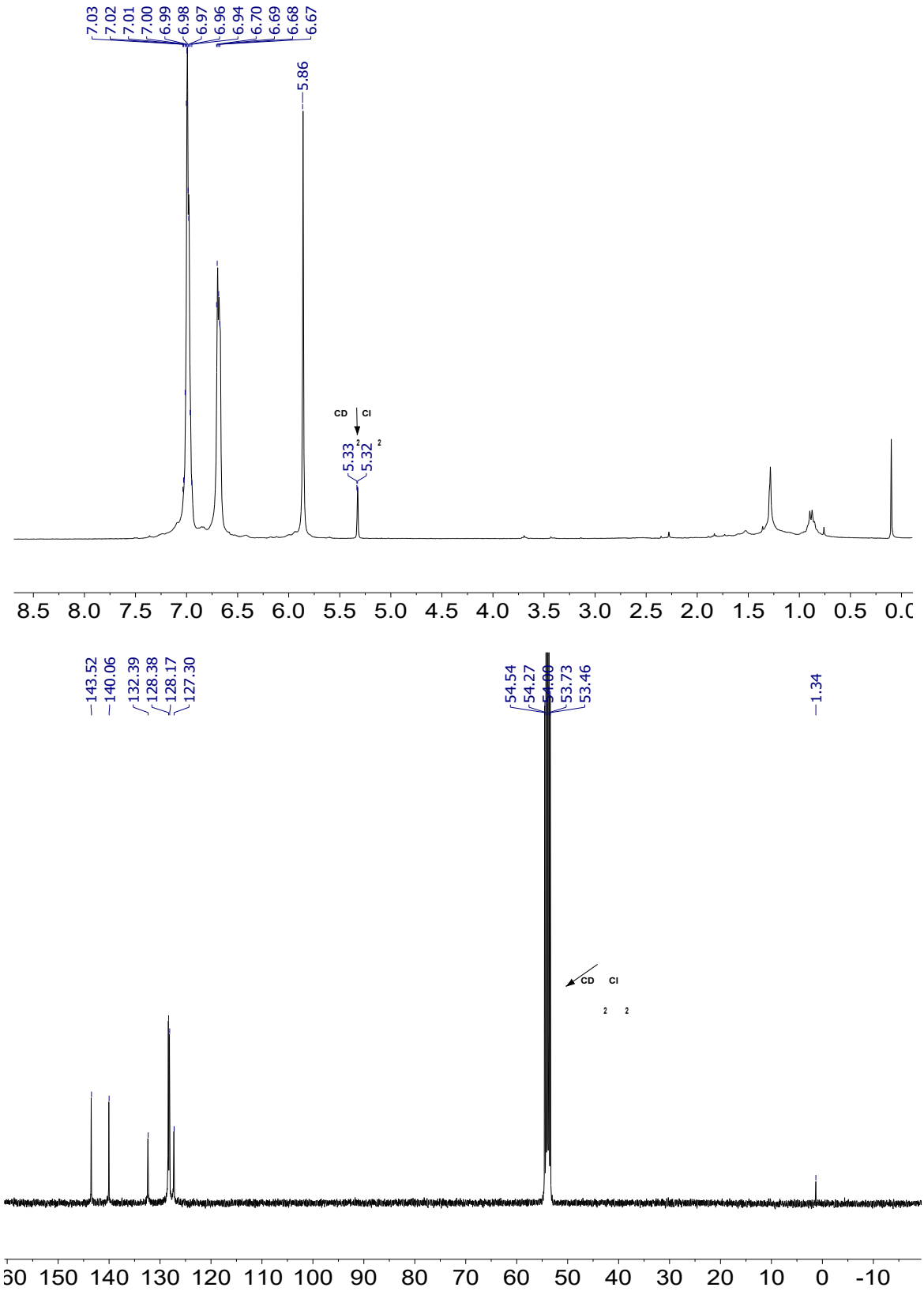


Figure S12. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of polyphenylacetylene in CD_2Cl_2 at 300 K.

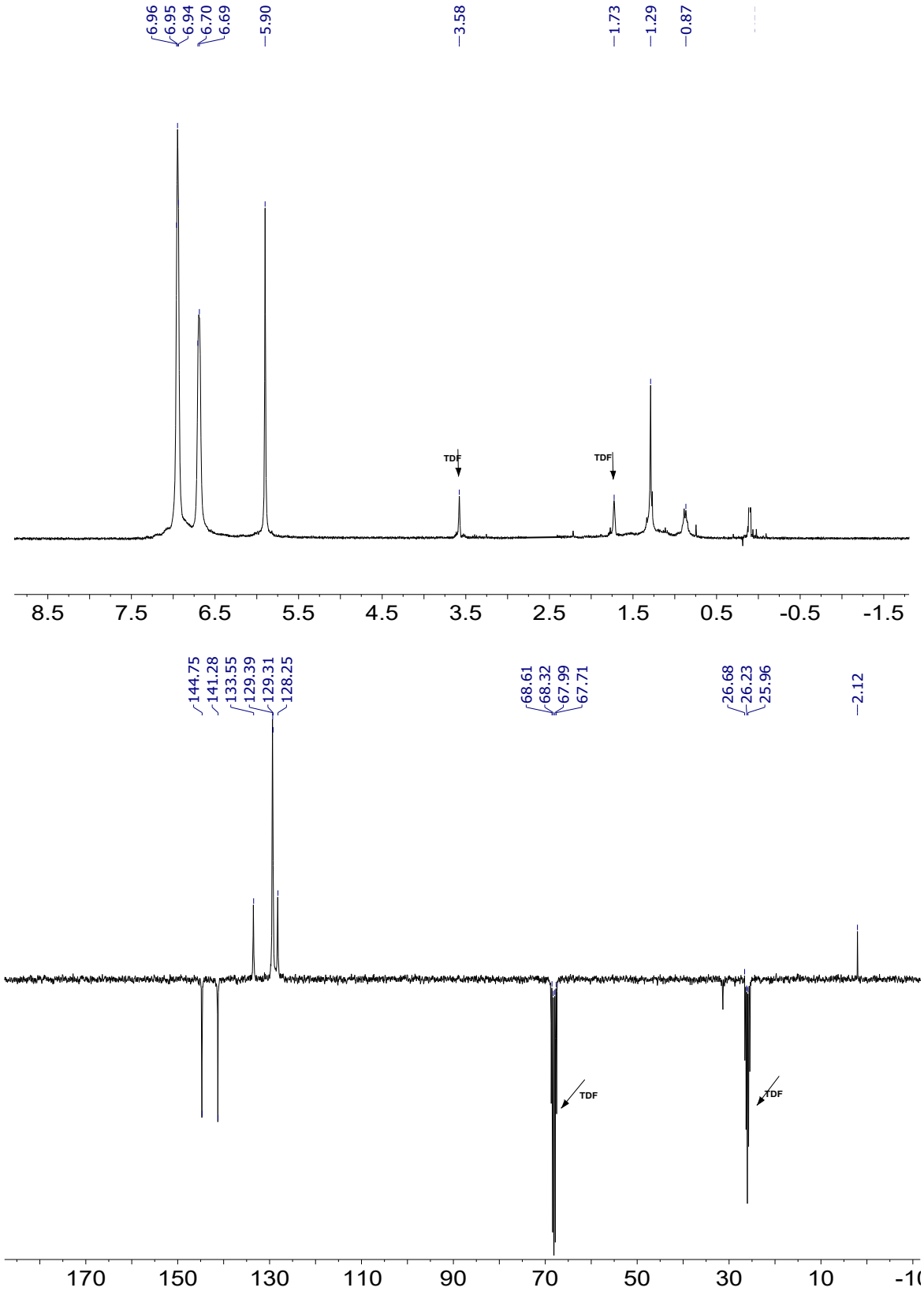


Figure S13. ^{1}H and $^{13}C\{^{1}H\}$-apt NMR spectra of polyphenylacetylene in THF-d_8 at 300 K.

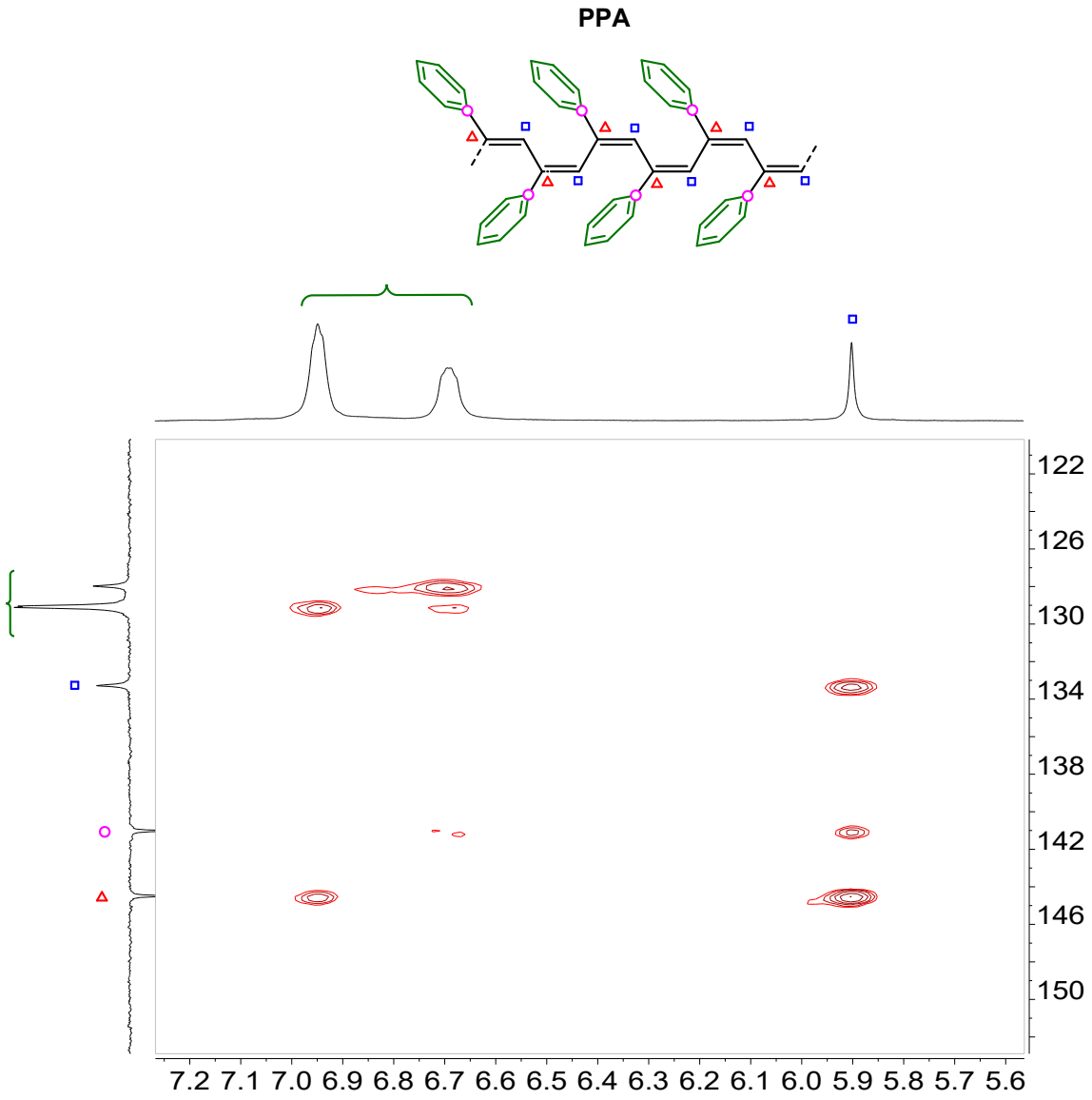


Figure S14. $^{1}H/^{13}C\{^{1}H\}$-HMBC NMR spectra of polyphenylacetylene in THF-d_8 at 300 K.

7.- Selected chromatograms and conformation plots for PPA samples.

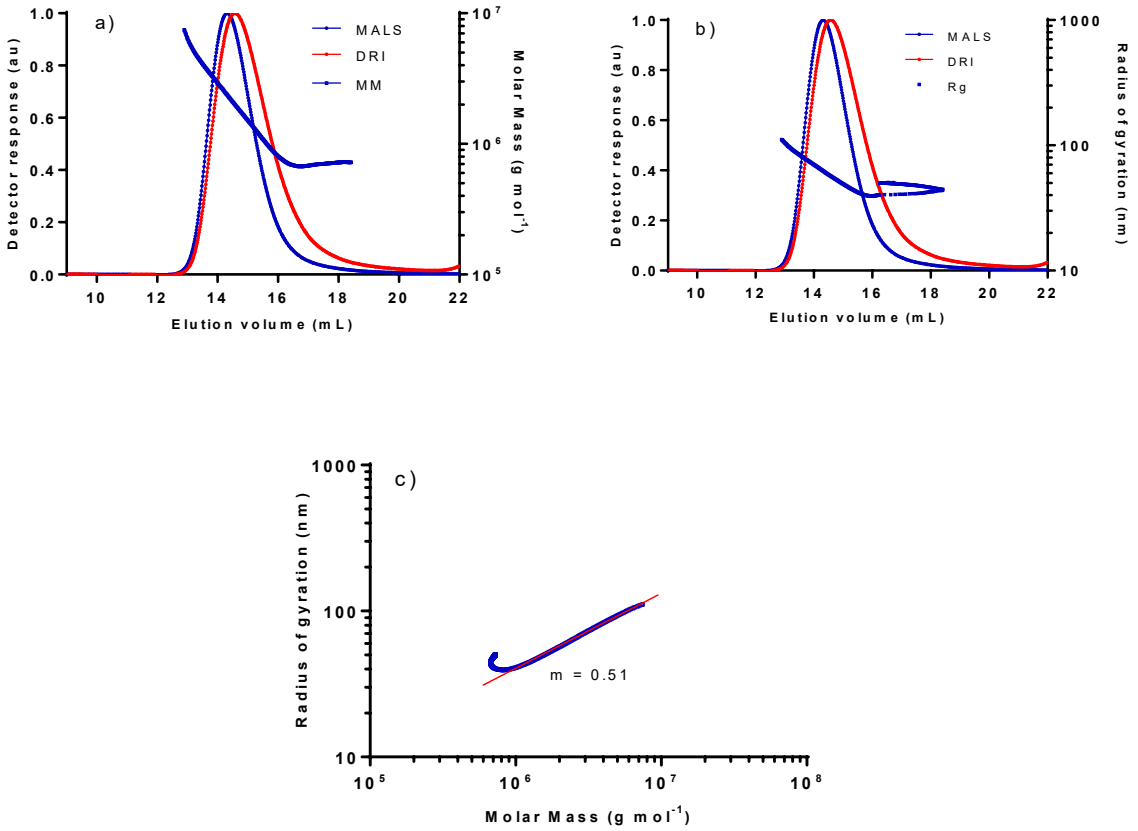


Figure S15. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [RhCl(nbd){κ*C*-MeIm$(CH_2)_3NMe_2$}] (**1**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

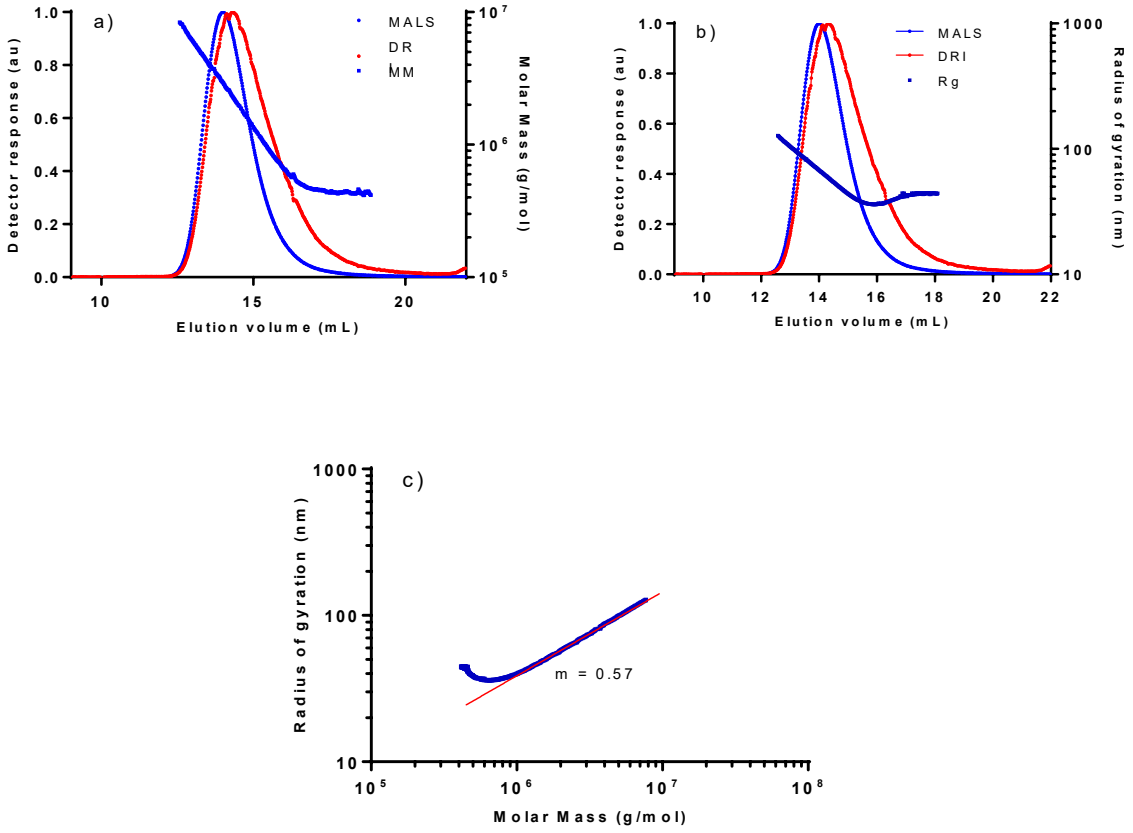


Figure S16. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [RhBr(nbd){κ*C*-MeIm$(CH_2)_3NH_2$}] (**2**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

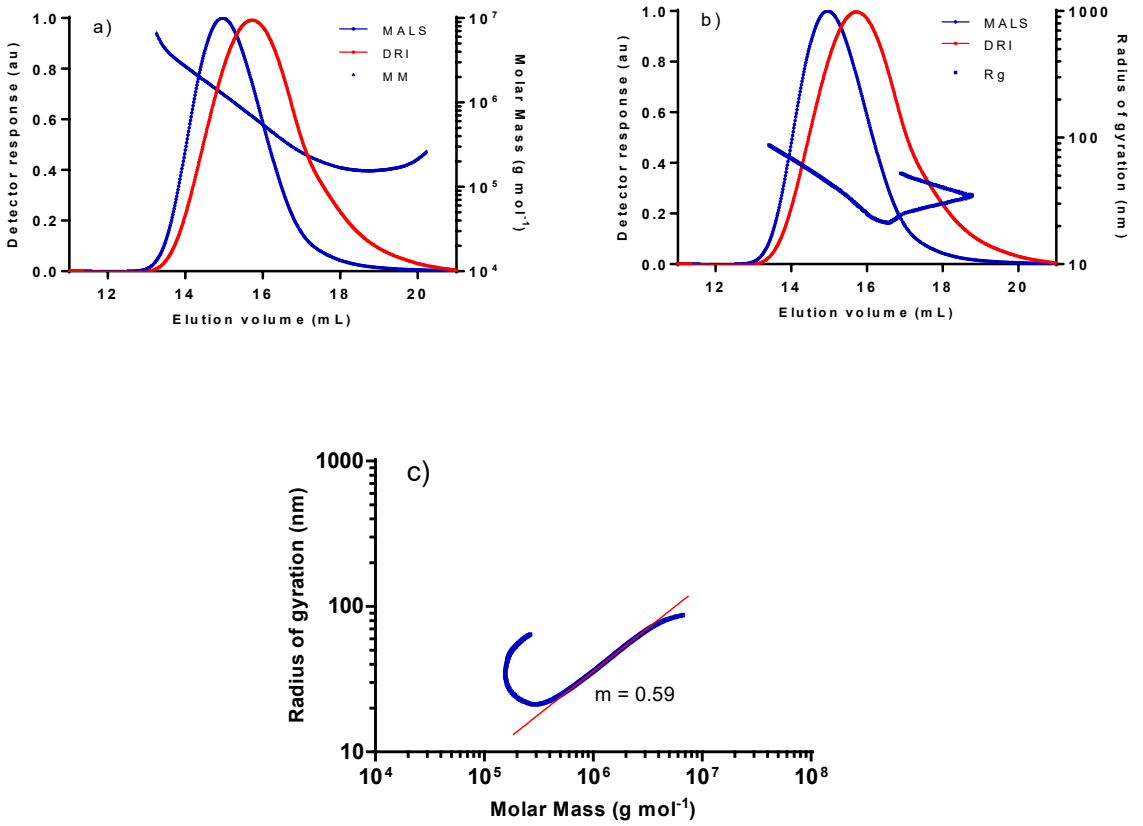


Figure S17. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [RhBr(nbd){κ*C*-MeIm(piridin-2-yl-methyl)}] (**3**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

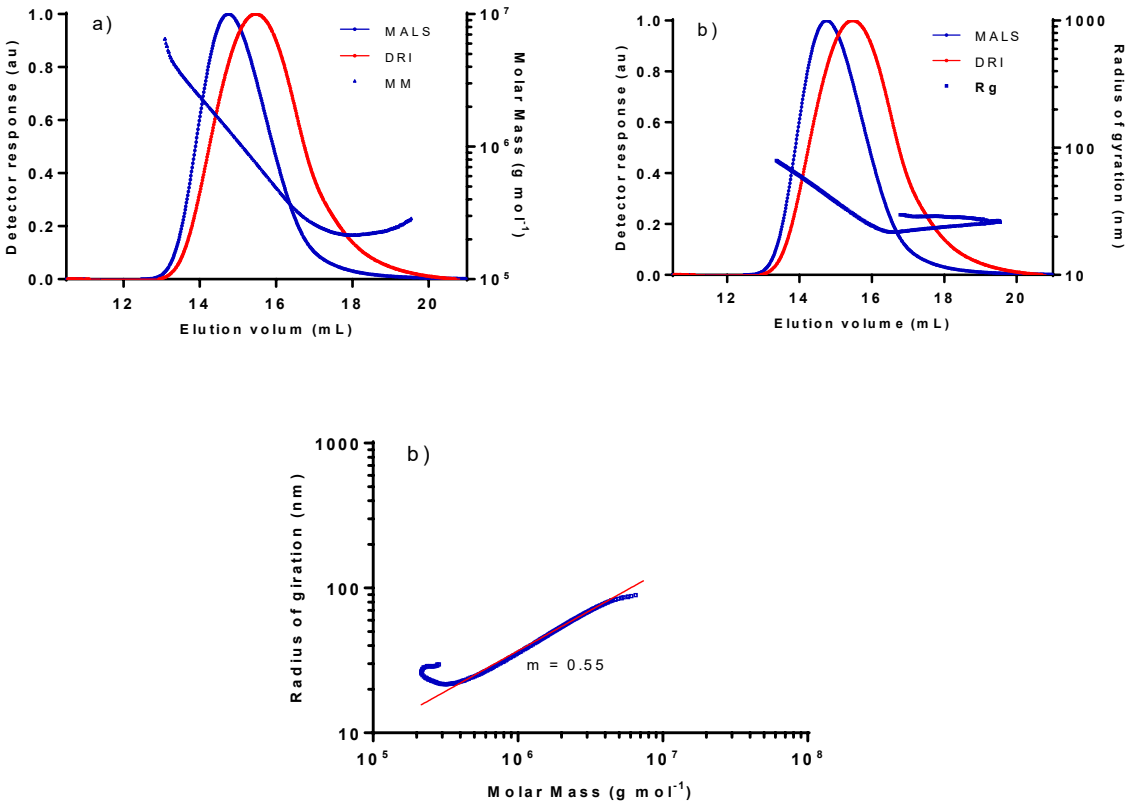


Figure S18. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [[RhCl(nbd){κ*C*-MeIm(quinolin-8-ylmethyl)}] (**4**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

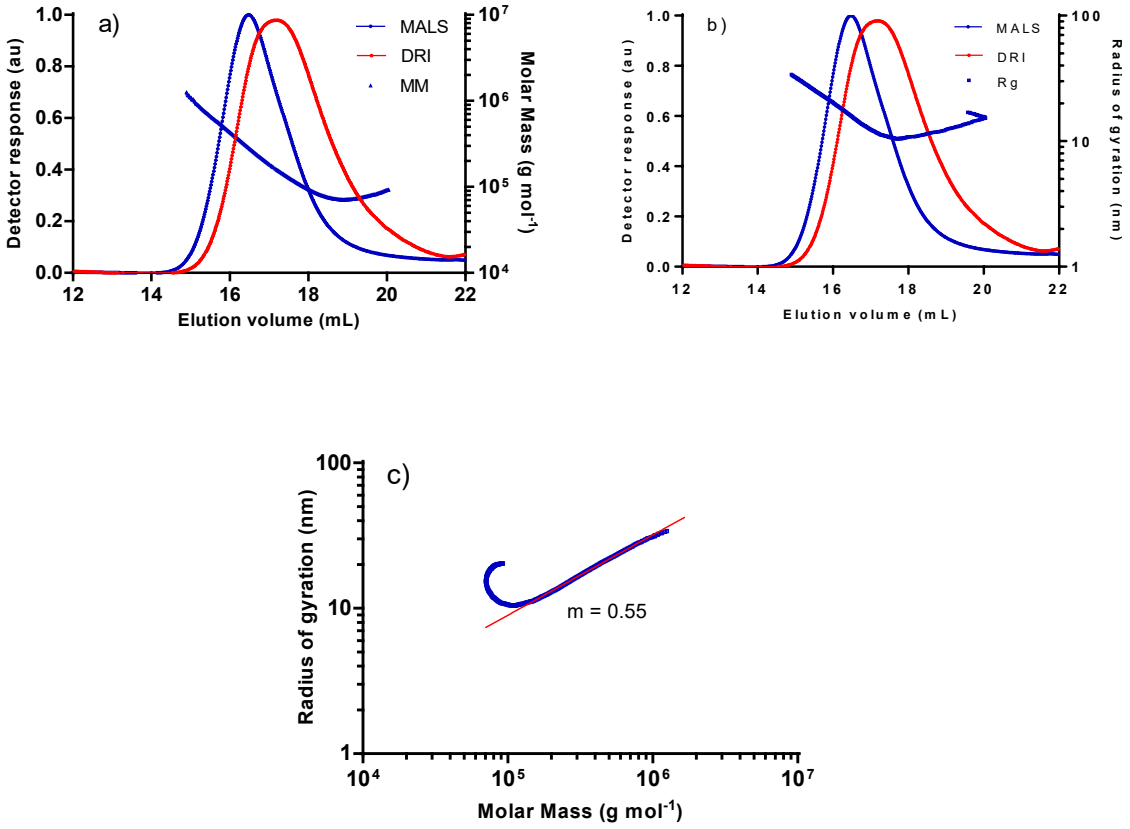


Figure S19. a SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [Rh(nbd){κ^2*C,N*-MeIm(CH$_2$)$_3$NMe$_2$)}][BF$_4$] (**5**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

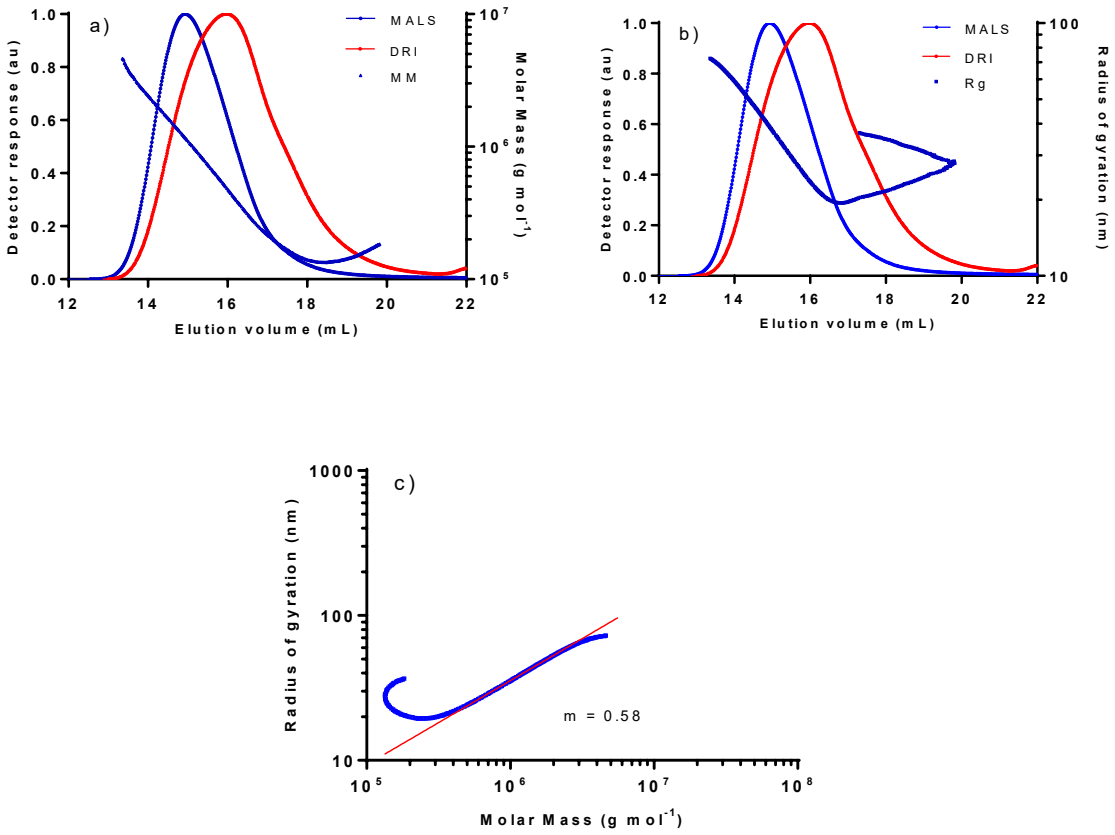


Figure S20. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [Rh(nbd){κ^2*C,N*-MeIm(CH$_2$)$_3$NH$_2$}][PF$_6$] (**6**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

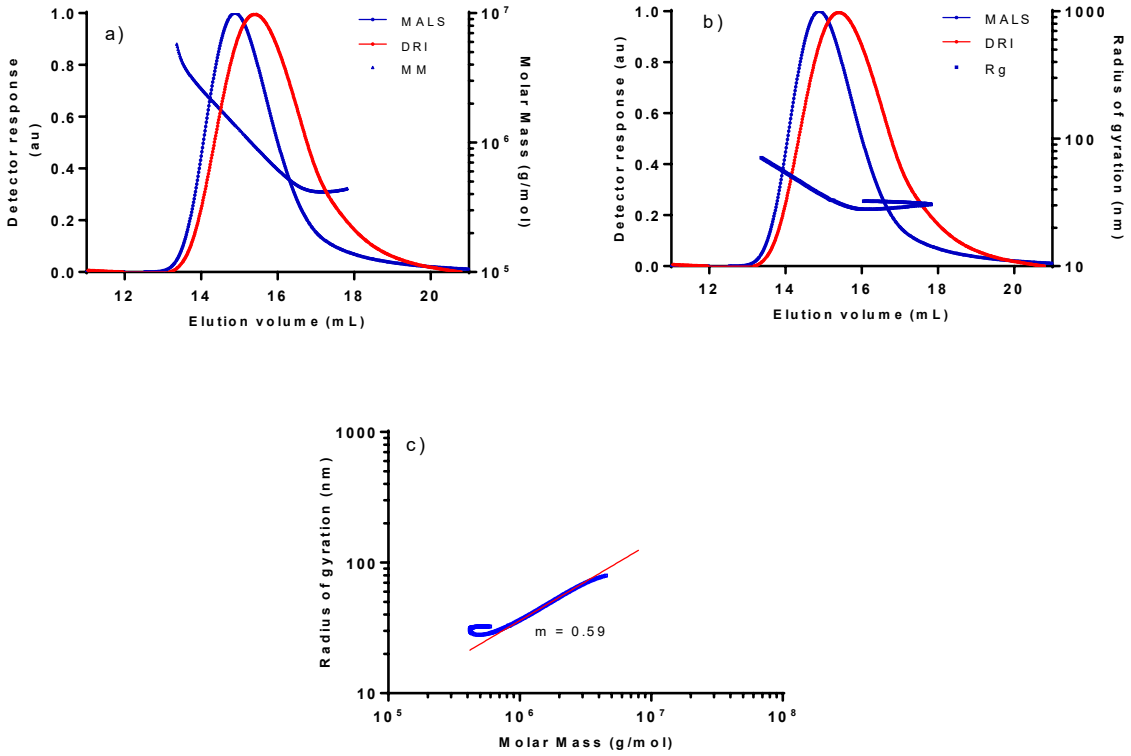


Figure S21. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [Rh(nbd){κ*C*-MeIm(pyridin-2-ylmethyl)}($OCMe_2$)][BF_4] (**7**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

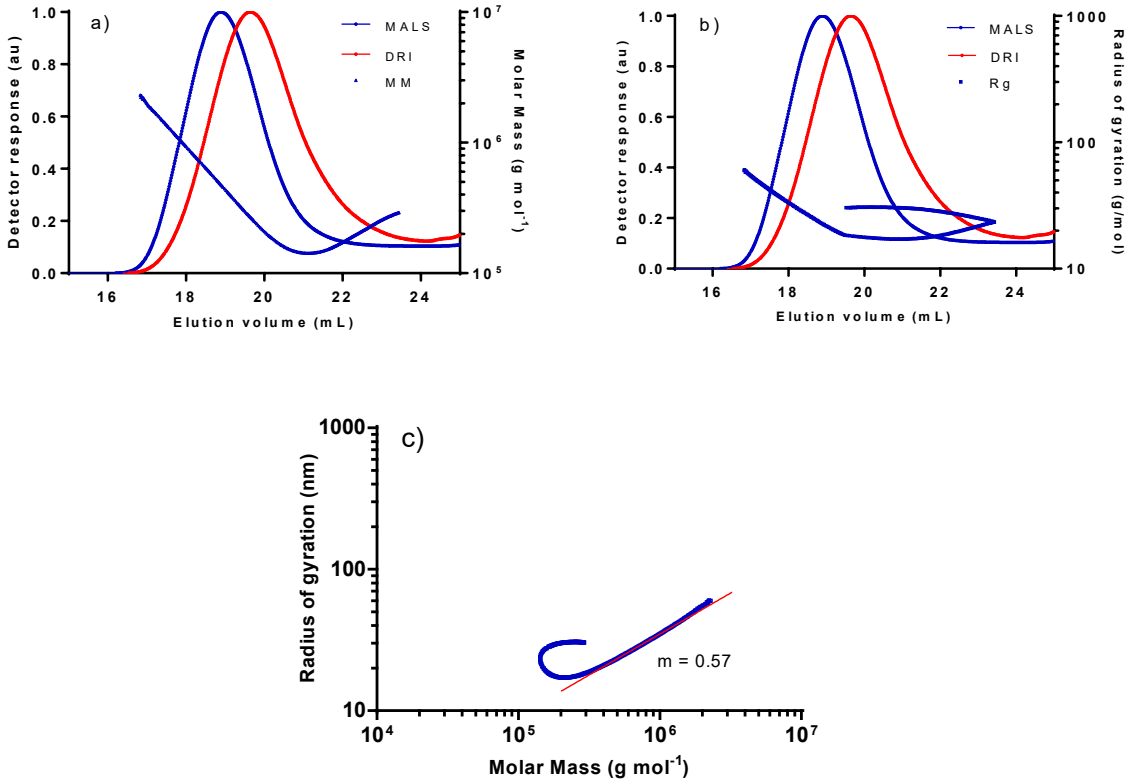


Figure S22. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [Rh(nbd){κ^2*C,N*-MeIm(quinolin-8-yl-methyl)}][PF_6] (**8**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

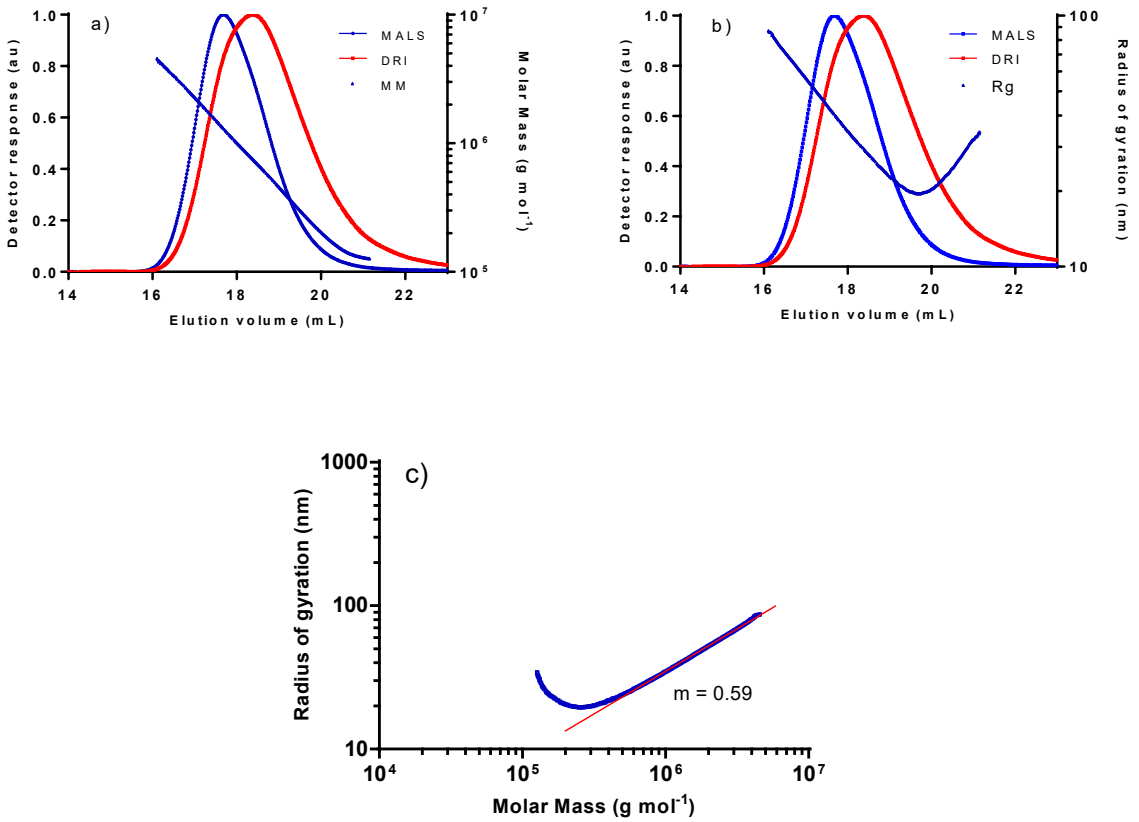


Figure S23. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [Rh(nbd){κ^2*C,N*-*t*-BuIm(CH$_2$)$_3$N-*t*-Bu}] (**9**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

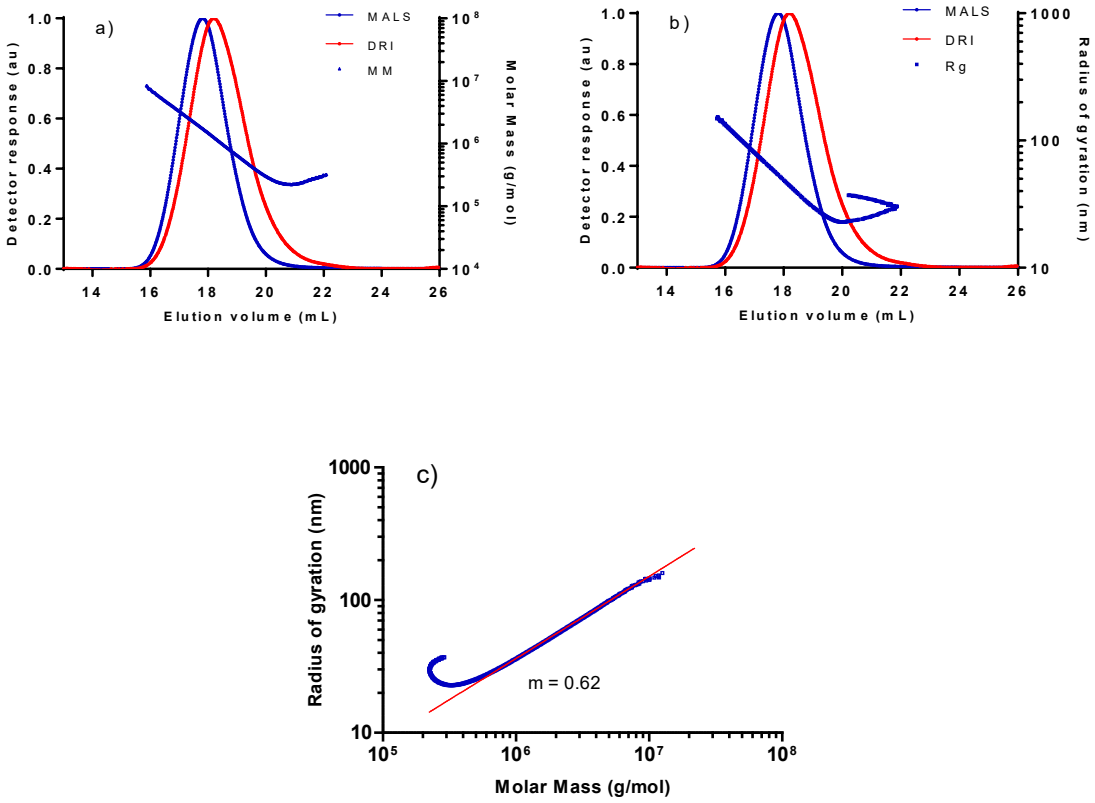


Figure S24. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [RhCl(nbd){κ*P*-$Ph_2P(CH_2)_3NMe_2$}] (**10**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

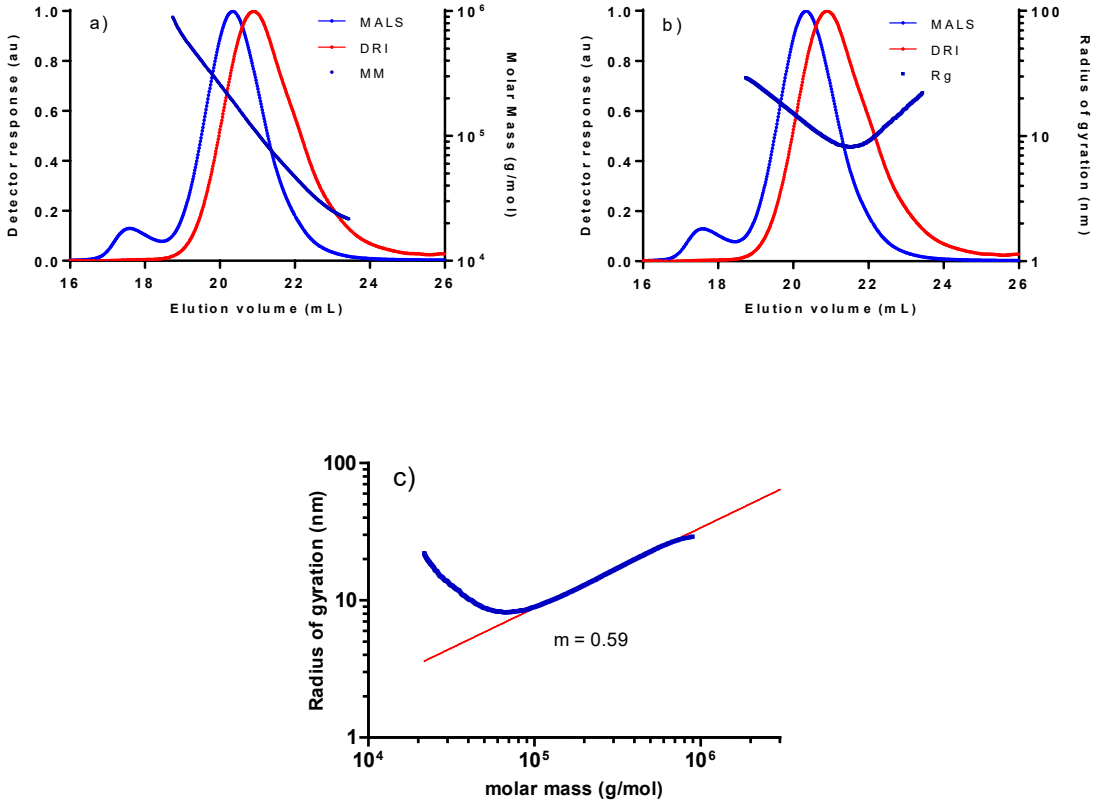


Figure S25. SEC chromatograms: light scattering detector response (90 degrees) (blue) and differential refractometer response (red), a) MM (molar mass) and b) radius of gyration (r_g) *vs* elution volume plots for a PPA sample prepared with catalyst [RhCl(cod){κ*P*-$Ph_2P(CH_2)_3NMe_2$}] (**12**) in THF. c) Log-log plot of the radius of gyration (r_g) vs MM.

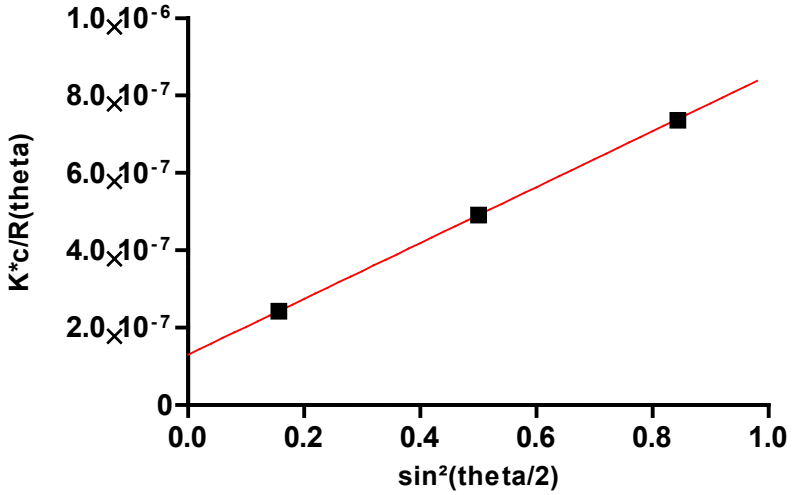


Figure S26. Angular-dependence of scattered light intensity for a SEC-MALS chromatogram of a PPA sample prepared with catalyst [RhBr(nbd){κ*C*-MeIm$(CH_2)_3NH_2$}] (**2**).

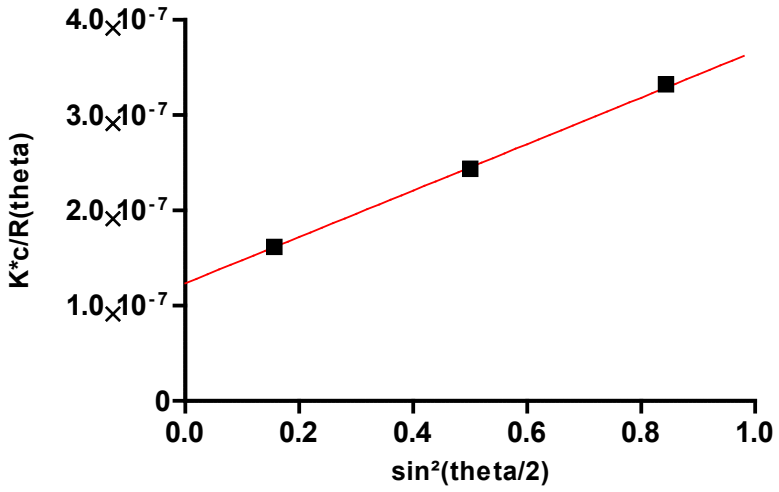


Figure S27. Angular-dependence of scattered light intensity for a SEC-MALS chromatogram of a PPA sample prepared with catalyst [RhCl(nbd){κ*C*-MeIm(quinolin-8-ylmethyl)}] (**4**).

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