Supporting Information

Hemilabile and Bimetallic Coordination in Rh and Ir Complexes of NCN Pincer Ligands

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Figure S1: 6 ^{1}H NMR (DMSO-d_6, 400 MHz)

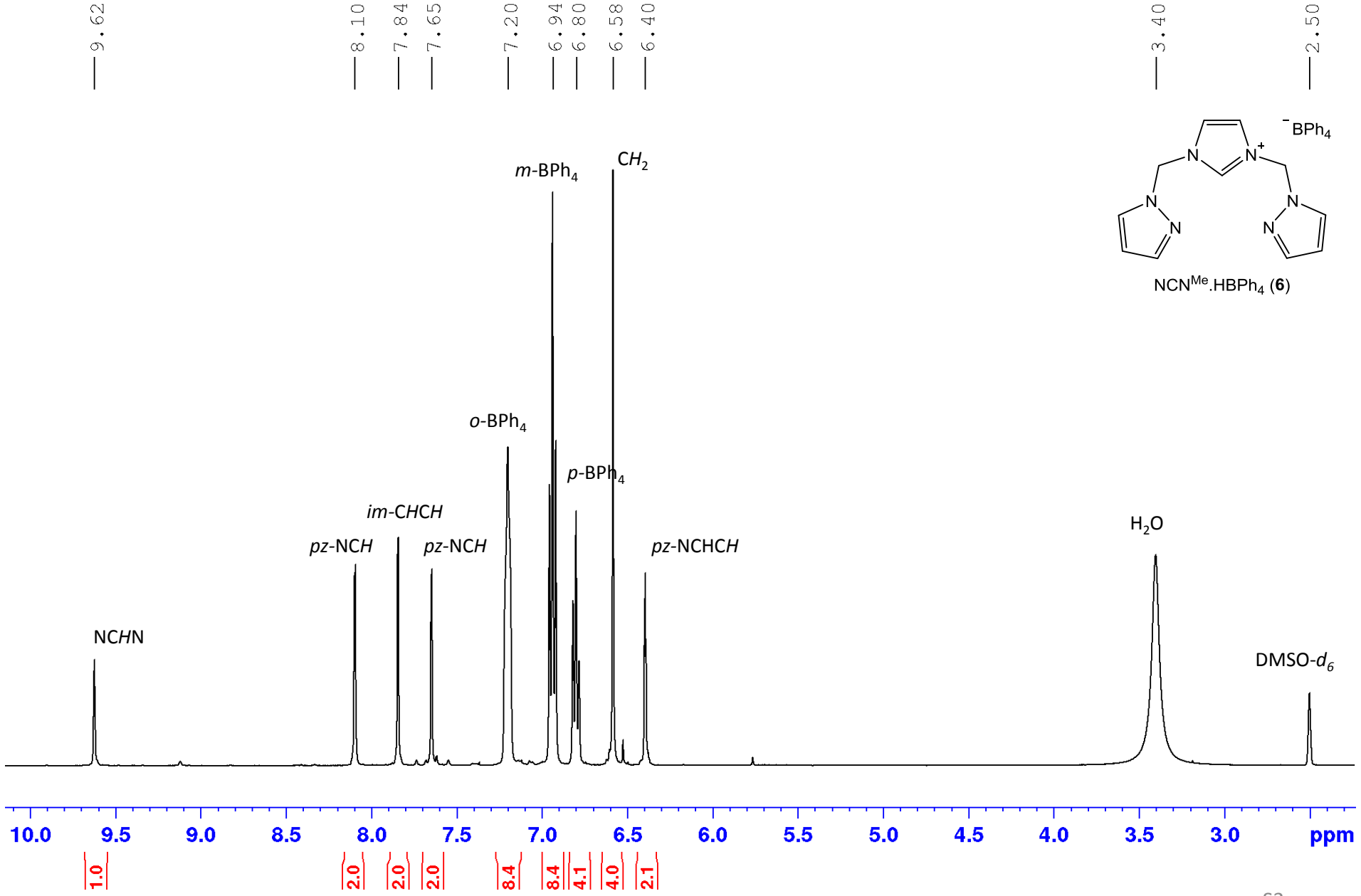

Figure S2: 6 ^{13}C NMR (DMSO-d_6, 100 MHz)

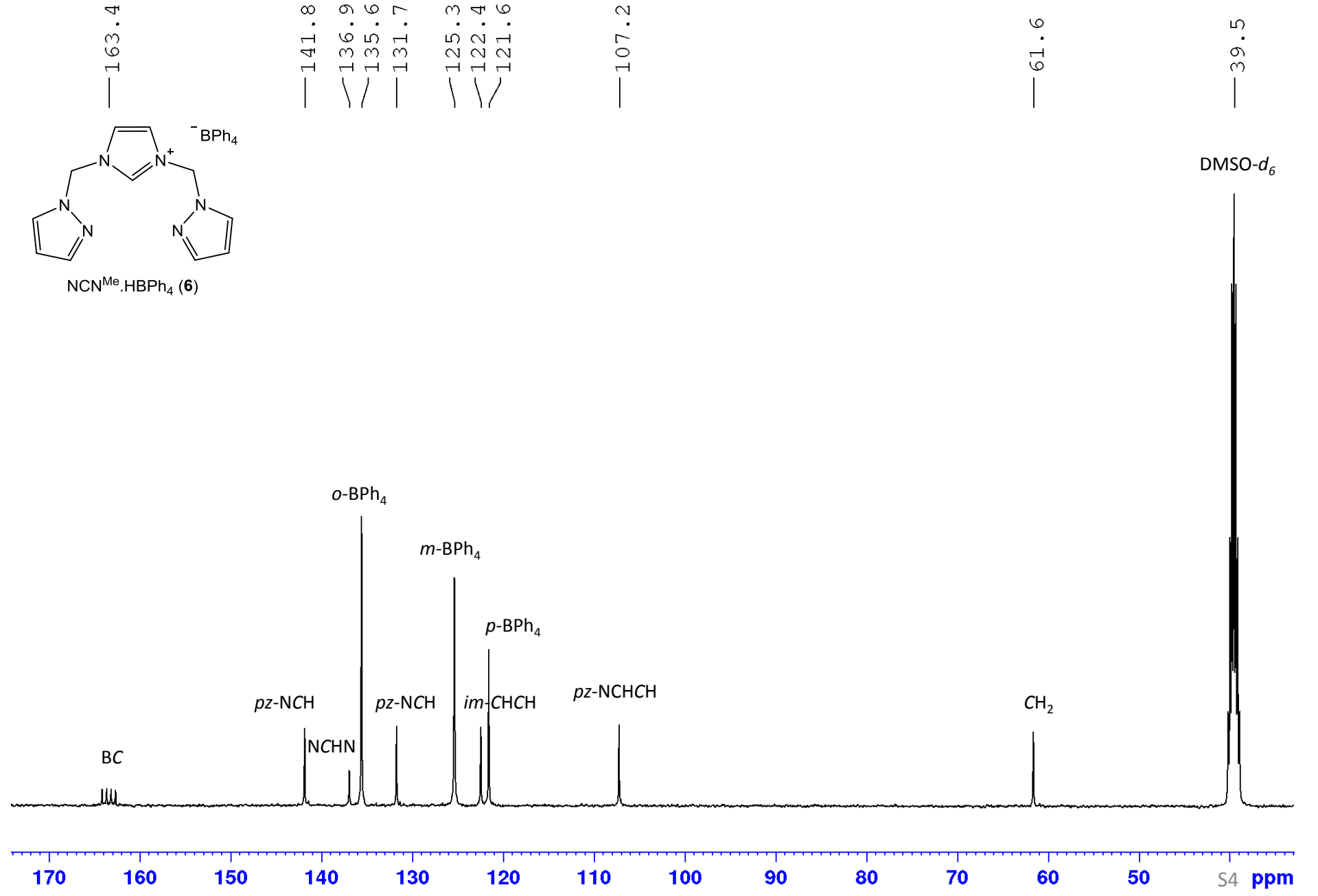

Figure S3: 7 ^{1}H NMR (DMSO-d_6, 400 MHz)

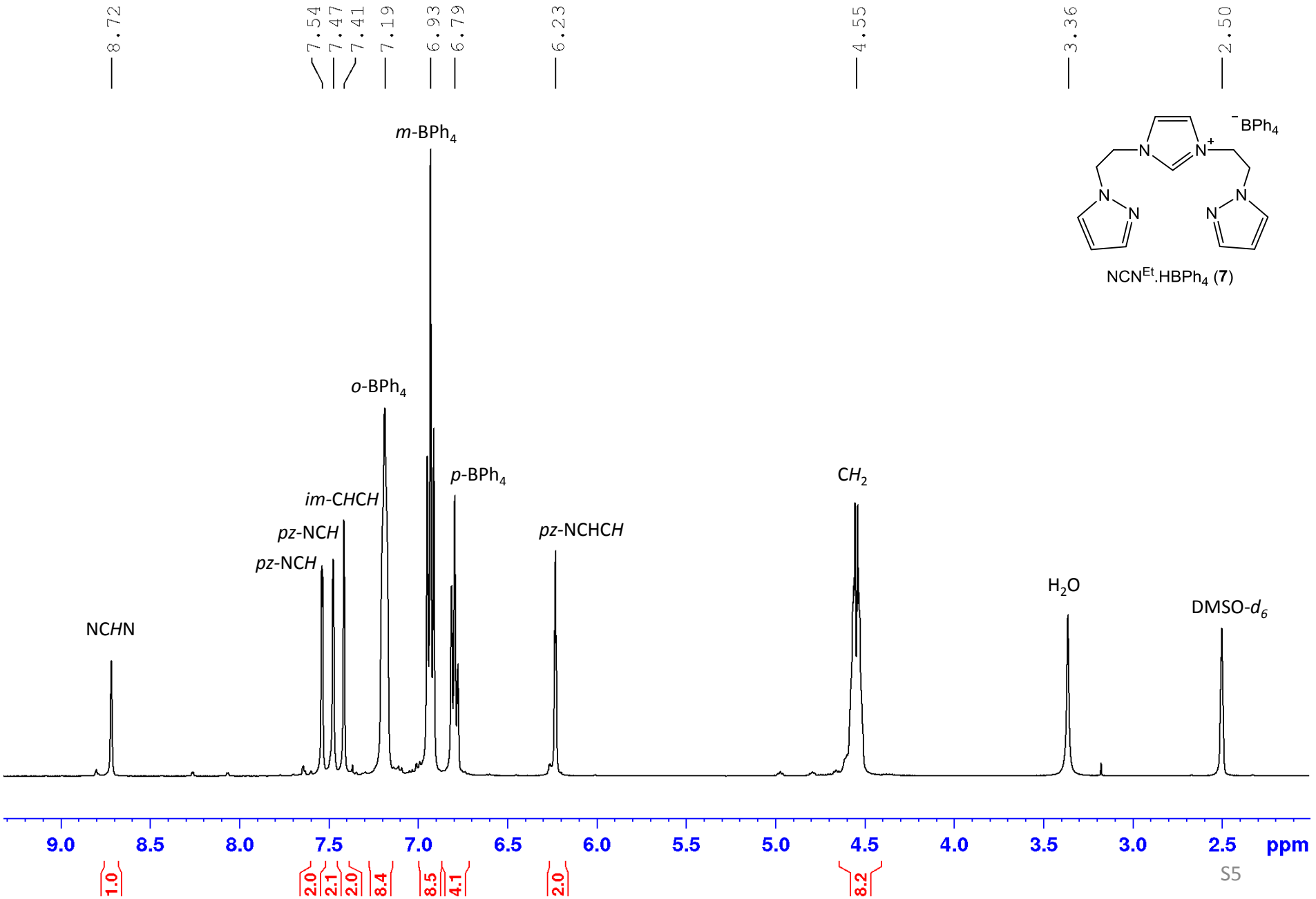

Figure S4: 7 ^{13}C NMR (DMSO-d_6, 100 MHz)

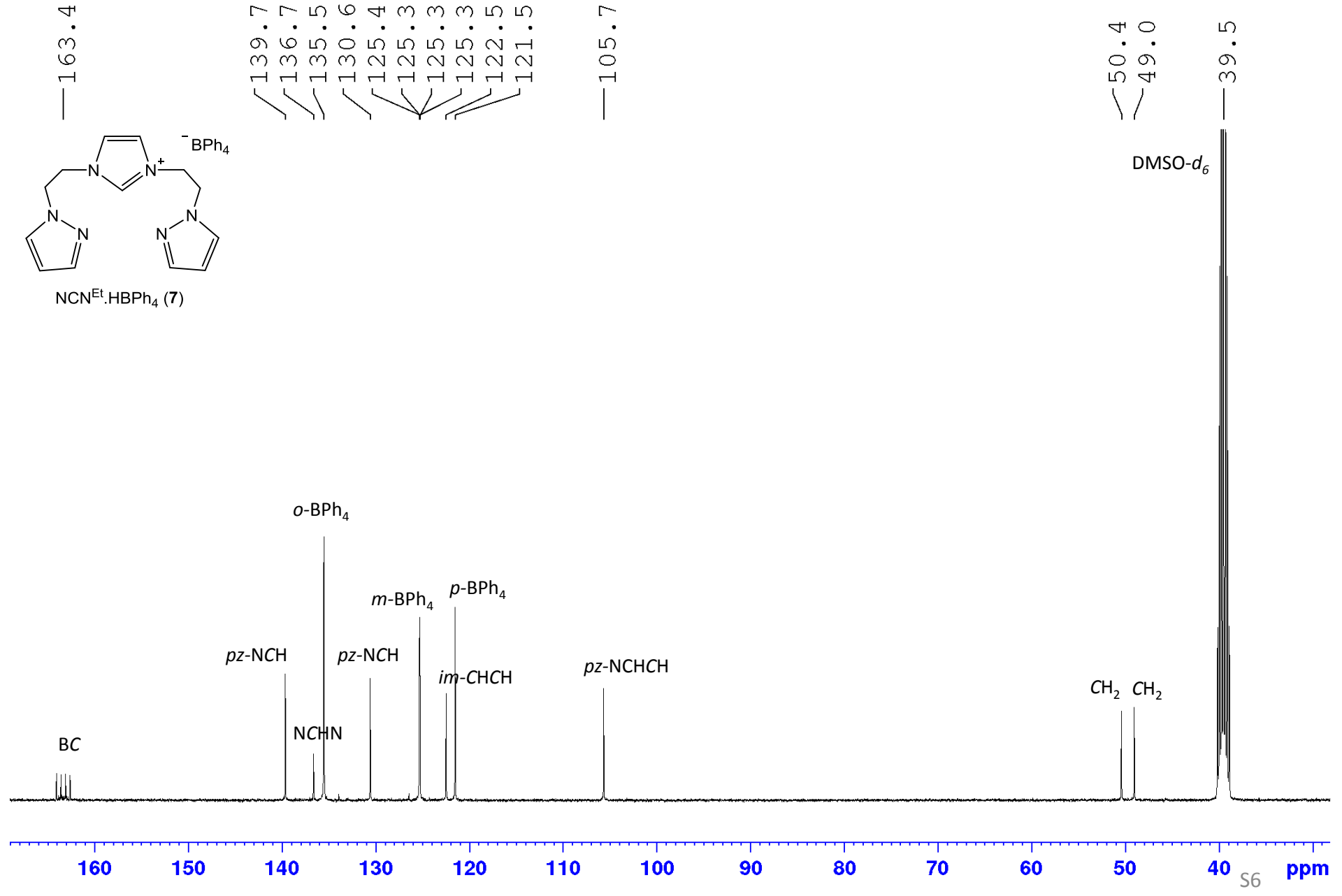

Figure S5: 8 ^{1}H NMR (DMSO-d_6, 400 MHz)

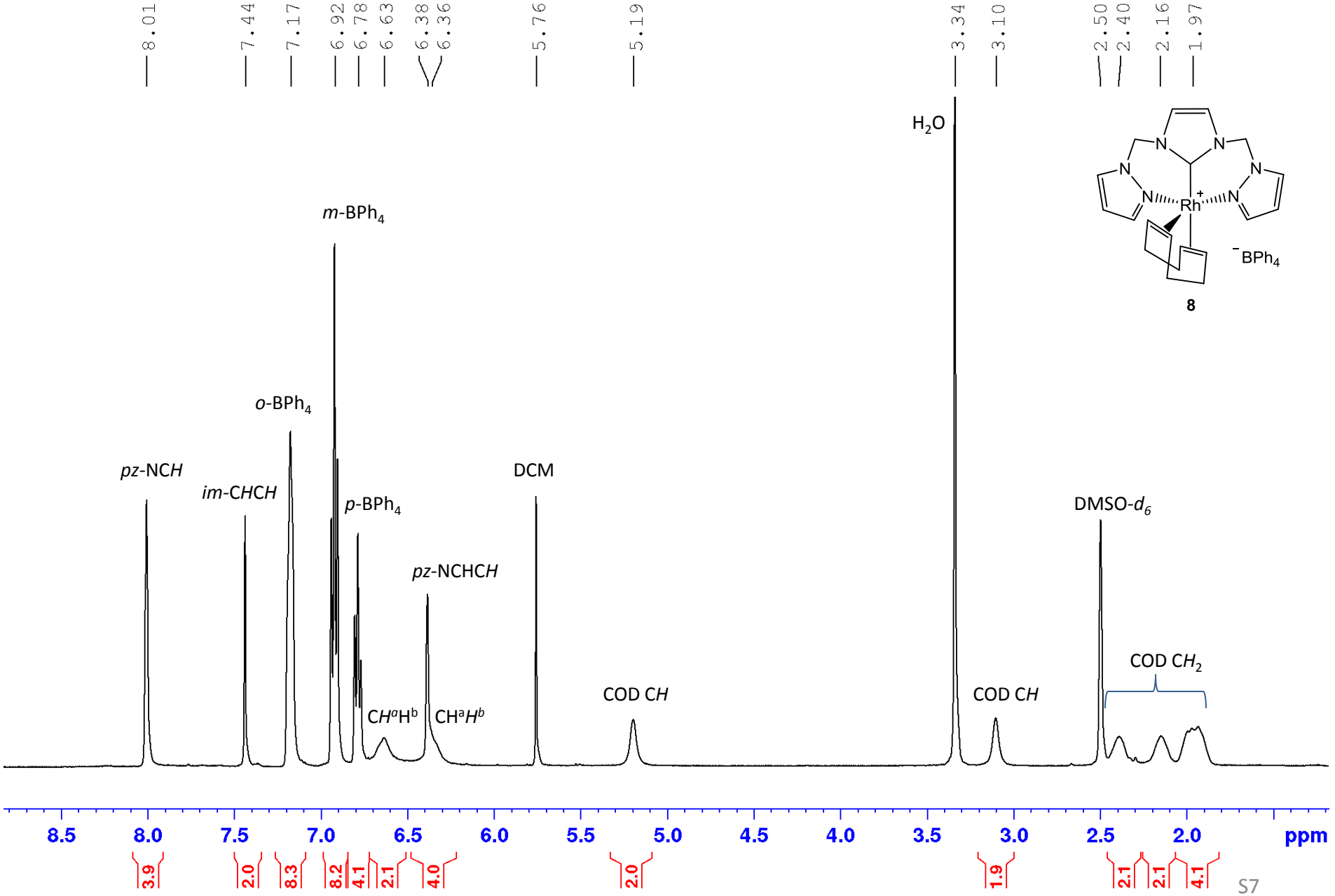

Figure S6: 8 ^{13}C NMR (DMSO-d_6, 100 MHz)

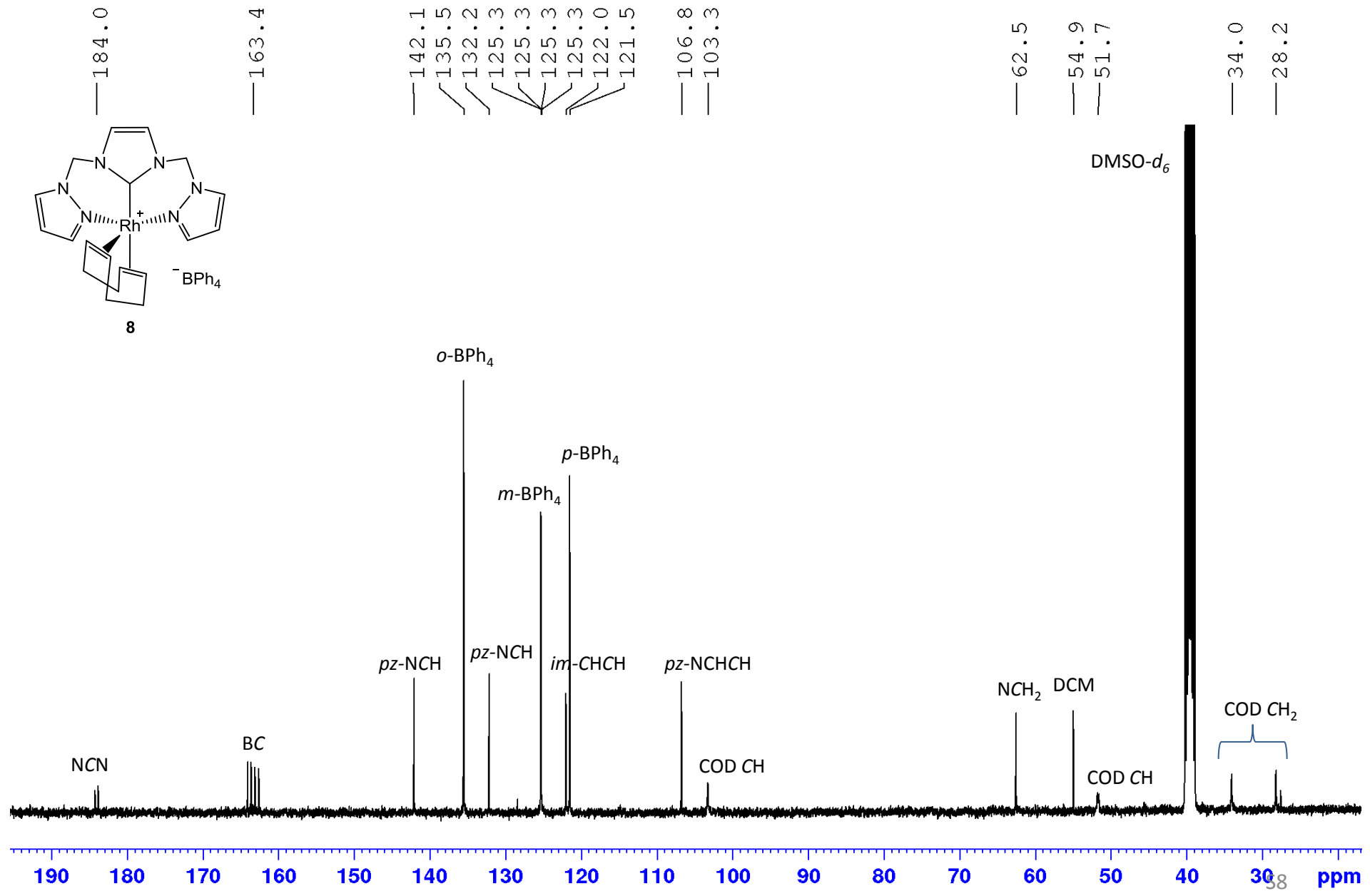

Figure S7: 9 ^{1}H NMR (DMSO-d_6, 400 MHz)

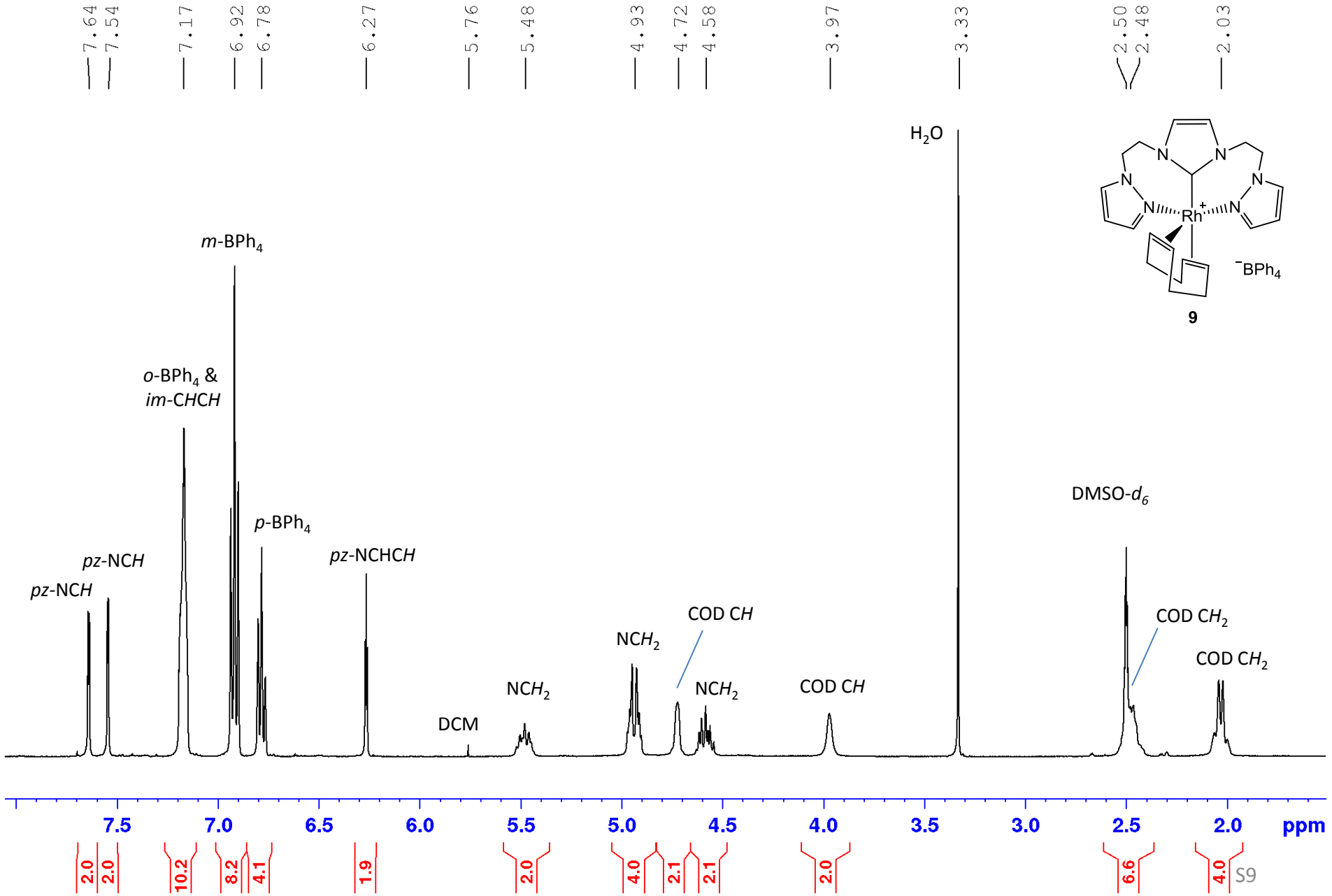

Figure S8: 9 ^{13}C NMR (DMSO-d_6, 100 MHz)

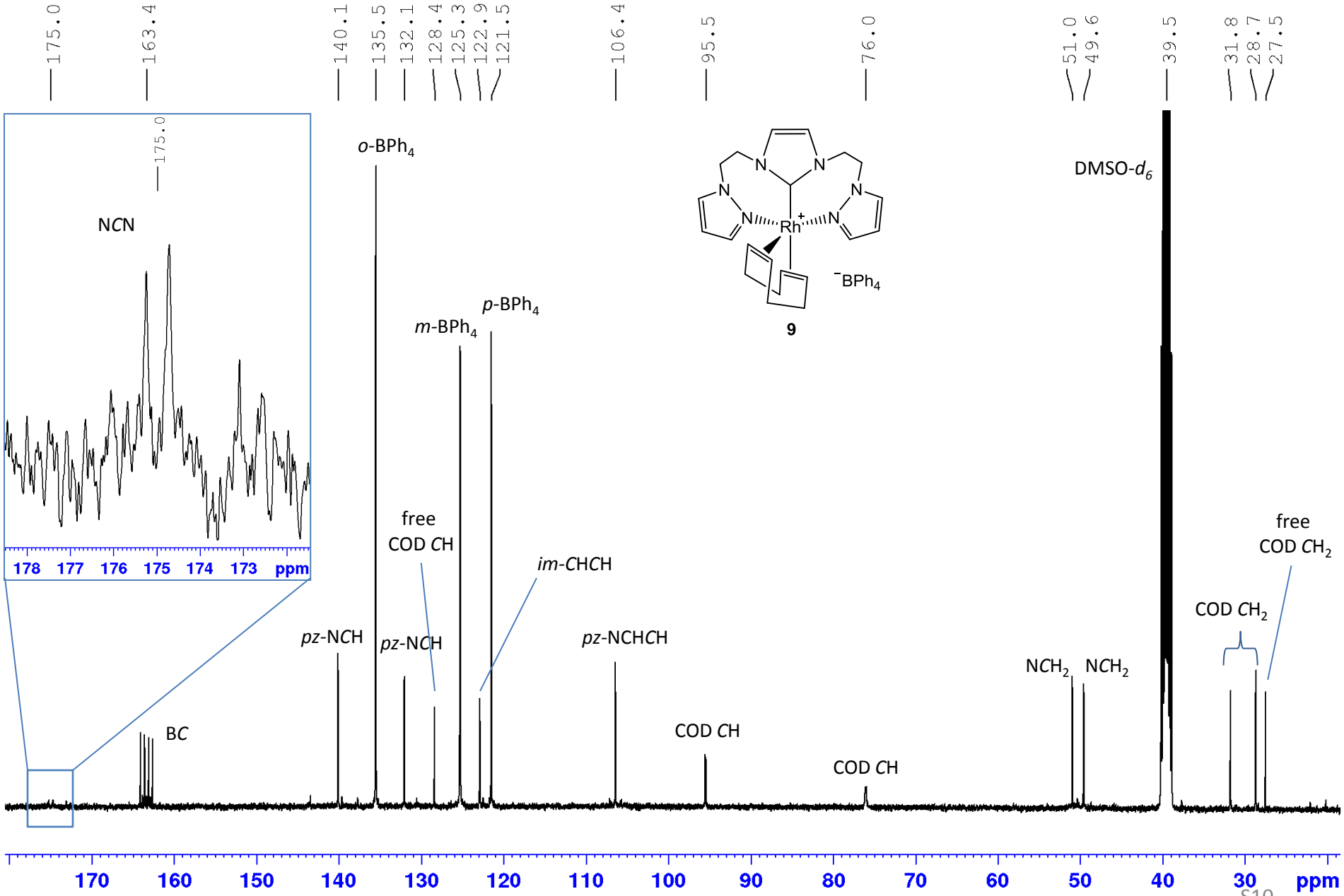

Figure S9: 10 ^{1}H NMR (DMSO-d_6, 400 MHz)

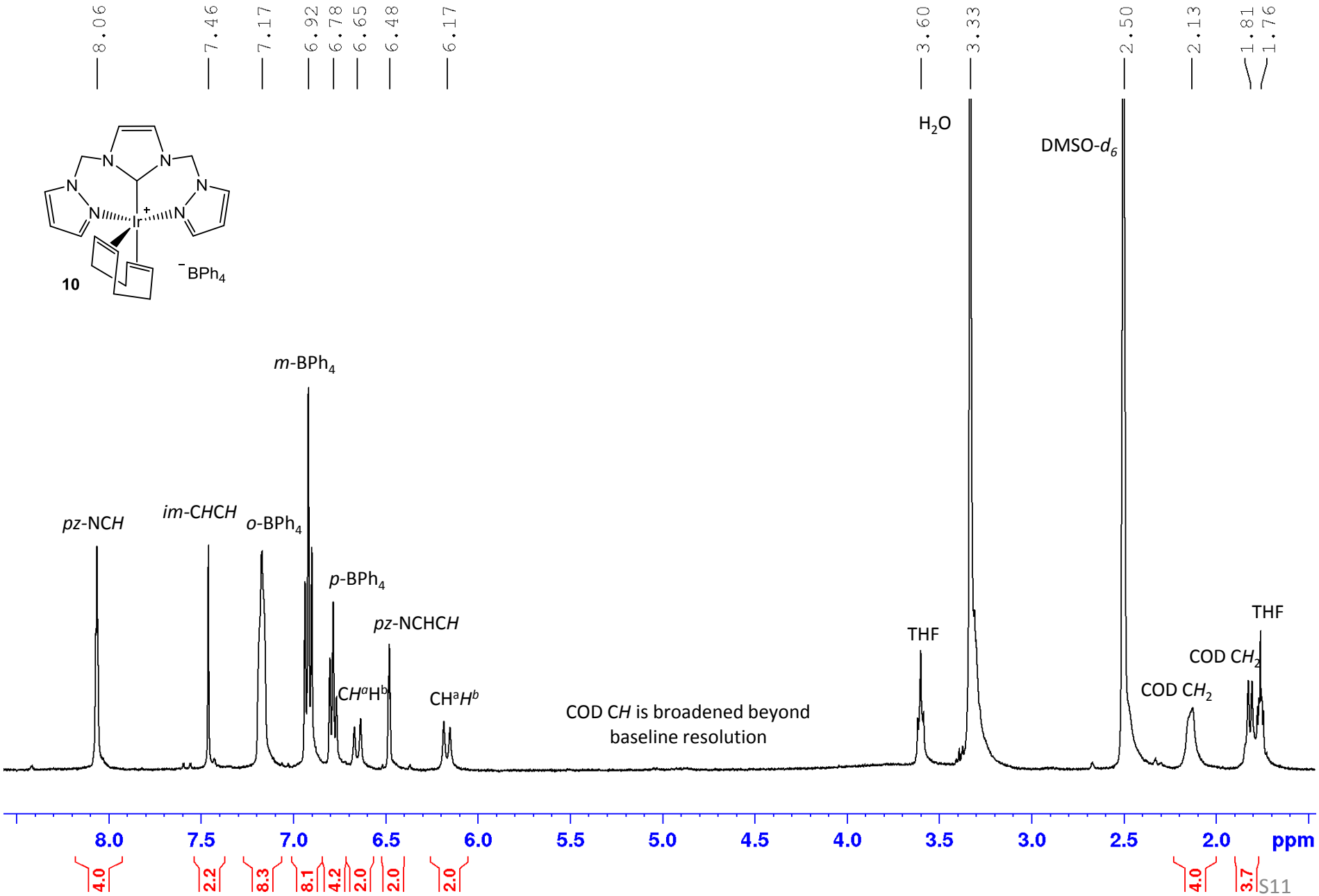

Figure S10: 10 ^{13}C NMR (DMSO-d_6, 100 MHz)

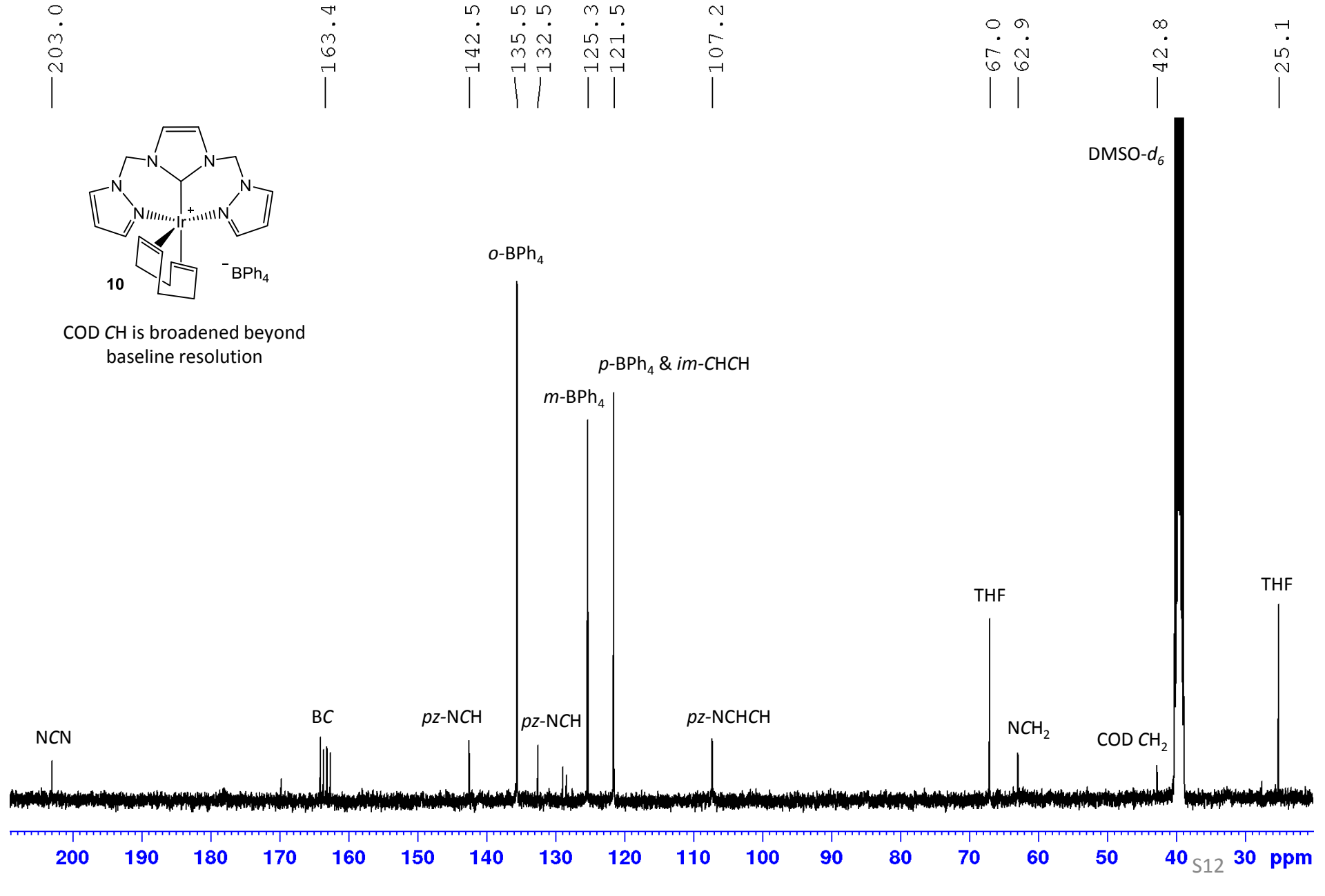

Figure S11: 11 ^{1}H NMR (DMSO-d_6, 400 MHz)

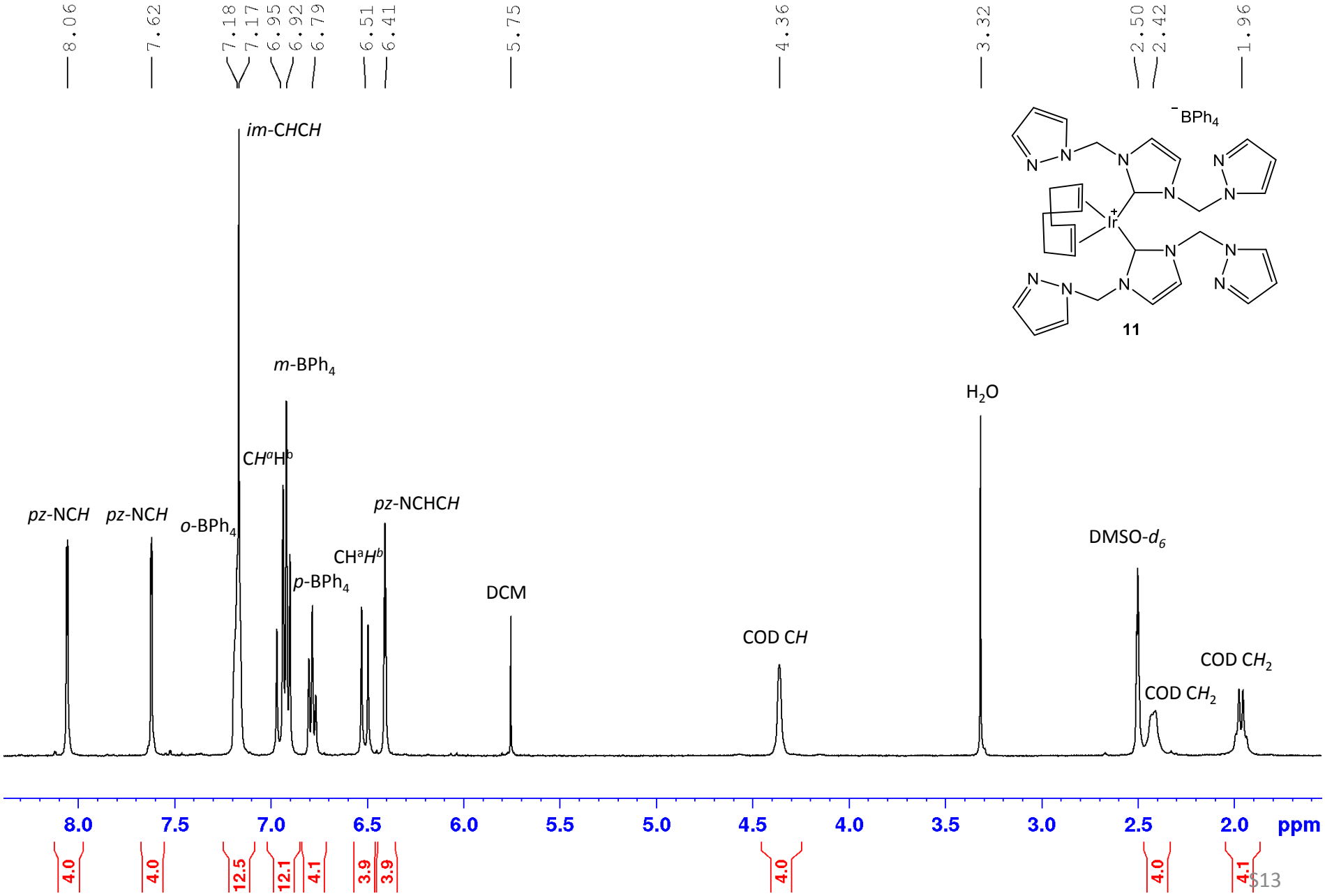

Figure S12: 11 ^{13}C NMR (DMSO-d_6, 100 MHz)

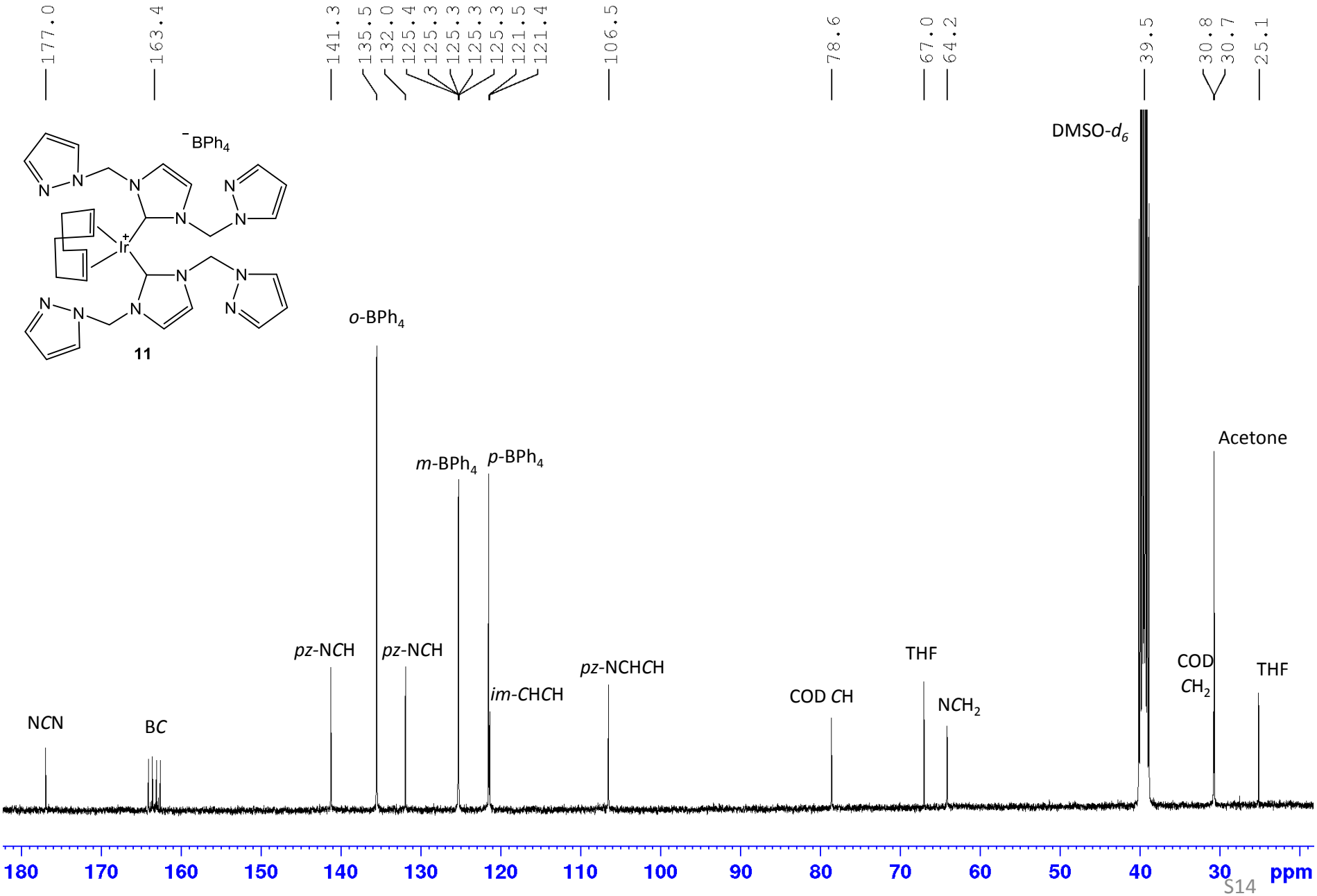

Figure S13: 12 ^{1}H NMR (DMSO-d_6, 600 MHz)

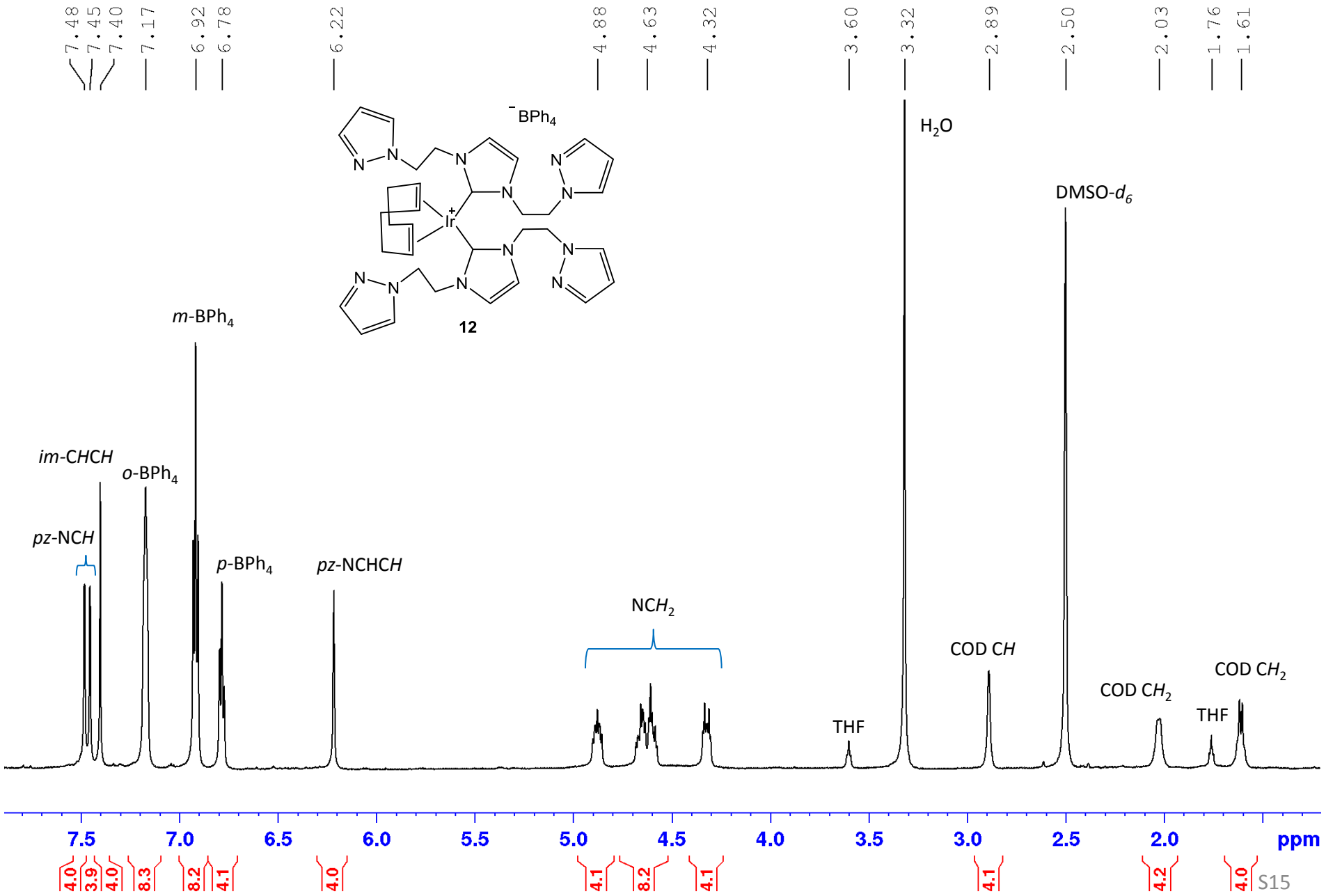

Figure S14: 12 ^{13}C NMR (DMSO-d_6, 100 MHz)

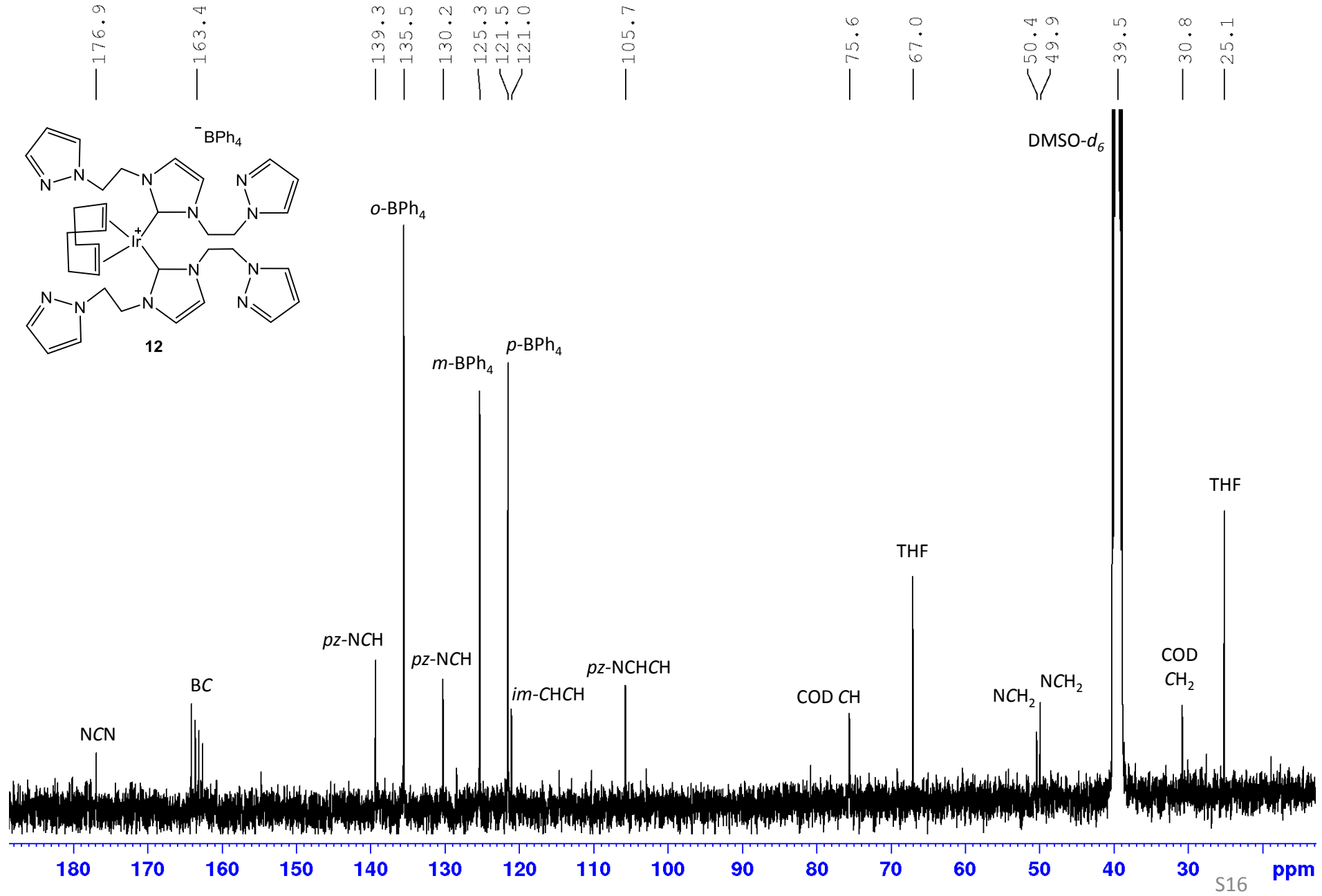

Figure S15: 13 ^{1}H NMR (Acetone-d_6, 400 MHz)

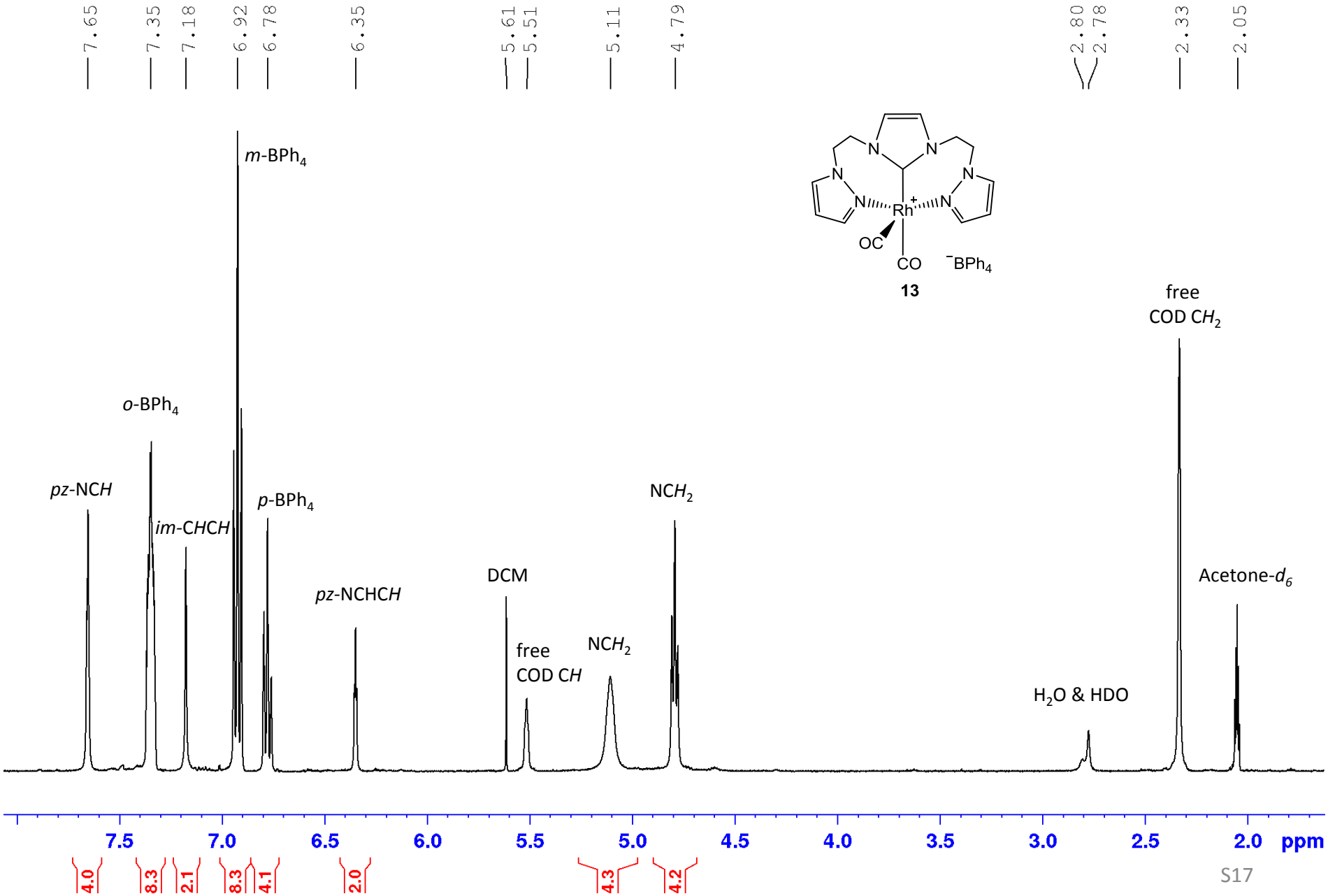

Figure S16: 13 ^{13}C NMR (Acetone-d_6, 100 MHz) [NB: ^{13}CO (99.5 %) used to enhance Ir-CO signal]

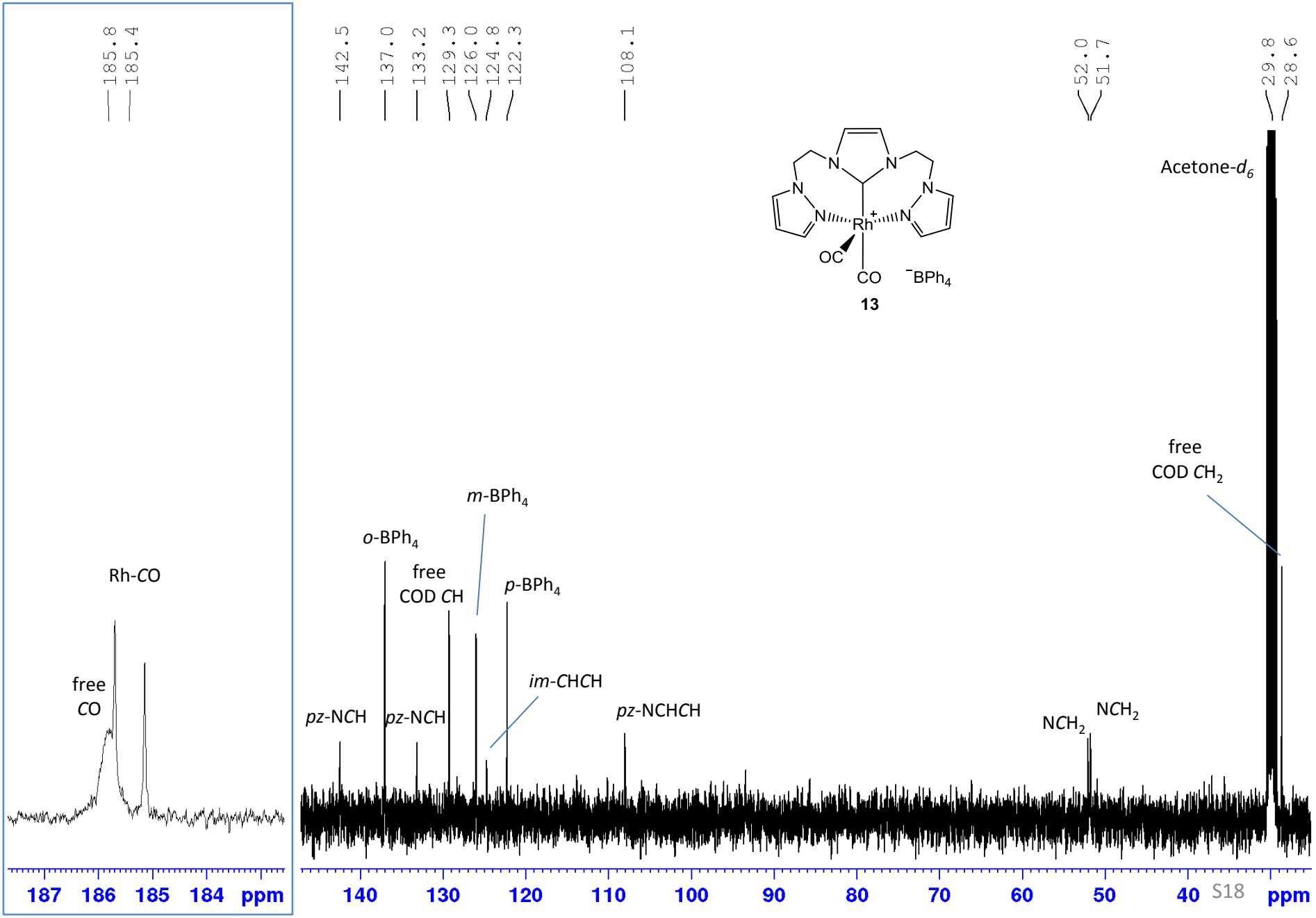

Figure S17: 14 ^{1}H NMR (Acetone-d_6, 400 MHz)

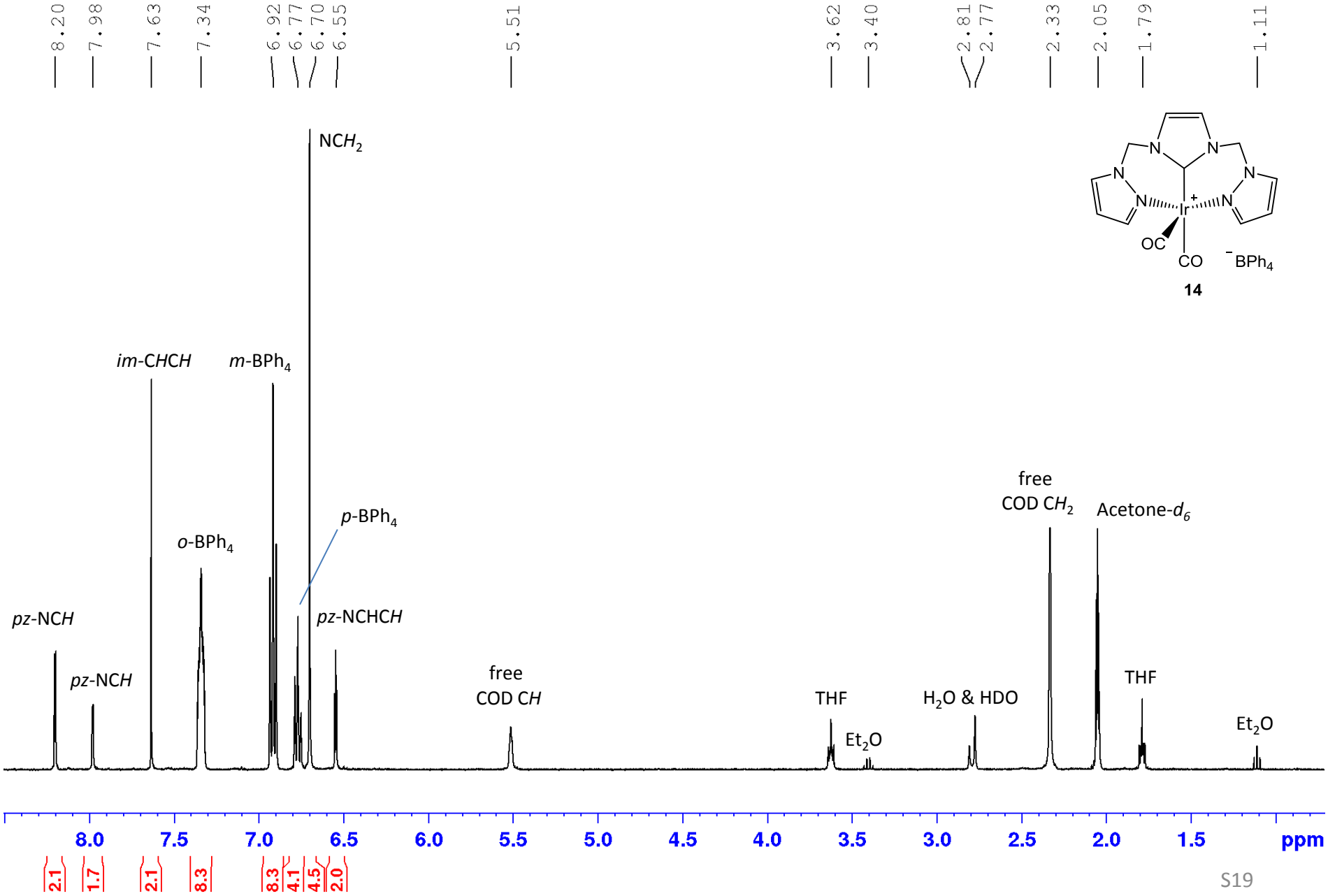

Figure S18: 14 ^{13}C NMR (Acetone-d_6, 100 MHz) [NB: ^{13}CO (99.5 %) used to enhance Ir-CO signal]

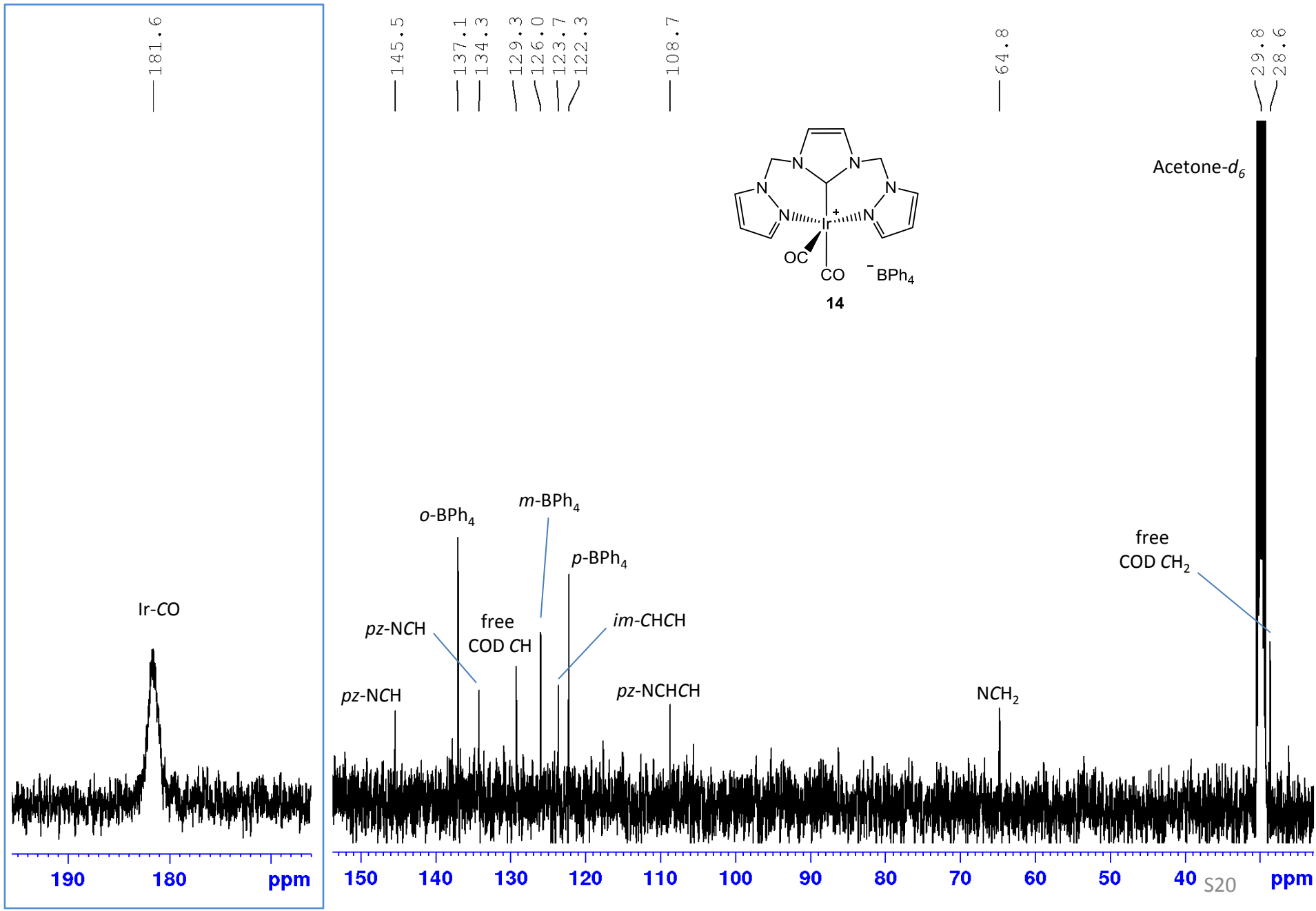

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Figure S19: 15 ^{1}H NMR (DMSO-d_6, 400 MHz)

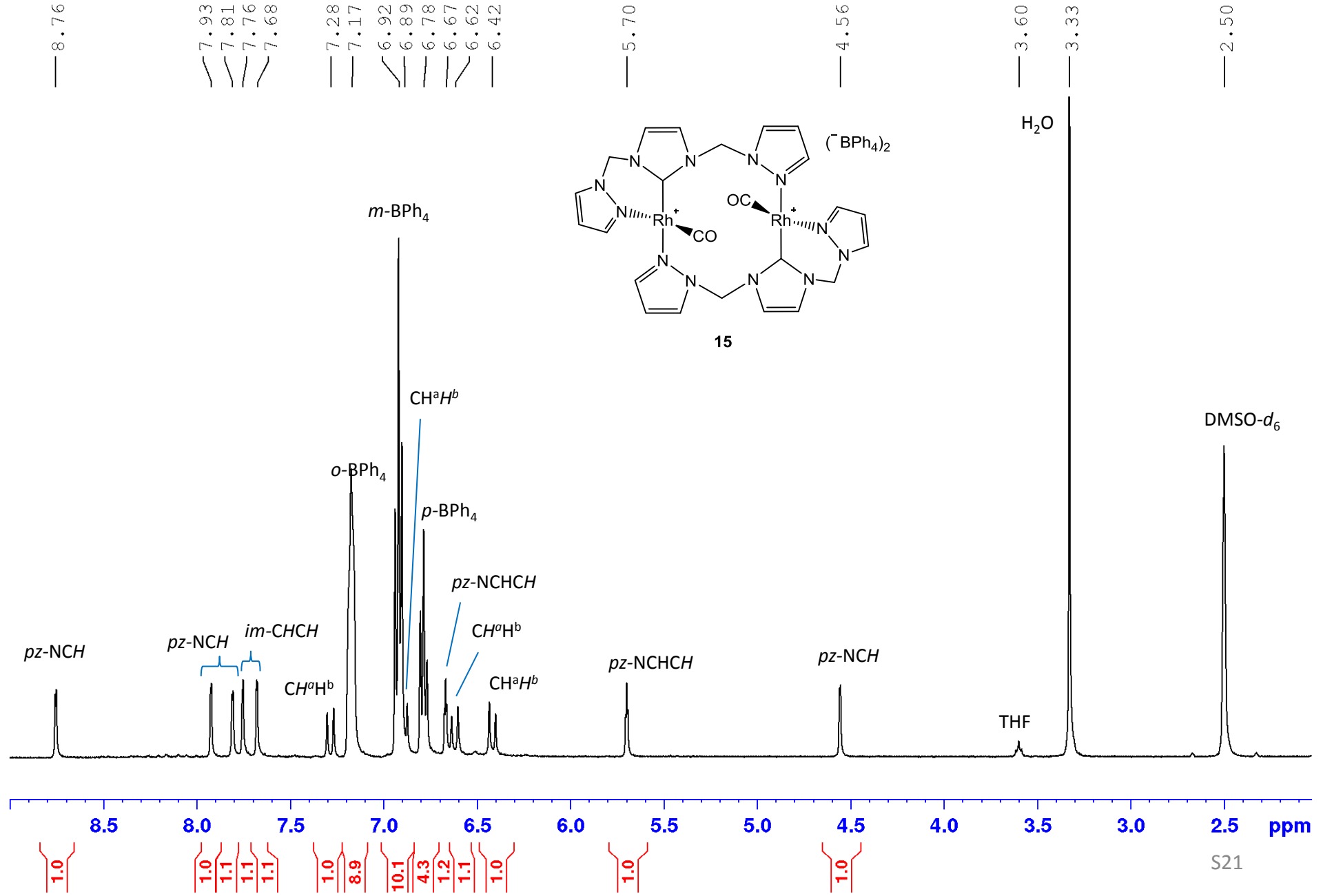


Figure S20: 15 ^{13}C NMR (DMSO-d_6, 150 MHz); [inset shows **15** generated *in situ* with ^{13}CO (99.5 %) (Acetone-d_6, 100 MHz)]

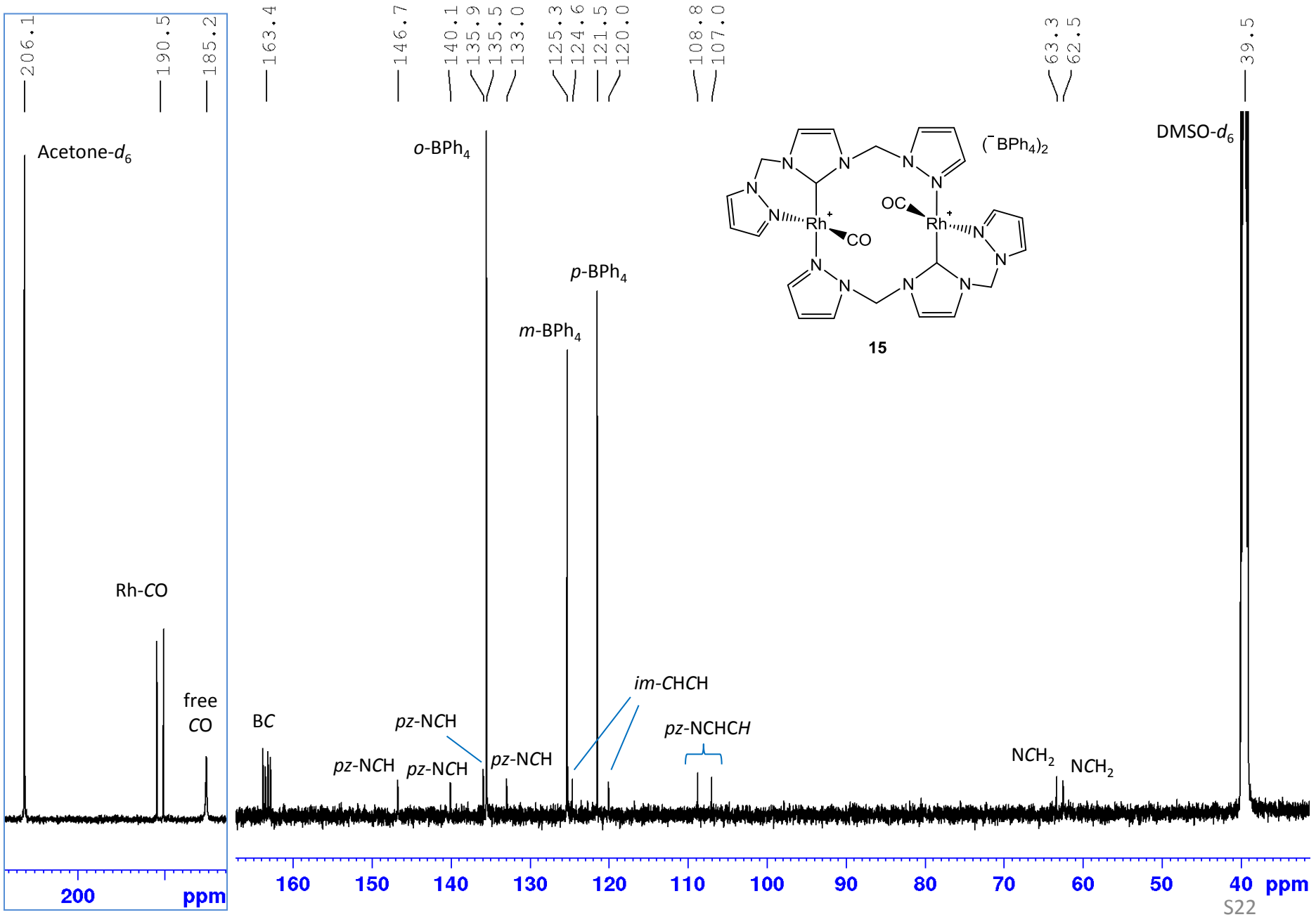
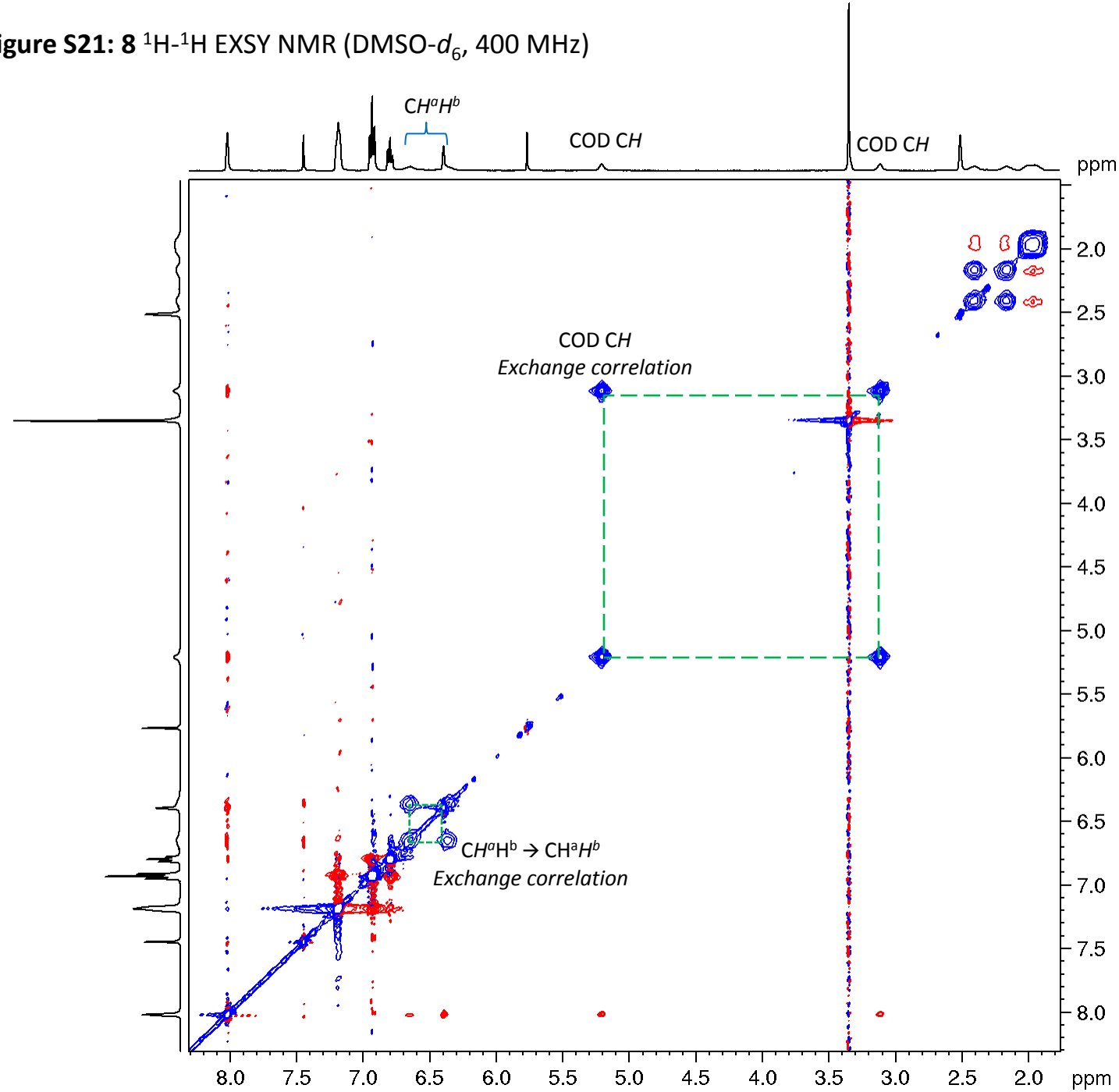


Figure S21: 8 ^{1}H-^{1}H EXSY NMR (DMSO-d_6, 400 MHz)



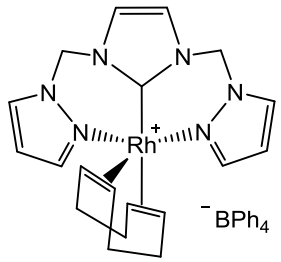
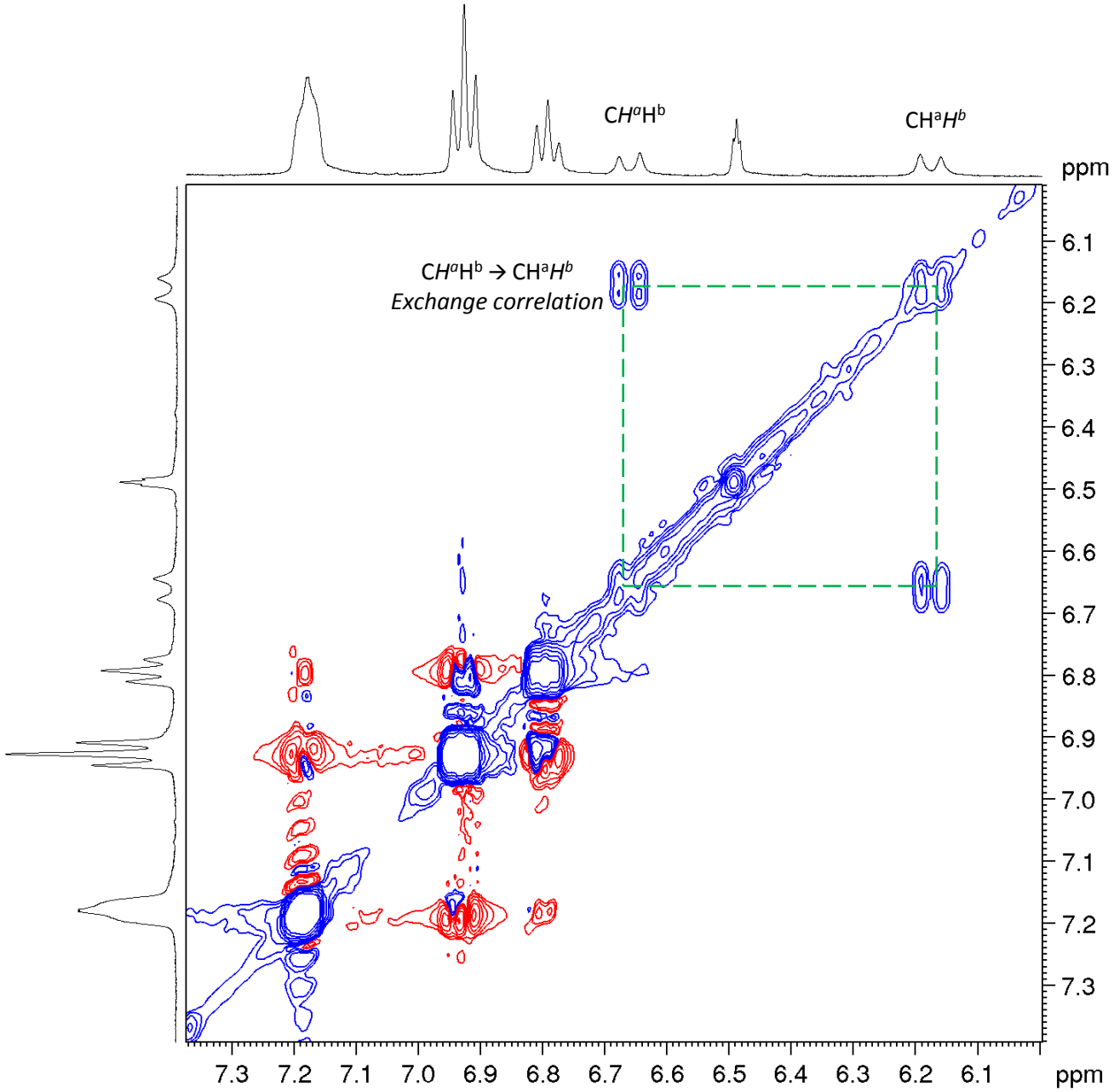


Figure S22: 10 ^{1}H-^{1}H EXSY NMR (DMSO-d_6, 400 MHz)



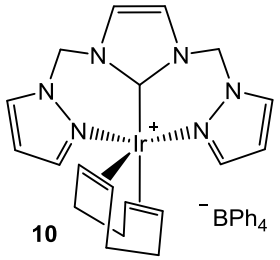
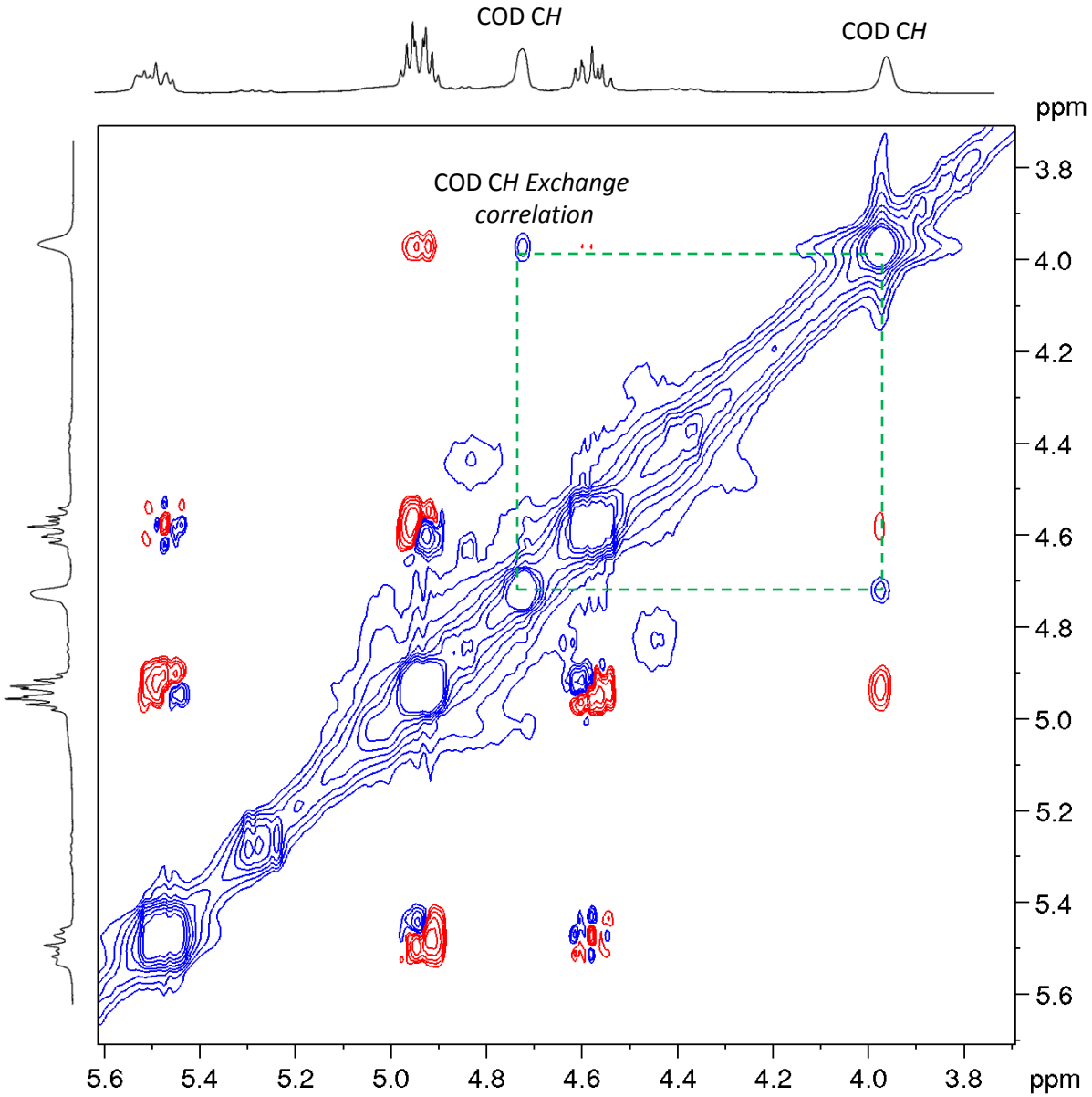
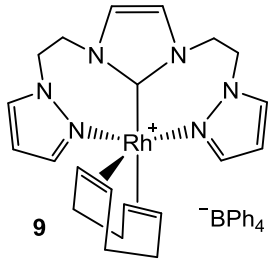


Figure S23: 9 ^{1}H-^{1}H EXSY NMR (DMSO-d_6, 400 MHz)





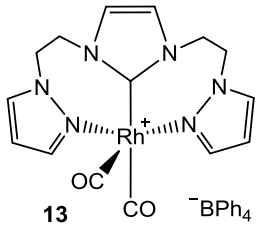


Figure S24: 13 ^{1}H NMR (Acetone-d_6, 400 MHz) [Low temperature NMR showing the CH_2 peaks broaden due to exchange between the diastereotopic pair CH^aH^b]

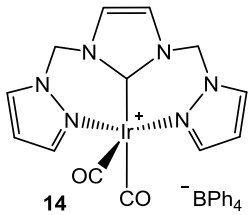


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Figure S25: 14 ^{1}H NMR (Acetone-d_6, 400 MHz) [Low temperature NMR showing the CH_2 peak split into the diastereotopic pair CH^aH^b]

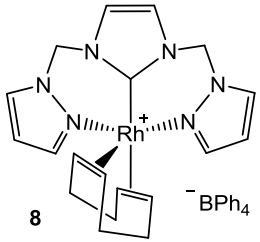

Figure S26: 8 ^{1}H NMR (DMSO-d_6, 400 MHz) [High temperature NMR showing COD C*H* peak broaden beyond baseline resolution]

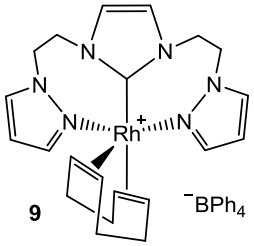

Figure S27: 9 ^{1}H NMR (DMSO-d_6, 400 MHz) [High temperature NMR showing little broadening of the COD C*H* peaks]

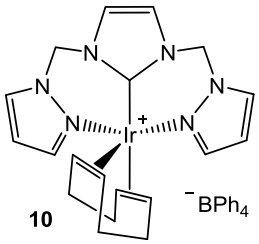

Figure S28: 10 ^{1}H NMR (Acetone-d_6, 600 MHz) [Low temperature NMR showing COD C*H* peak resolve from baseline]

Figure S29: 8 HRMS (Top= measured; Bottom= calculated)

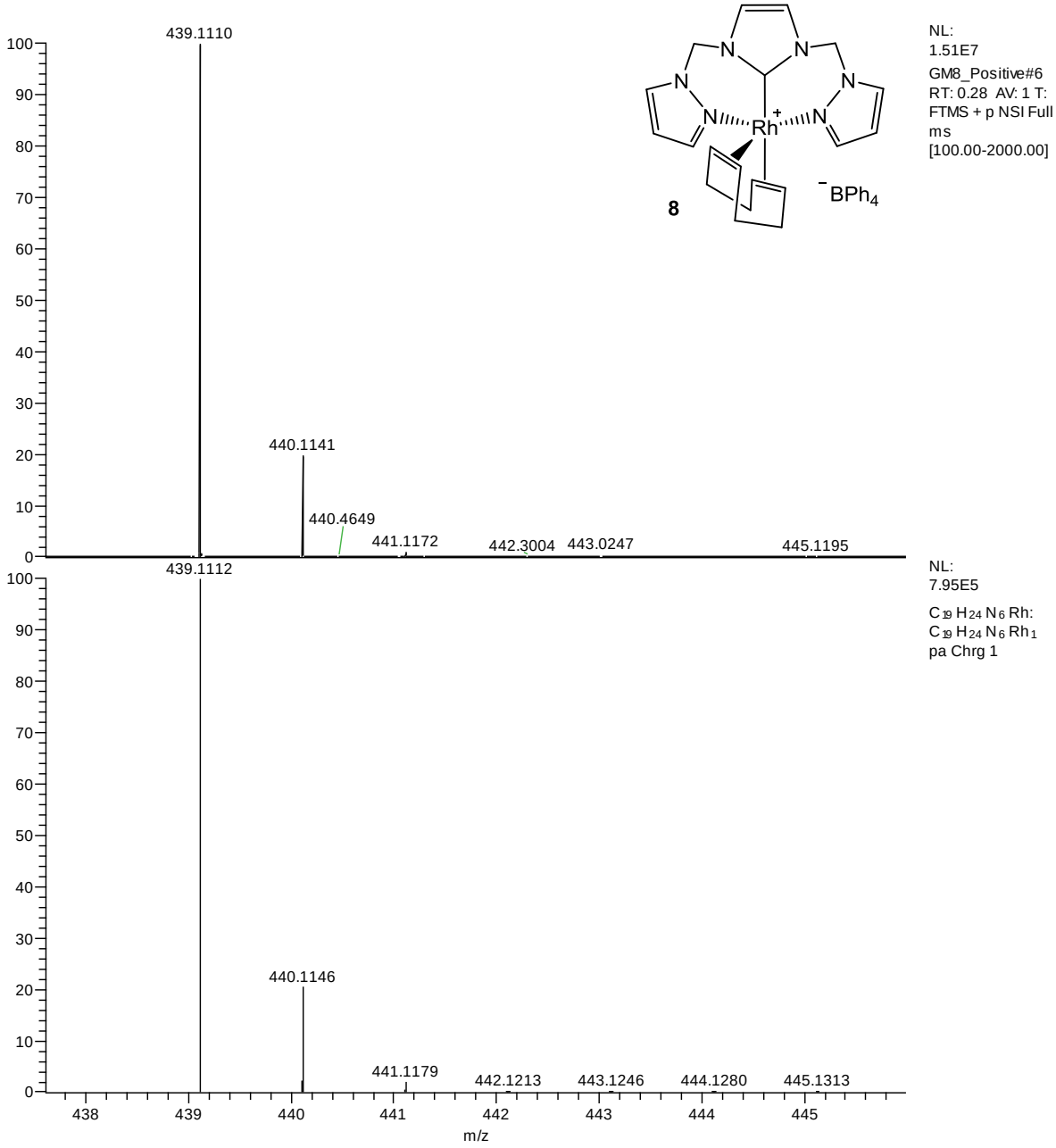

Figure S30: 9 HRMS (Top= measured; Bottom= calculated)

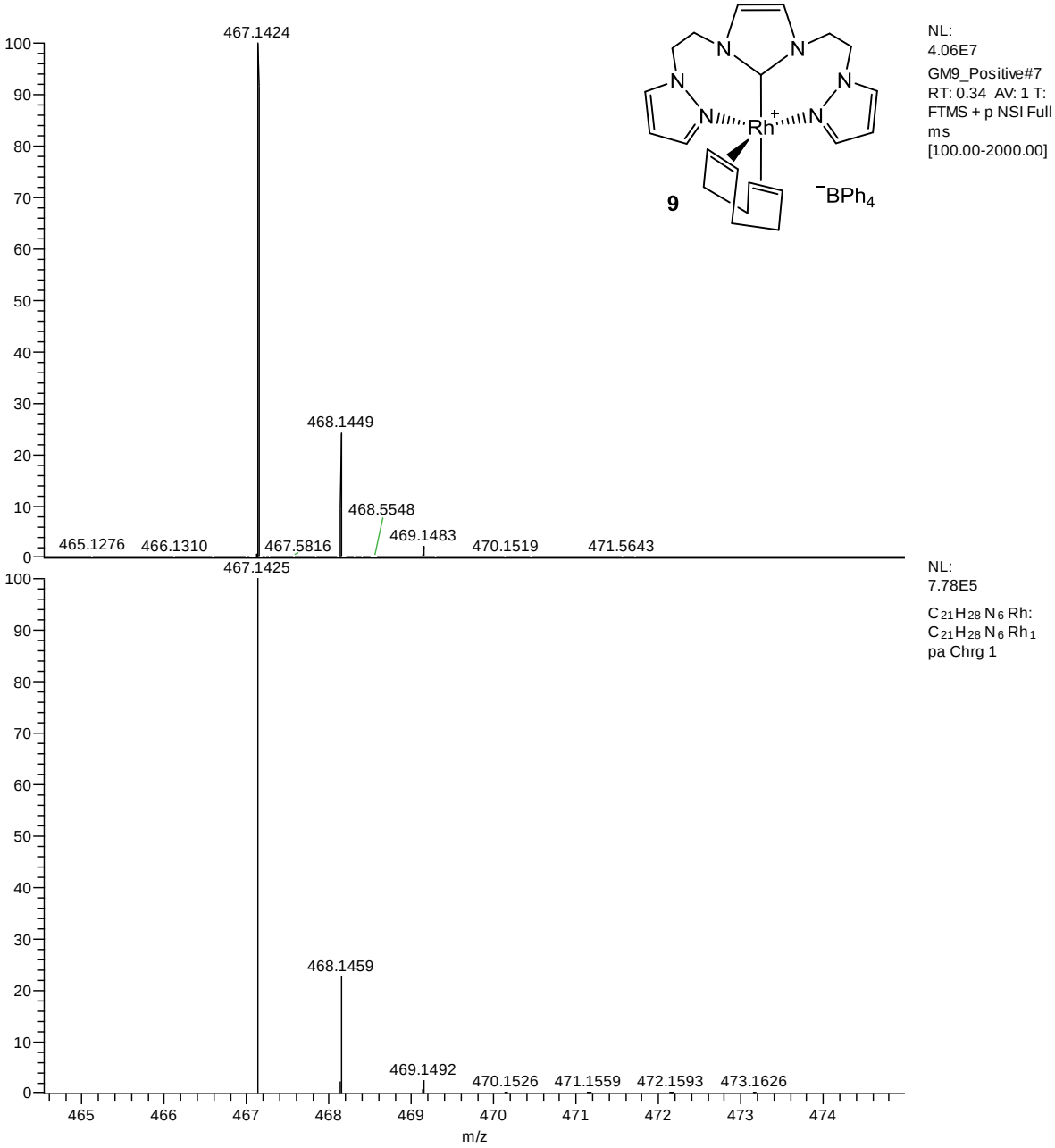

Figure S31: 10 HRMS (Top= measured; Bottom= calculated)

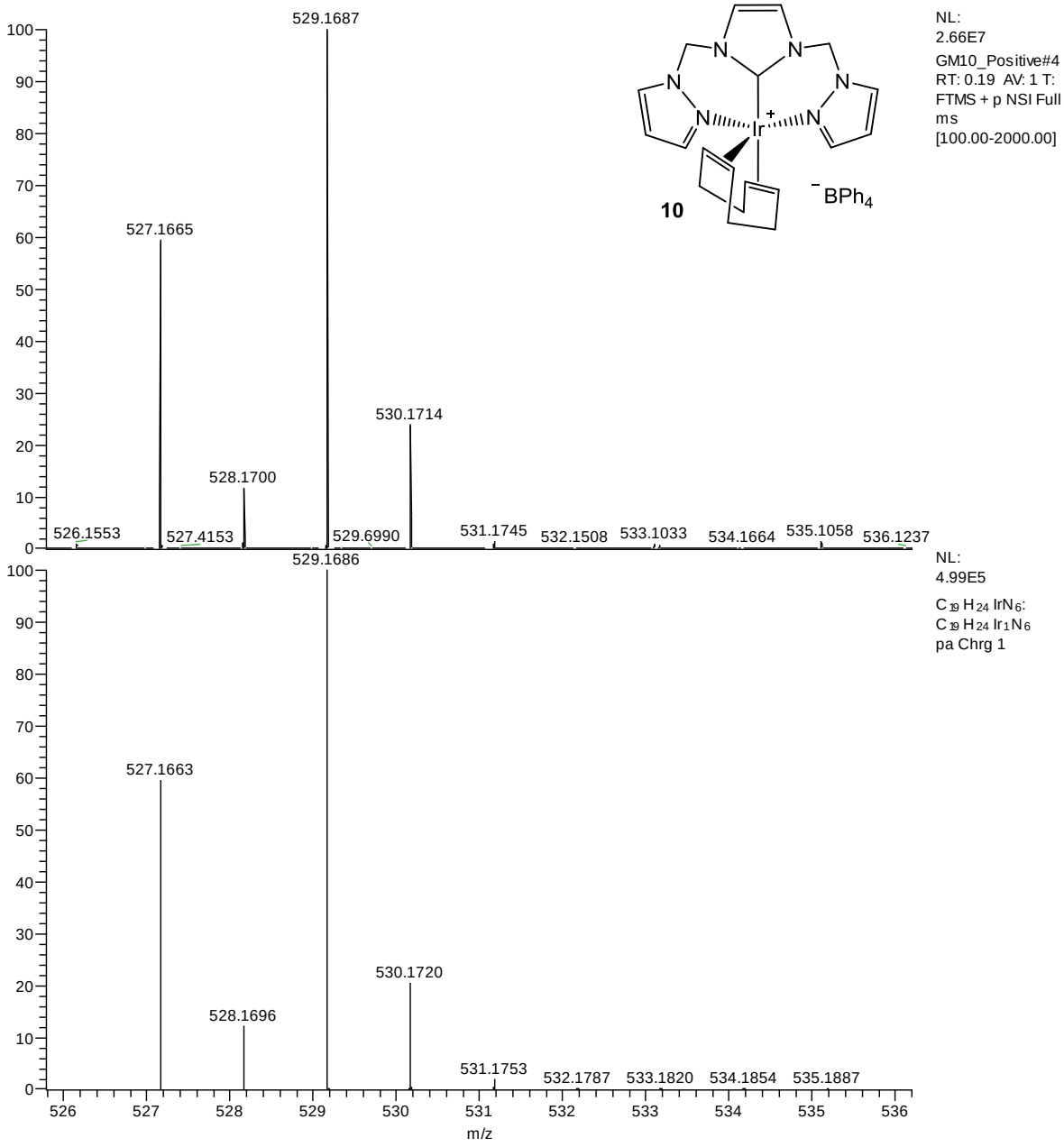

Figure S32: 15 HRMS (Top= measured; Bottom= calculated)