

Supplementary Material

First isolation of a Wheland intermediate in the azo-coupling reaction, its X-Ray crystal structure determination and products from its evolution

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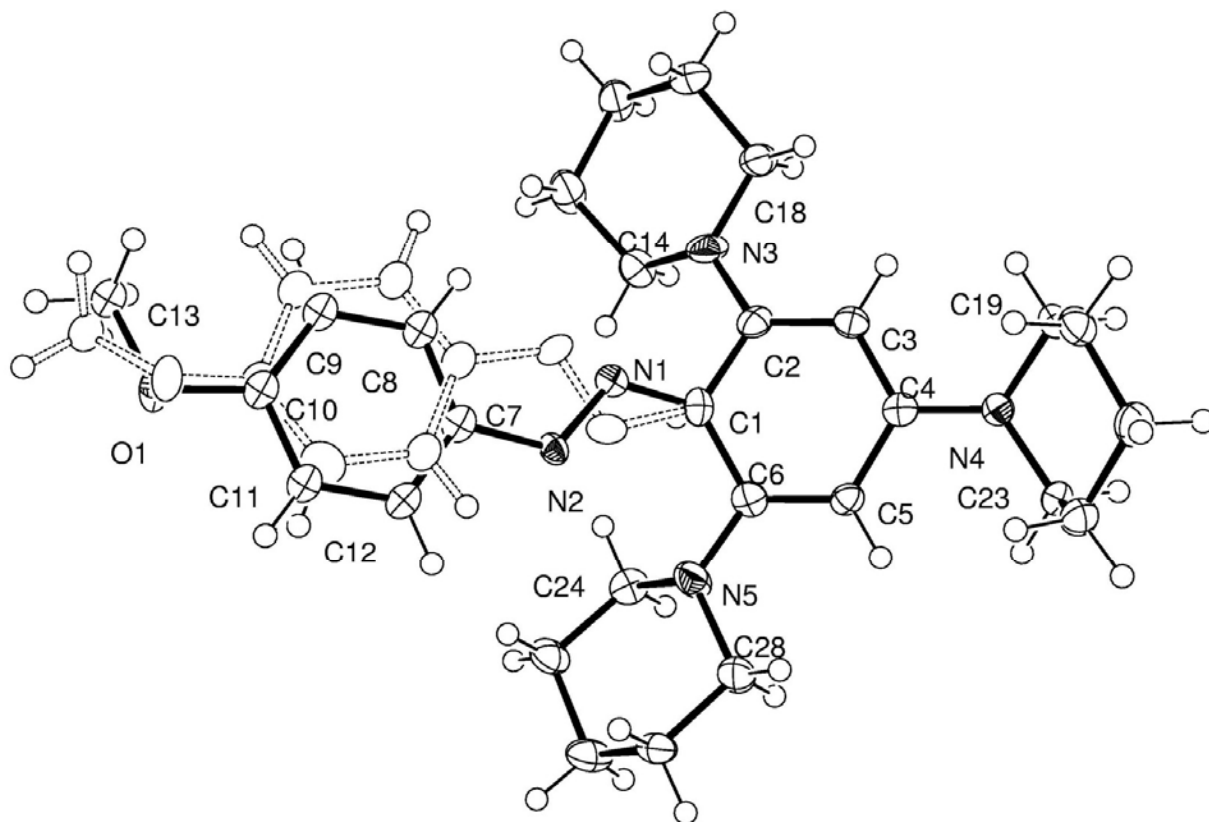


Figure S1. ORTEP drawing of **W** (cation only). Broken lines indicate the minor conformer arising by the 'pedal motion'.

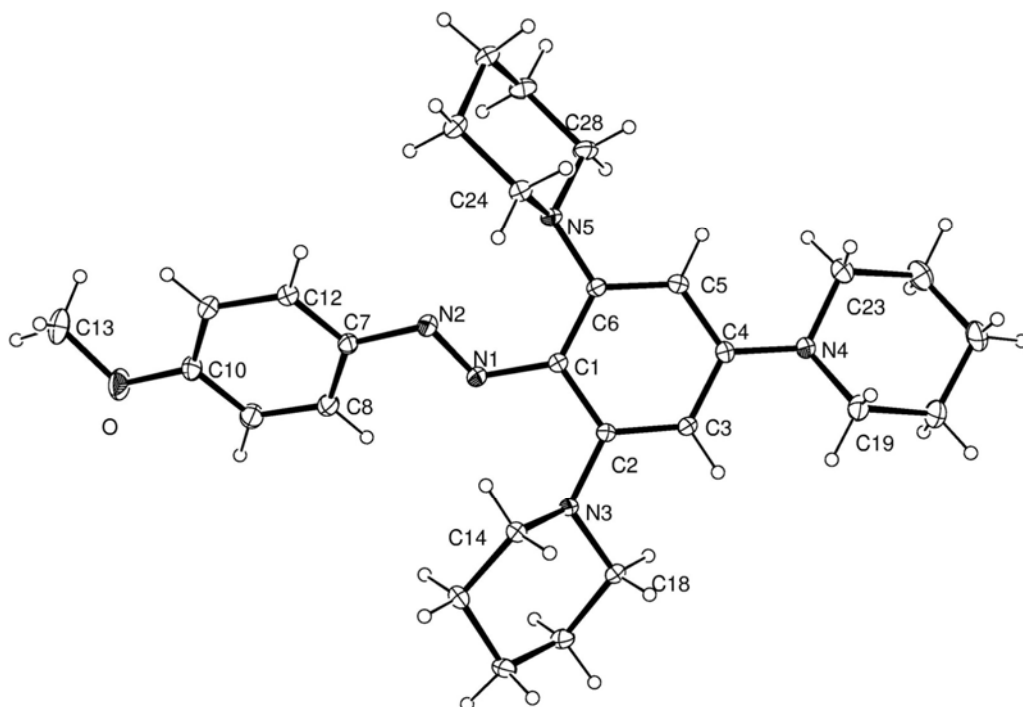


Figure S2. ORTEP drawing of compound **P**.

Cartesian coordinates of W and P structures optimized at B3LYP/6-31G(d)

Compound W

N	-1.00924500	0.09378200	-1.00466300
N	-1.05083700	-0.11692100	0.23193200
C	-2.33203500	-0.17663100	0.81019800
C	-3.54447800	-0.04020400	0.11053800
H	-3.52267500	0.12228300	-0.96157800
C	-4.75588200	-0.11443700	0.78175800
C	-4.77354300	-0.32755200	2.17593900
C	-3.56246800	-0.46578400	2.87941500
H	-3.60266900	-0.62969100	3.95096500
C	-2.35979100	-0.39192900	2.20057300
H	-1.41525600	-0.49648000	2.72524800
O	-5.89382400	-0.41482900	2.92045900
C	-7.16710200	-0.28606200	2.28805500
H	-7.27712100	0.69681900	1.81502000
H	-7.90209000	-0.39009300	3.08638400
H	-7.32132800	-1.07566400	1.54331000
N	0.39959600	2.60197300	-1.33359500
N	4.09832100	0.20174100	0.61403000
N	0.58425000	-2.29700300	-1.55224100
C	0.41060300	0.15080100	-1.50583700
H	0.32889600	0.20526300	-2.59721600
C	1.05852800	1.44771800	-1.03777200
C	2.24446000	1.40793900	-0.33871800
H	2.75380700	2.32976900	-0.11427000
C	2.91504000	0.18162000	-0.04972000
C	2.36806400	-1.05730000	-0.49732900
H	2.89752800	-1.96402900	-0.26162100
C	1.17105400	-1.12786300	-1.17487700
C	-0.58455700	2.72251000	-2.43173600
H	-0.95912300	1.73824900	-2.69950000
H	-0.06585000	3.14533000	-3.30692100
C	-1.76702100	3.61943800	-2.05267300
H	-2.33981600	3.12998000	-1.25473100
H	-2.42679900	3.70202000	-2.92423700
C	-1.28914400	4.99818700	-1.59042500
H	-0.81721600	5.52677200	-2.43087800
H	-2.13594700	5.61262900	-1.26588200
C	-0.28227200	4.83169000	-0.45036900
H	-0.78745700	4.41517600	0.43056400
H	0.14071300	5.79788500	-0.15179500
C	0.87844700	3.90291500	-0.83298700
H	1.51232600	4.37452900	-1.59999500
H	1.49239200	3.73736600	0.05117500
C	4.56932000	1.33084700	1.43688000
H	3.84512300	2.14149300	1.41218700
H	5.51112800	1.70468200	1.01158200
C	4.77910200	0.88056300	2.89400800
H	3.80031400	0.63182300	3.32447500
H	5.17481400	1.72925400	3.46416300
C	5.71794400	-0.32837700	2.99671200
H	5.77342100	-0.67783900	4.03334200

H	6.73557600	-0.02675900	2.71118200
C	5.24946500	-1.45851700	2.06967000
H	5.98342200	-2.27238800	2.04585700
H	4.30382700	-1.88264600	2.43220800
C	5.05259400	-0.92164300	0.64703900
H	6.00875100	-0.52850100	0.27245500
H	4.74510600	-1.69832000	-0.04971600
C	-0.45201300	-2.37691800	-2.60558700
H	0.04574200	-2.64013000	-3.55277500
H	-0.92640900	-1.40619000	-2.72882100
C	-1.52939300	-3.41705700	-2.28456400
H	-2.22879100	-3.45486000	-3.12783500
H	-2.09603400	-3.08166200	-1.40643400
C	-0.91112300	-4.79144100	-2.01831400
H	-1.68305400	-5.51520700	-1.73526500
H	-0.44155400	-5.17040200	-2.93722400
C	0.13774700	-4.66804100	-0.91140900
H	-0.35351000	-4.40339700	0.03382000
H	0.65679500	-5.61980600	-0.74929200
C	1.19340100	-3.60042200	-1.23046700
H	1.83788400	-3.48791500	-0.36024200
H	1.82263400	-3.92133700	-2.07538600
H	-5.68117700	-0.00870400	0.22776200

Compound P

N	1.02991700	0.32295300	0.05760200
N	1.87224100	-0.57925400	0.35985300
C	-1.12436300	1.30025400	0.21194500
N	-4.54420300	-0.05433700	-0.34170900
C	-3.15558700	-0.01704000	-0.11355900
C	-2.50498900	1.22203700	0.03779100
H	-3.08624000	2.13300200	-0.01081300
C	0.34389900	2.82273700	1.48051300
H	0.82768200	1.90168400	1.80117700
H	-0.31182000	3.16283800	2.30648100
N	-0.47385600	2.54342600	0.28927100
C	-0.32911100	0.10219600	0.24377700
N	-0.28500700	-2.37047800	0.25448000
C	3.19197700	-0.26350600	-0.05206400
C	4.22625000	-1.02805000	0.49787200
H	3.97376900	-1.80264700	1.21584200
C	-1.00212500	-1.16082500	0.18625900
O	7.13273500	0.51859900	-1.18352500
C	-2.38962100	-1.18802700	-0.02170300
H	-2.88464600	-2.14876800	-0.03875700
C	0.27517800	-2.72291800	1.56965700
H	-0.53593500	-3.09056700	2.22837000
H	0.69338400	-1.82183400	2.01621600
C	5.87043800	0.20861500	-0.76491500
C	3.51799300	0.74303700	-0.98402700
H	2.71359700	1.32375800	-1.42187700
C	1.39322500	3.89807500	1.19249800

H	2.10149300	3.50337300	0.45348600
H	1.95762900	4.10634100	2.11042700
C	-1.17133800	3.73099100	-0.19697600
H	-1.90060300	4.10972000	0.54725900
H	-1.73292900	3.46053200	-1.09560300
C	4.83707400	0.97483400	-1.33370300
H	5.10304400	1.74034100	-2.05675200
C	-0.85075900	-3.53177400	-0.43550100
H	-1.25127400	-3.19855000	-1.39756200
H	-1.68885300	-3.98031100	0.13440500
C	5.55990500	-0.79762100	0.15732600
H	6.33789600	-1.40247200	0.60900400
C	0.84590300	-5.02712900	0.68773900
H	0.08477900	-5.53856000	1.29632400
H	1.65648900	-5.74861100	0.52559600
C	-5.15520000	-1.32064900	-0.74119300
H	-5.30990600	-1.98655400	0.13037800
H	-4.47325600	-1.83218400	-1.42530100
C	-0.16950300	4.84417600	-0.53506700
H	0.44775700	4.51025000	-1.37905100
H	-0.72170700	5.73336500	-0.86555500
C	8.21600500	-0.23276300	-0.66182500
H	8.29418800	-0.12688600	0.42853400
H	9.11542500	0.17383200	-1.12820700
H	8.12712200	-1.29809800	-0.91345200
C	0.22326300	-4.60458700	-0.64846200
H	-0.22636900	-5.46557600	-1.15972100
H	1.00004000	-4.19841200	-1.30857900
C	0.73115900	5.17506100	0.66094300
H	0.12405000	5.62905900	1.45867000
H	1.48699800	5.91845700	0.37883300
C	1.36031800	-3.79295800	1.43899900
H	1.71709900	-4.06815200	2.44016300
H	2.20258900	-3.35342000	0.89324100
C	-6.49667400	-1.08170000	-1.44709400
H	-6.30410100	-0.55960200	-2.39336800
H	-6.94585000	-2.05138100	-1.69592900
C	-5.41574500	0.74095500	0.53471400
H	-4.90783300	1.66691900	0.80553000
H	-5.60017300	0.19035100	1.47750100
C	-6.75576000	1.04797500	-0.13949600
H	-7.38966900	1.60987500	0.55807600
H	-6.57628400	1.69165900	-1.01071300
C	-7.44864400	-0.24609500	-0.58374300
H	-8.37240800	-0.02417500	-1.13186900
H	-7.73971000	-0.82537300	0.30509200

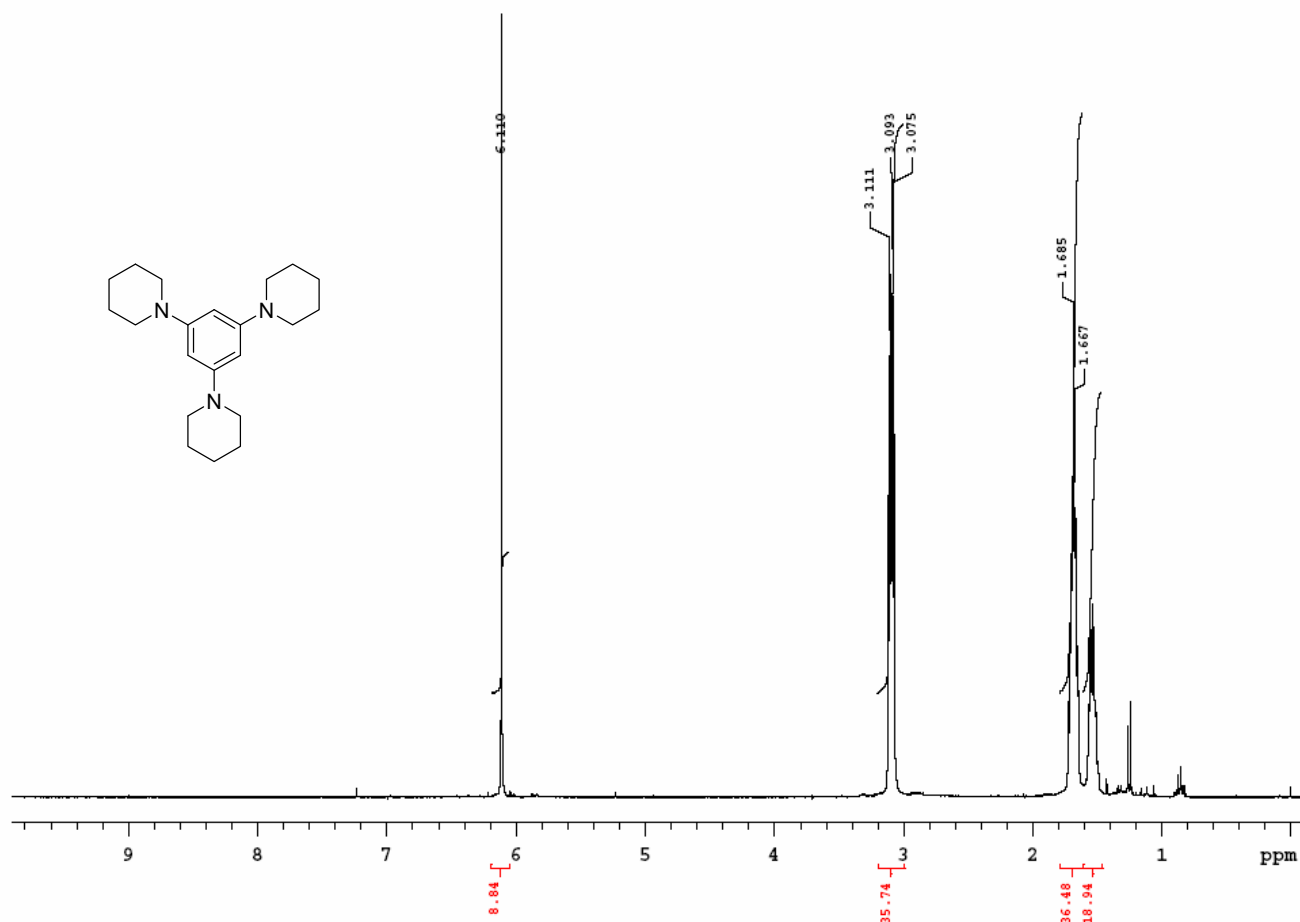


Figure S3. ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectrum of compound of 1,3,5-tris(1-piperidinyl)benzene (**1**).

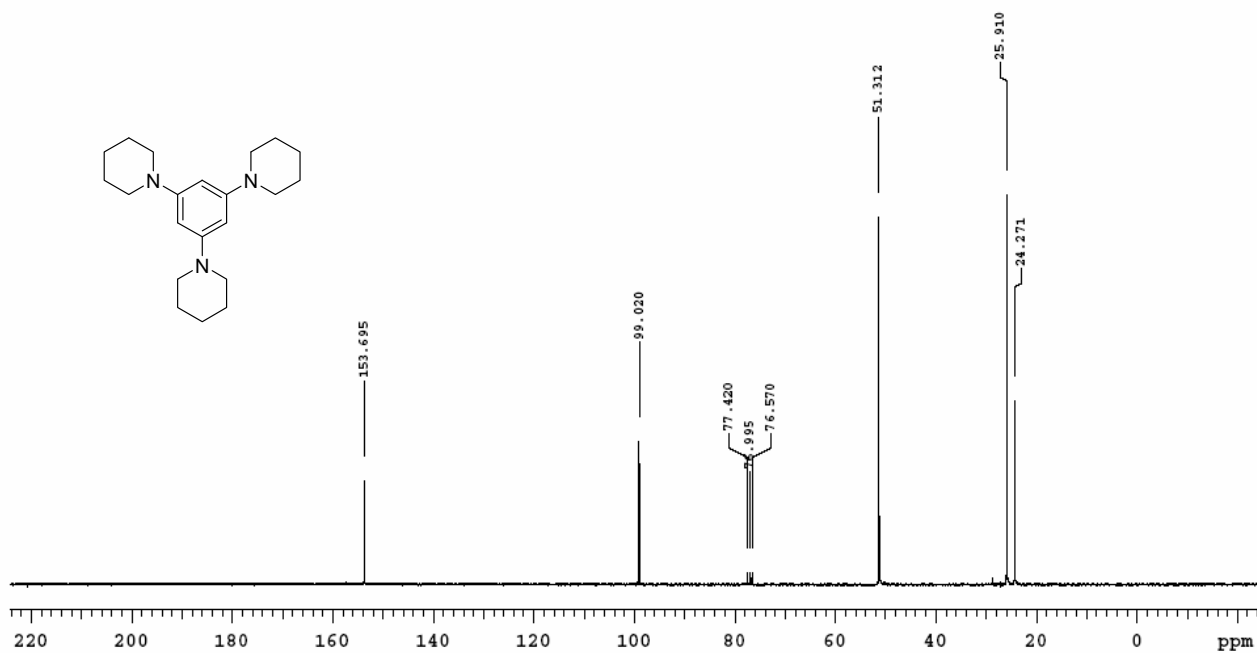


Figure S4. ^{13}C NMR (75.46 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectrum of compound of 1,3,5-Tris(1-piperidinyl)benzene (**1**).

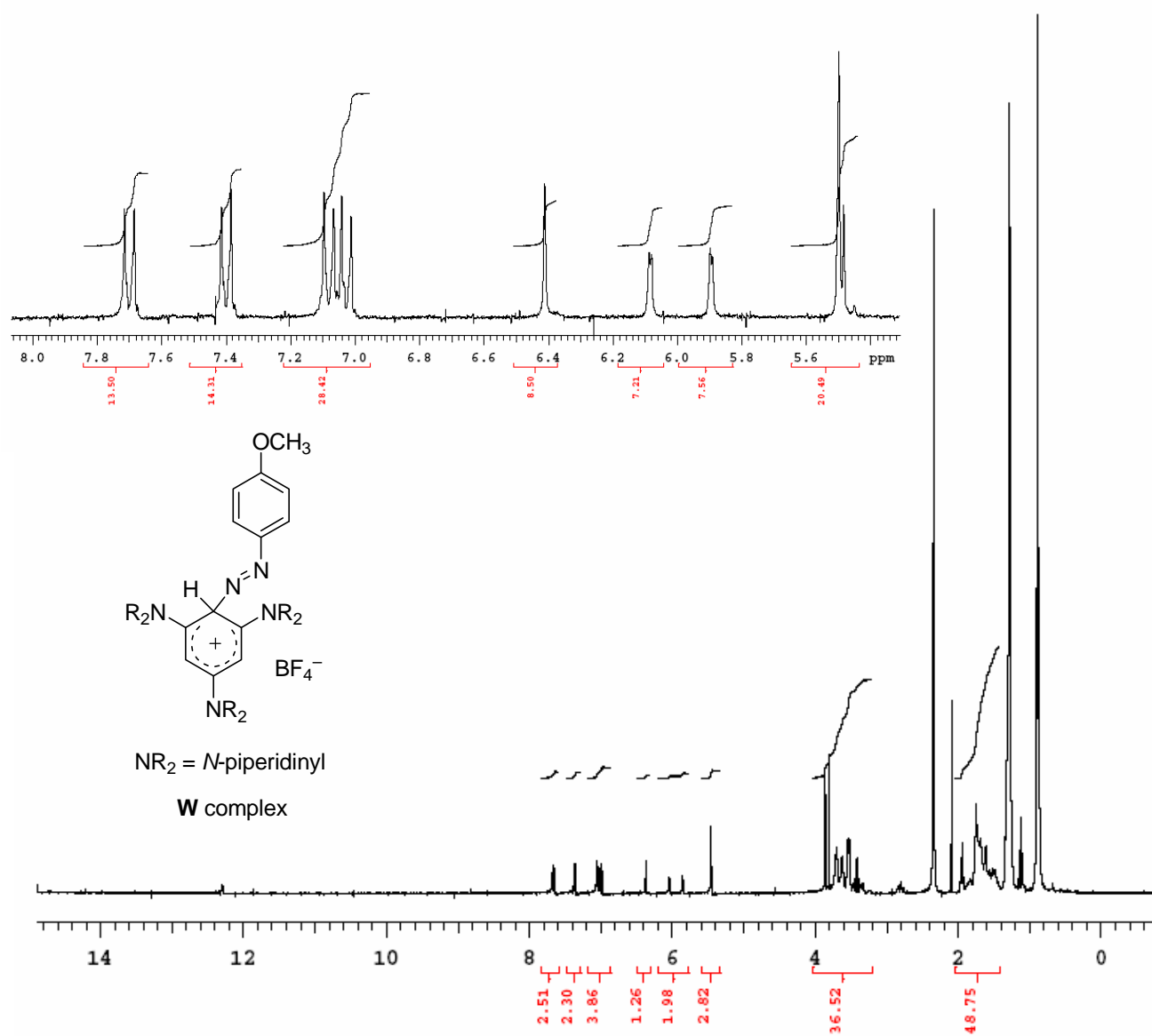


Figure S5. ^1H NMR (300 MHz, CD_3CN , -40°C) spectrum (and expanded view) of **W** [with presence of PH^+ (spectrum recorded after time used to record ^{13}C NMR spectrum) and presence of acetone, dichloromethane, and *n*-hexane used as solvents].

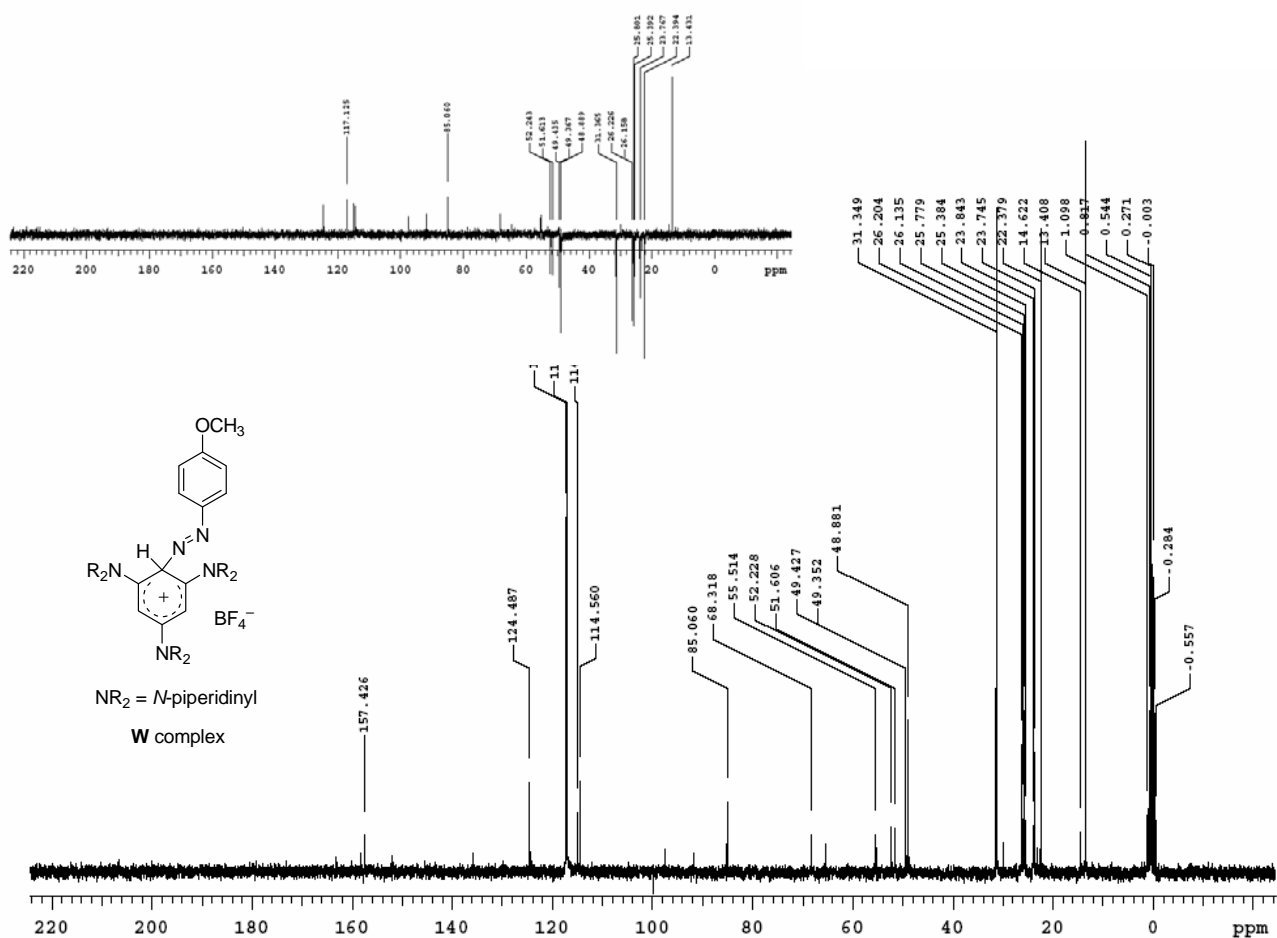


Figure S6. ^{13}C NMR (75.46 MHz, CD_3CN , -40°C) (and DEPT) of **W** [with traces of **PH**⁺ (spectrum recorded immediately after precipitation of **W**) and of acetone/dichloromethane/hexane used as solvents].

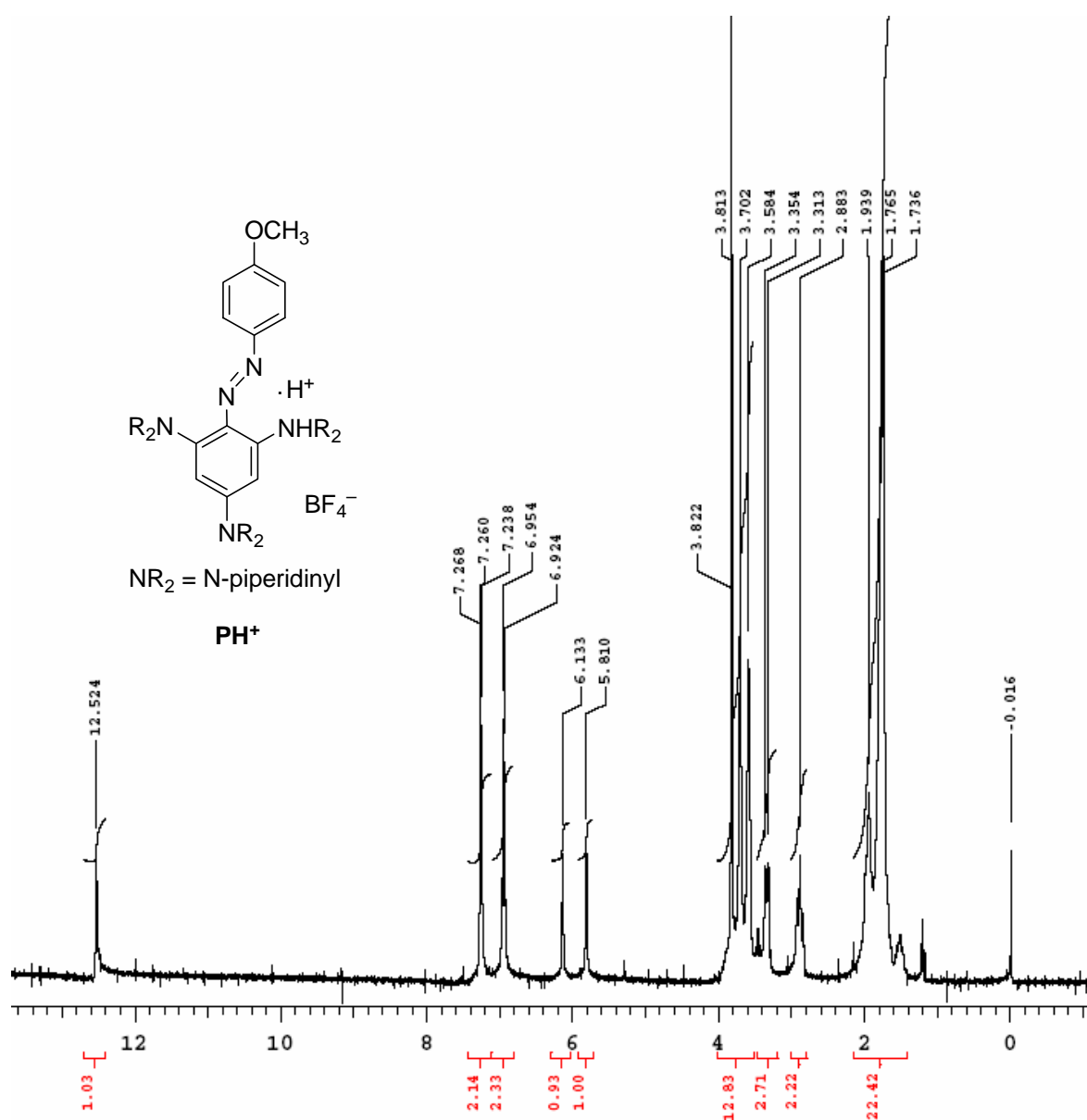


Figure S7. ¹H NMR (300 MHz, CDCl₃, 25 °C) spectrum of compound **PH**⁺.

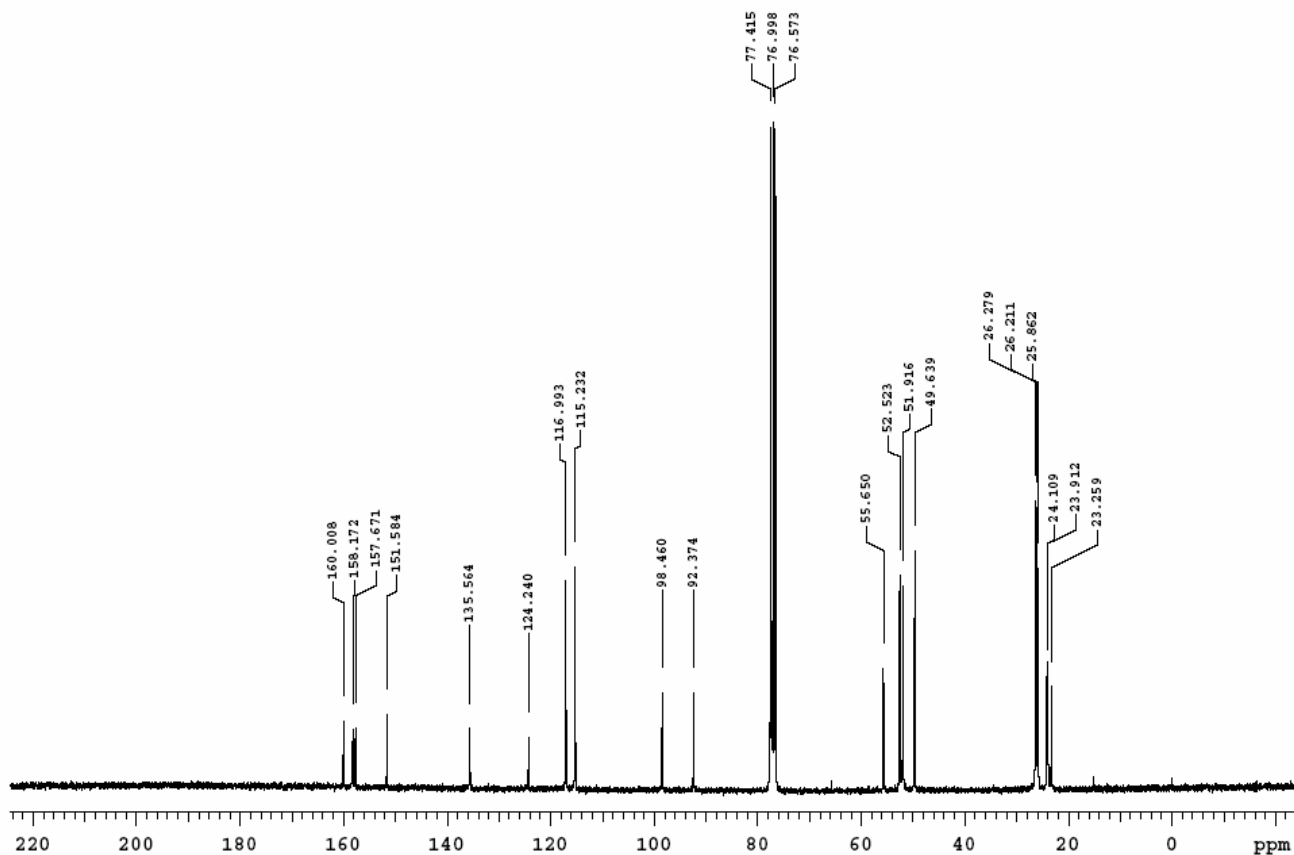


Figure S8. ^{13}C NMR (75.46 MHz, CDCl_3 , +40 °C) of compound PH^+ .

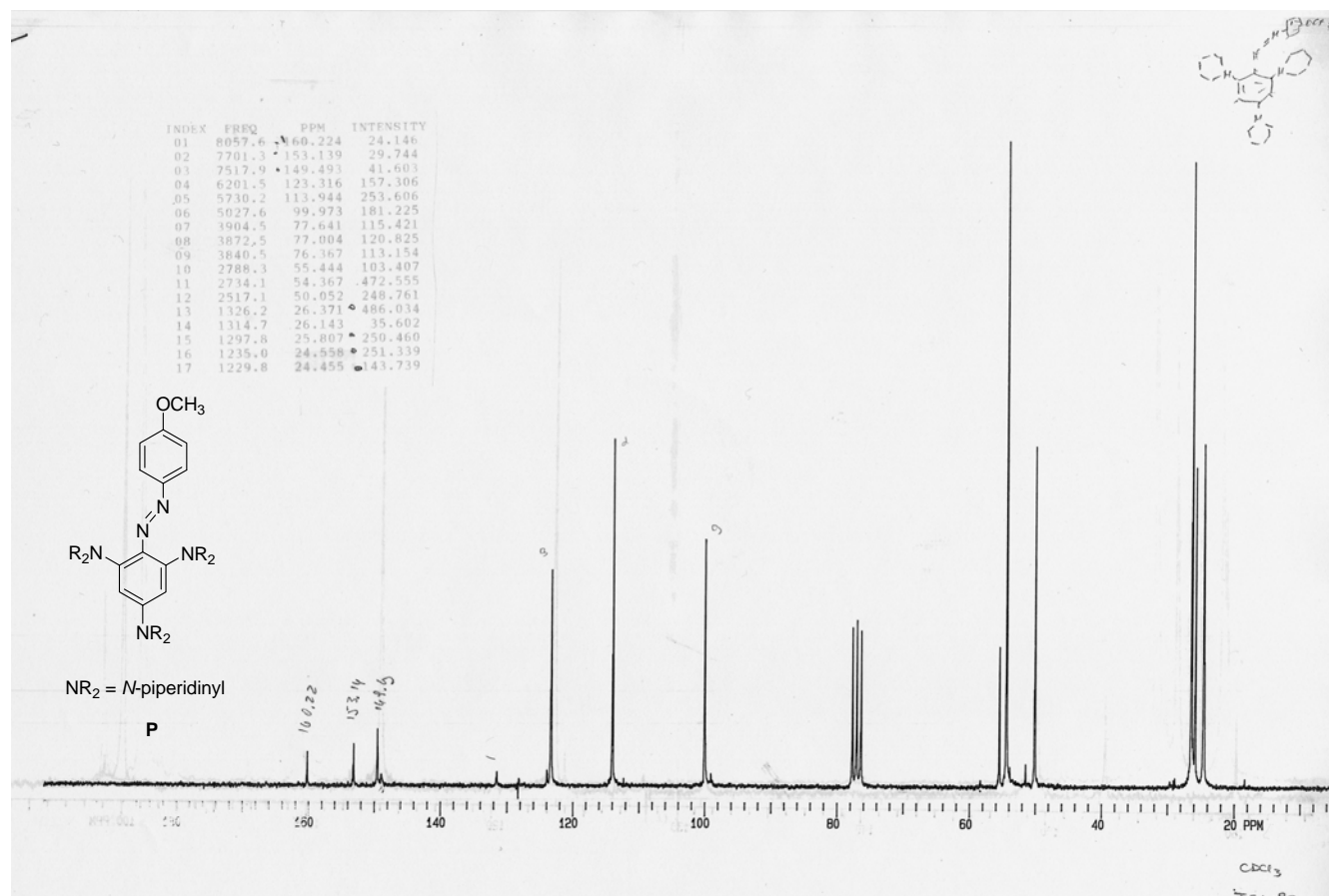


Figure S9. ¹³C NMR (75.46 MHz, CDCl₃, +40 °C) of compound P.

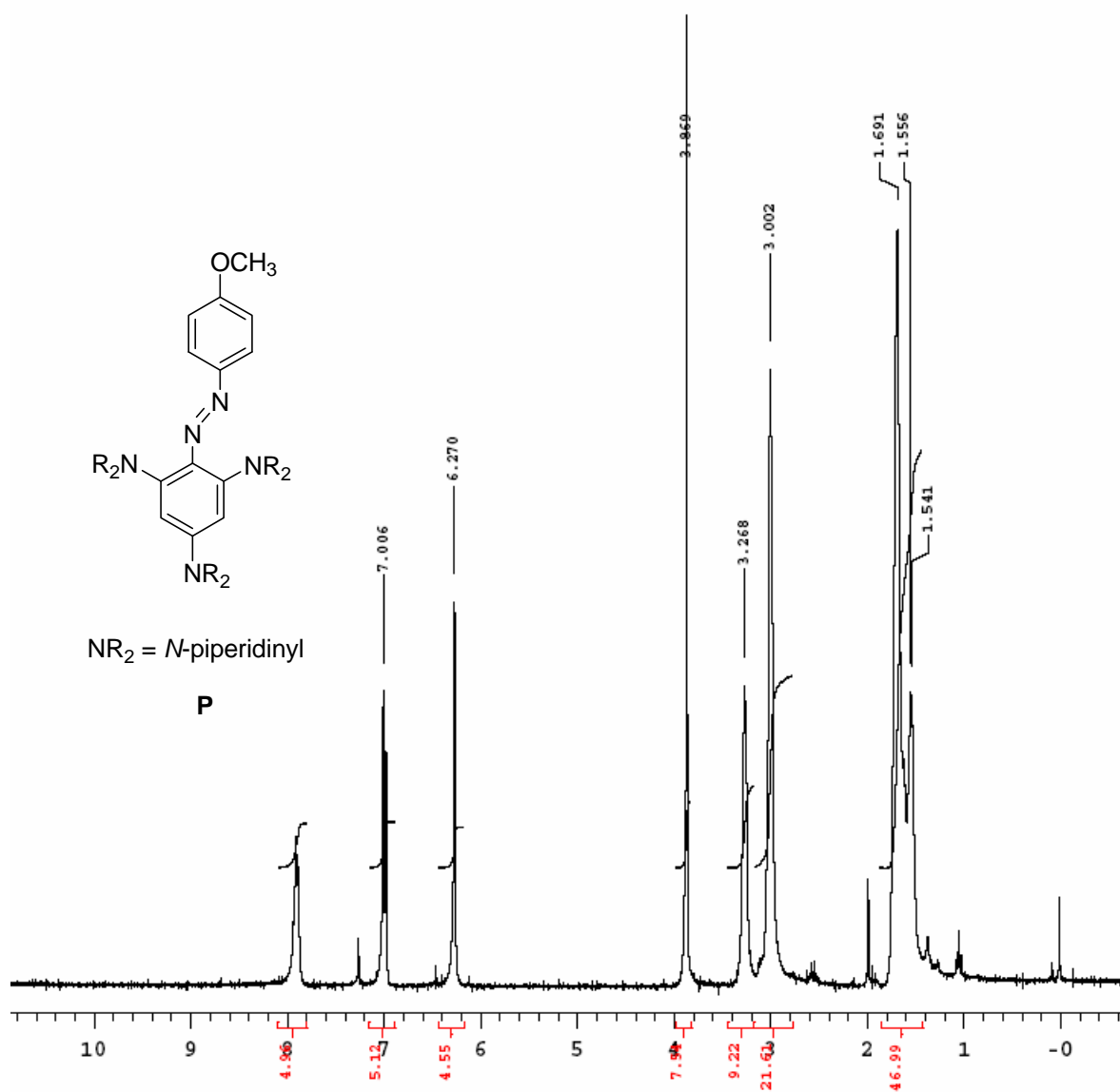


Figure S10. ^1H NMR (300 MHz, CDCl_3 , 25 °C) spectrum of compound **P**.