SUPPORTING INFORMATION

NMR SPECTROSCOPY AND ESI-MS

- **Ligand $SiHMe_2$(*o*-C_6H_4SMe) (L1)**

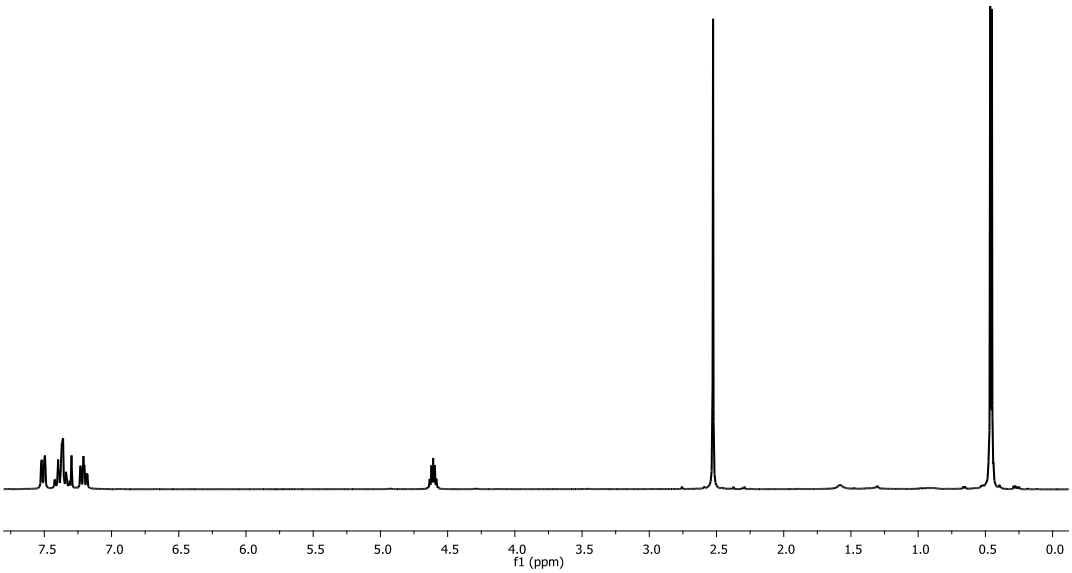

Figure 1. ^1H NMR spectrum of **L1** in $CDCl_3$.

- **Ligand SiHMe(*o*-$C_6H_4SMe)_2$ (L2)**

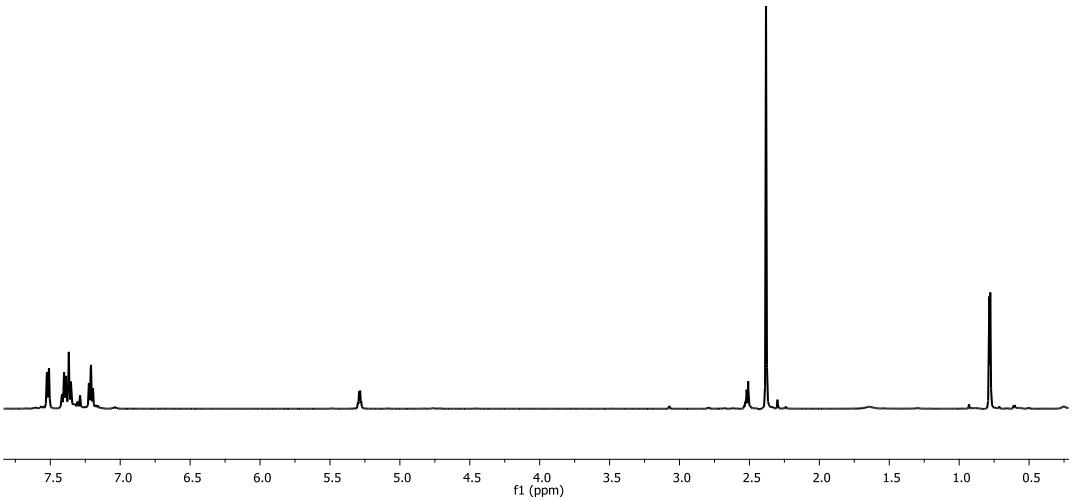

Figure 2. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

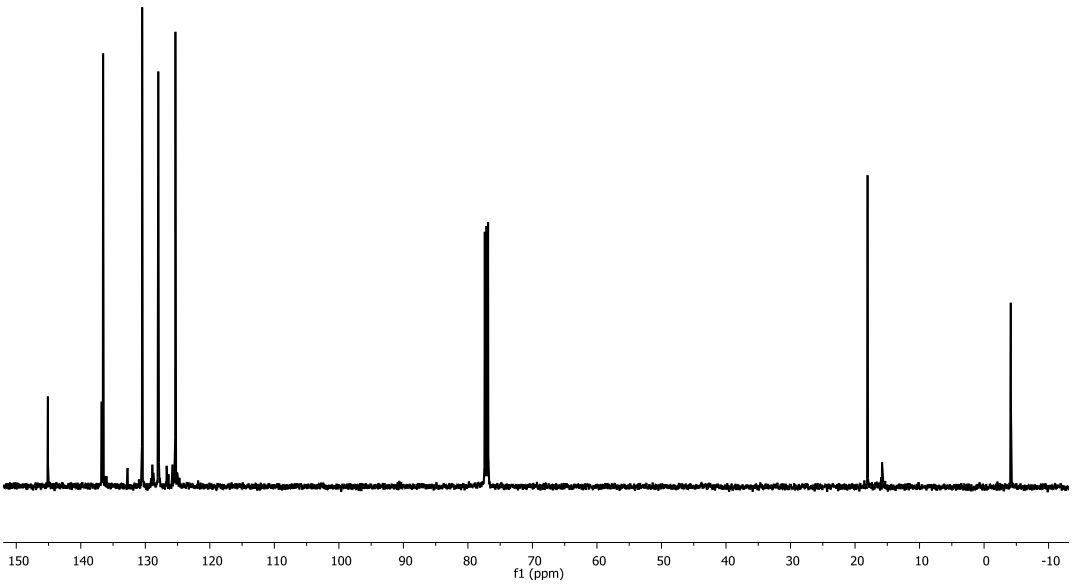

Figure 3. $^{13}C\{^{1}H\}$ NMR spectrum of **L2** in $CDCl_3$.

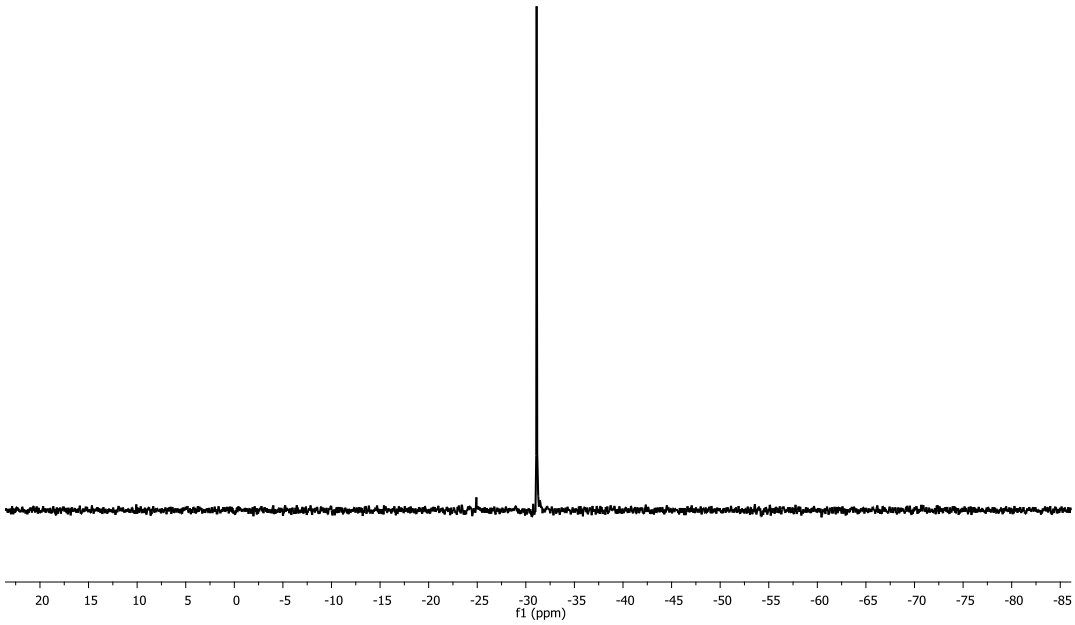

Figure 4. $^{29}Si\{^{1}H\}$ NMR spectrum of **L2** in $CDCl_3$.

- **Ligand $SiMe_2(o\text{-}C_6H_4SMe)_2$ (L3)**

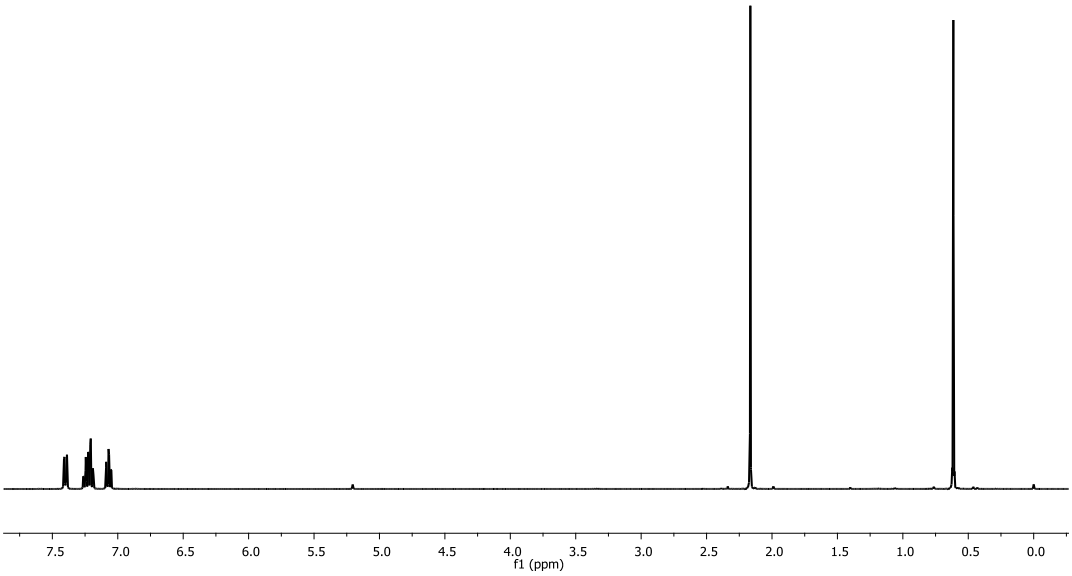

Figure 5. ^1H NMR spectrum of **L3** in CD_2Cl_2.

- **Compound [RhCl(SiMe$_2$(*o*-C$_6$H$_4$SMe))$_2$]$_2$ (1)**

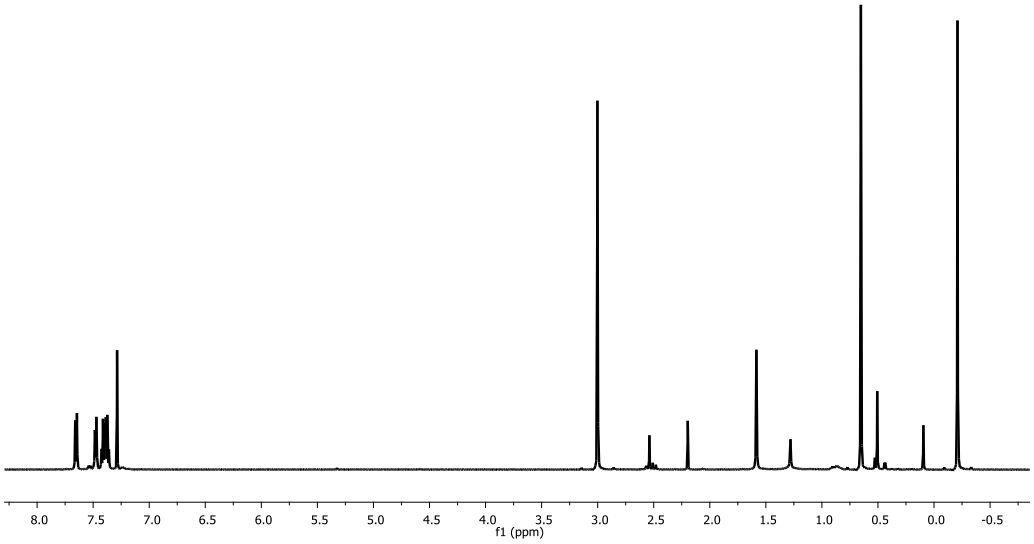

Figure 6. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

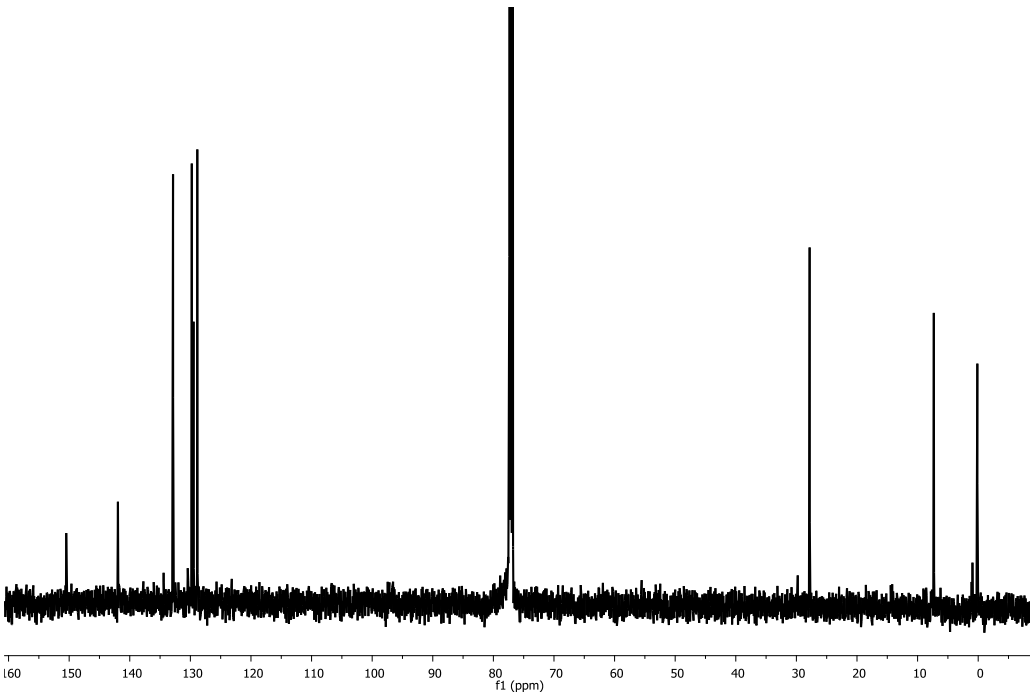

Figure 7. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.

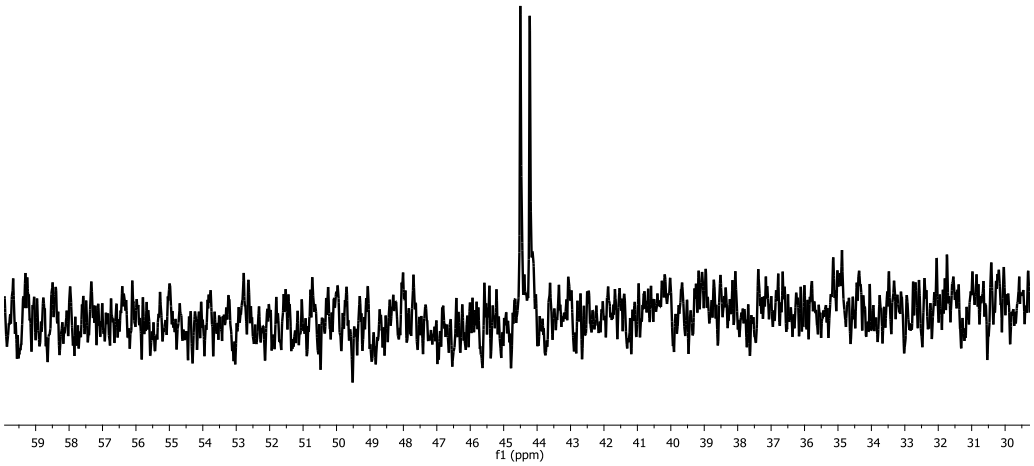

Figure 8. $^{29}Si\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.

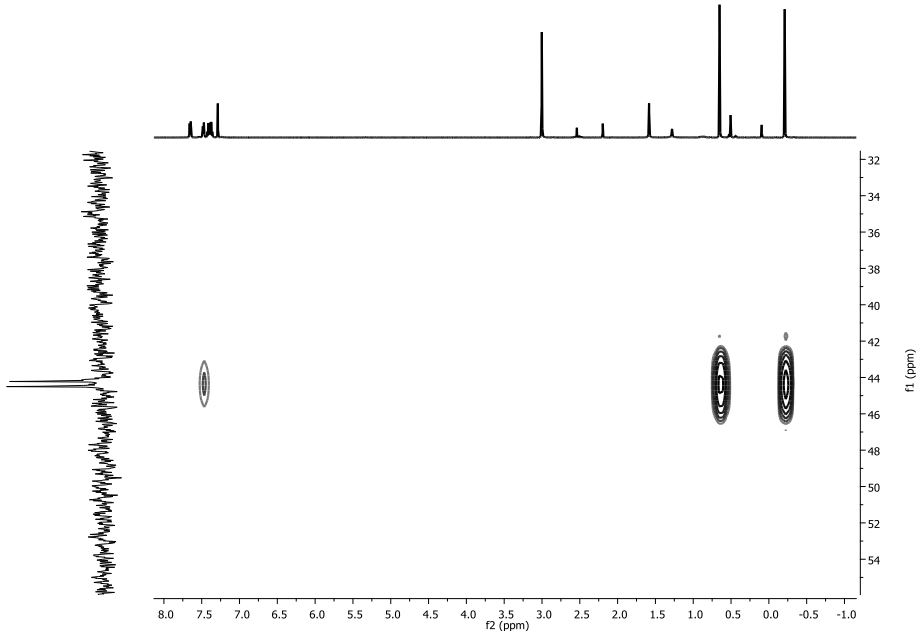

Figure 9. $^{29}Si\{^{1}H\}$-^{1}H NMR correlation for compound **1**.

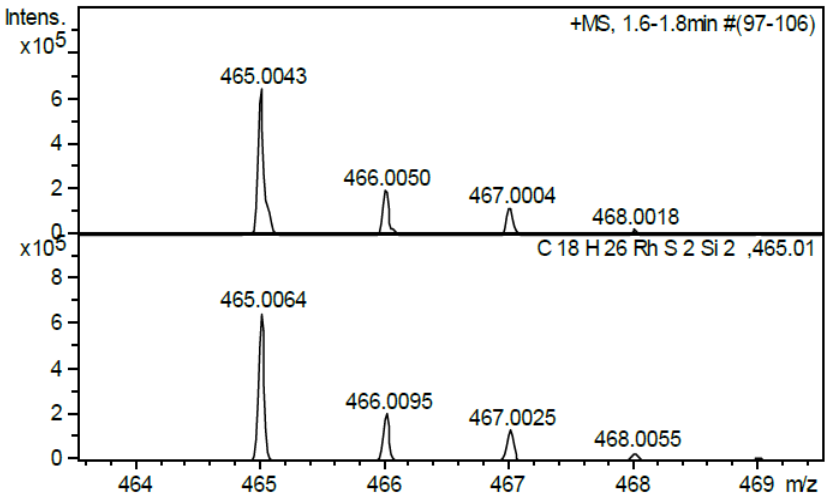

Figure 10. Found (top) and calculated (bottom) ESI-MS of compound **1**.

- **Compound [(cod)Rh(μ-Cl)$_2$Rh(SiMe$_2$(*o*-C$_6$H$_4$SMe))$_2$] (2)**

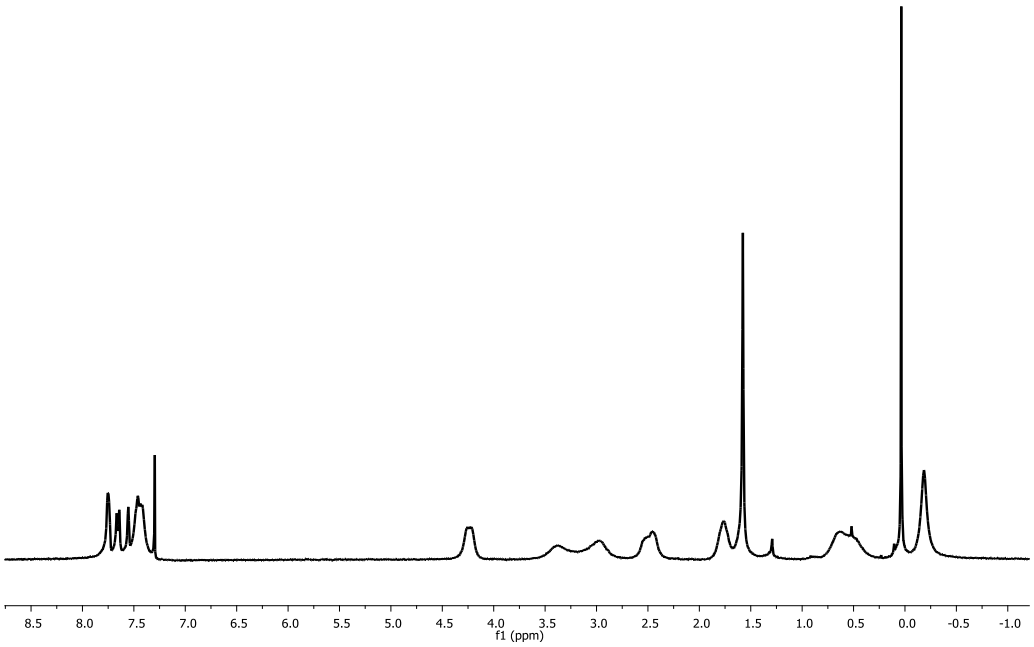

Figure 11. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

- **Compound [RhCl(η^3-cyclooctenyl)(SiMe(*o*-$C_6H_4SMe)_2$)] (3)**

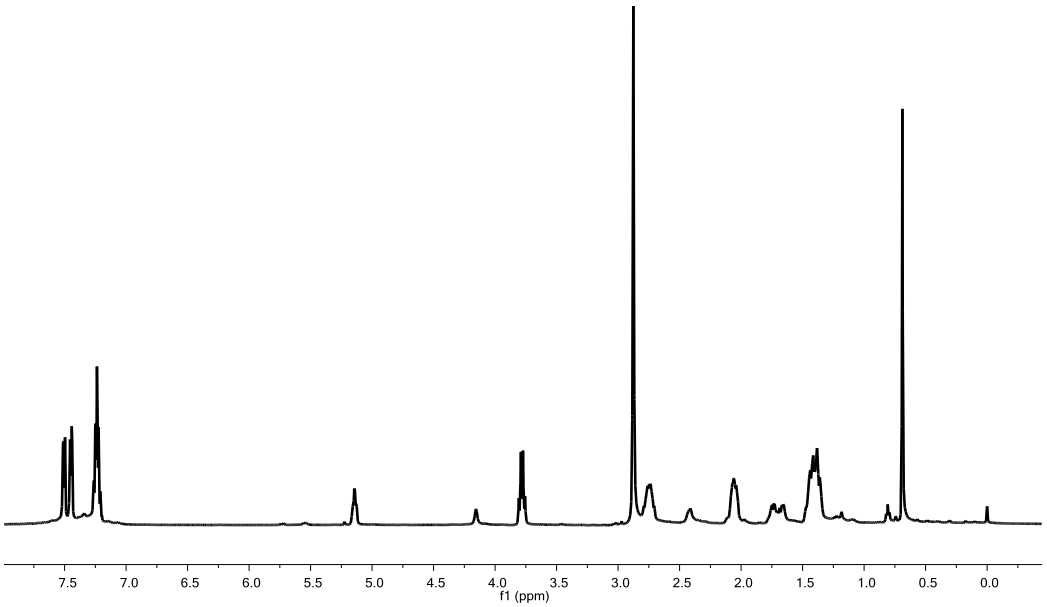

Figure 12. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

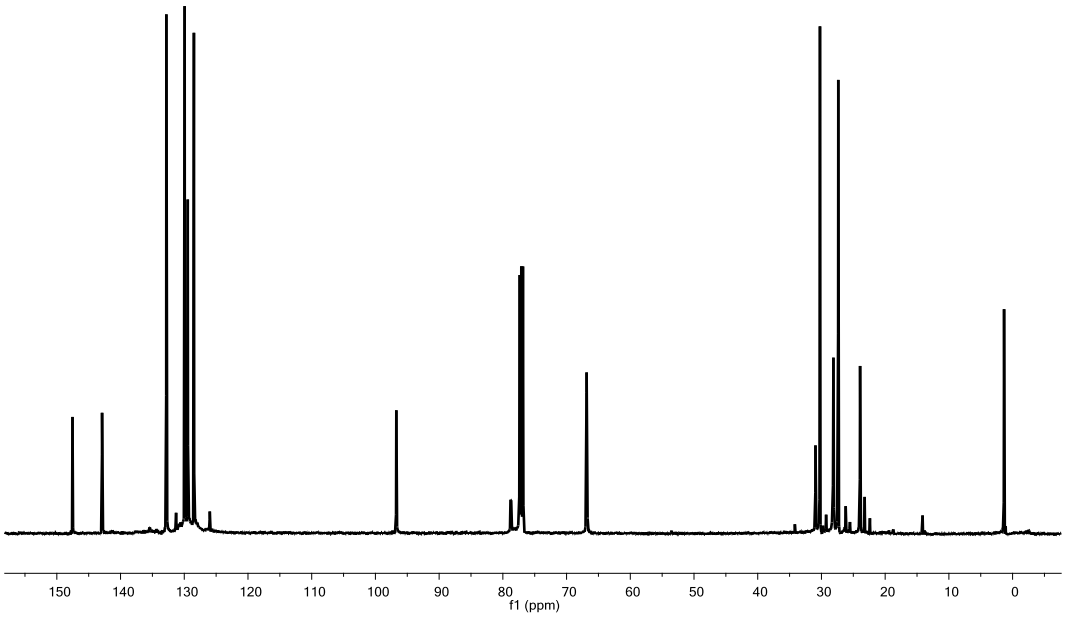

Figure 13. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

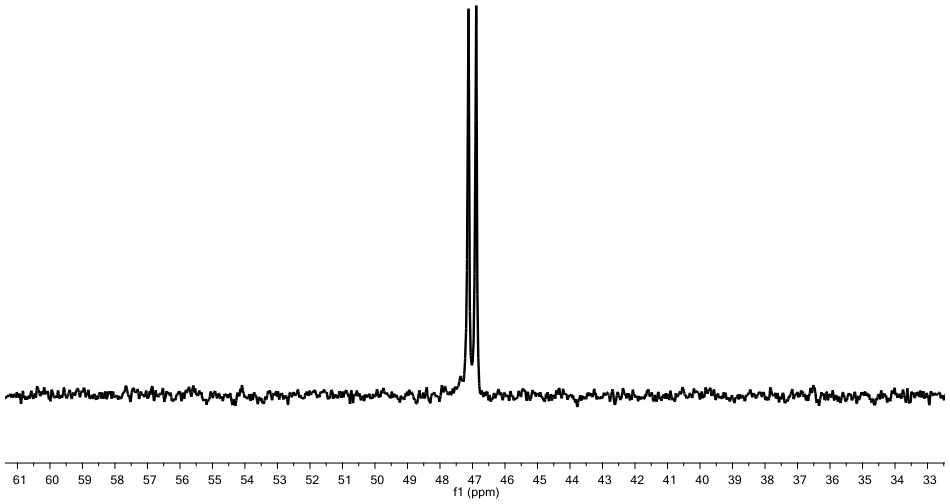

Figure 14. $^{29}Si\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$.

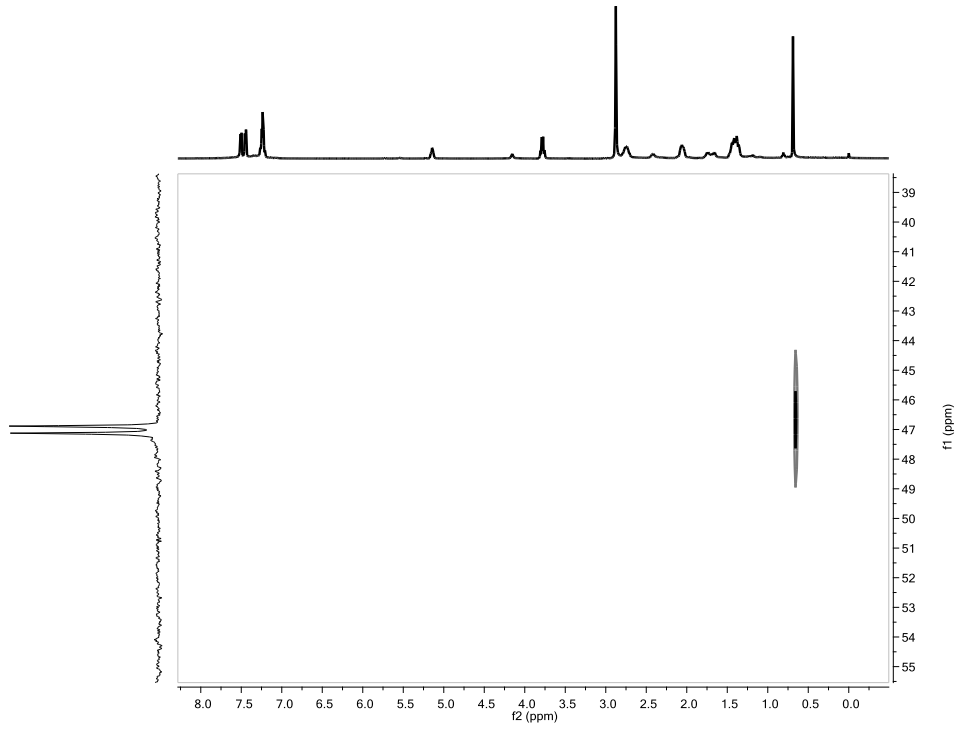

Figure 15. $^{29}Si\{^{1}H\}$ - ^{1}H NMR correlation for compound **3**.

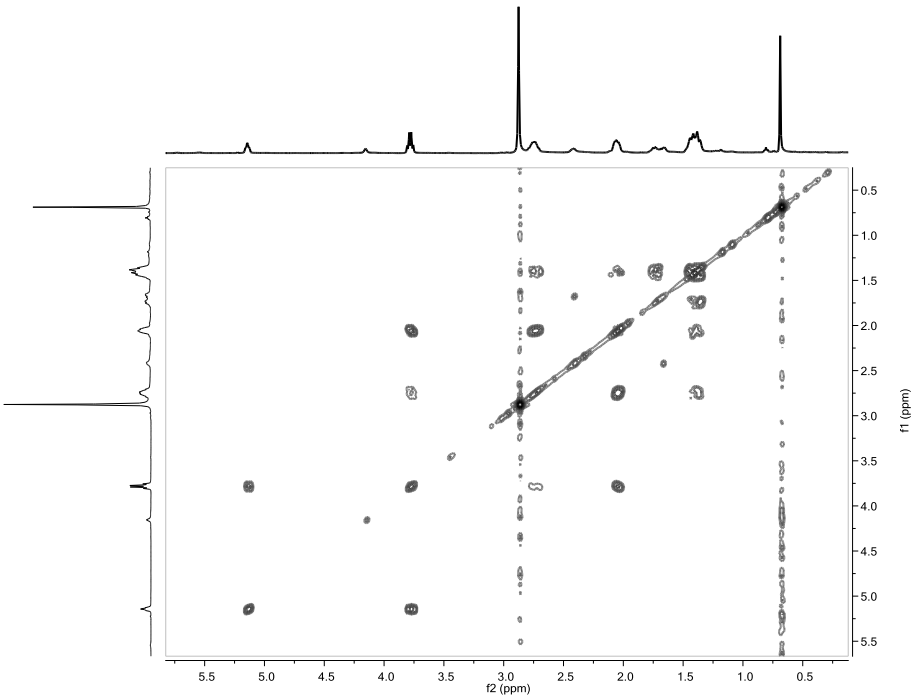

Figure 16. ^{1}H - ^{1}H NMR correlation for compound **3**.

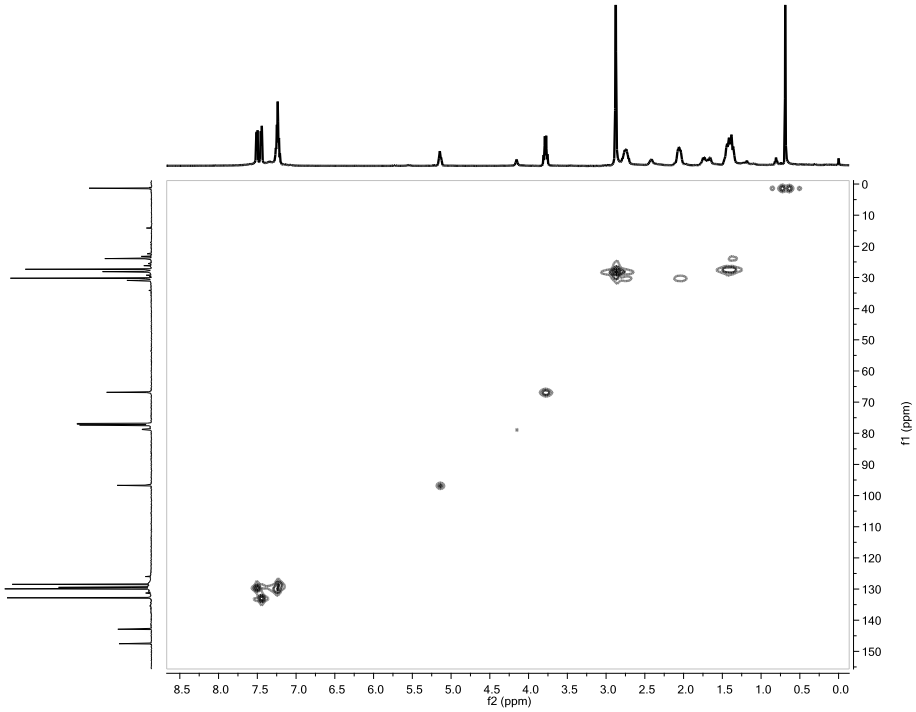

Figure 17. ^{1}H – $^{13}C\{^{1}H\}$ NMR correlation for compound **3**.

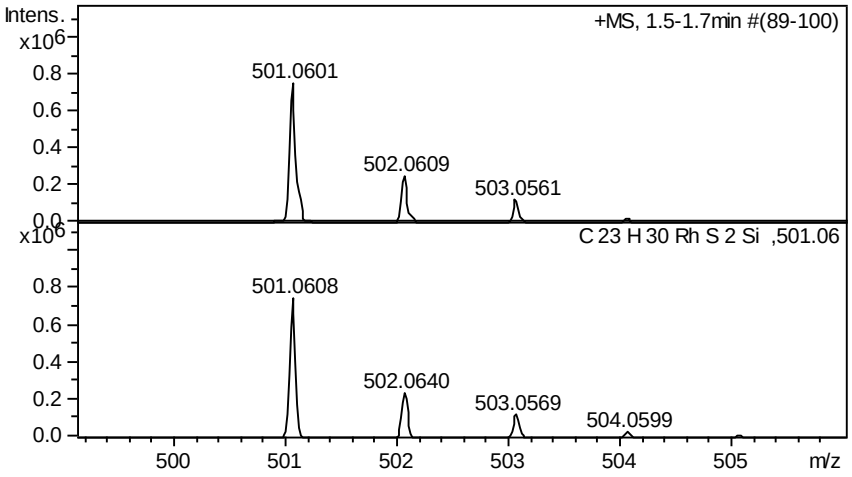

Figure 18. Found (top) and calculated (bottom) ESI-MS of compound **3**.

- **Compound [Rh(η^3-cyclooctenyl)(SiMe(*o*-$C_6H_4SMe)_2$)]BAr^F_4 (4)**

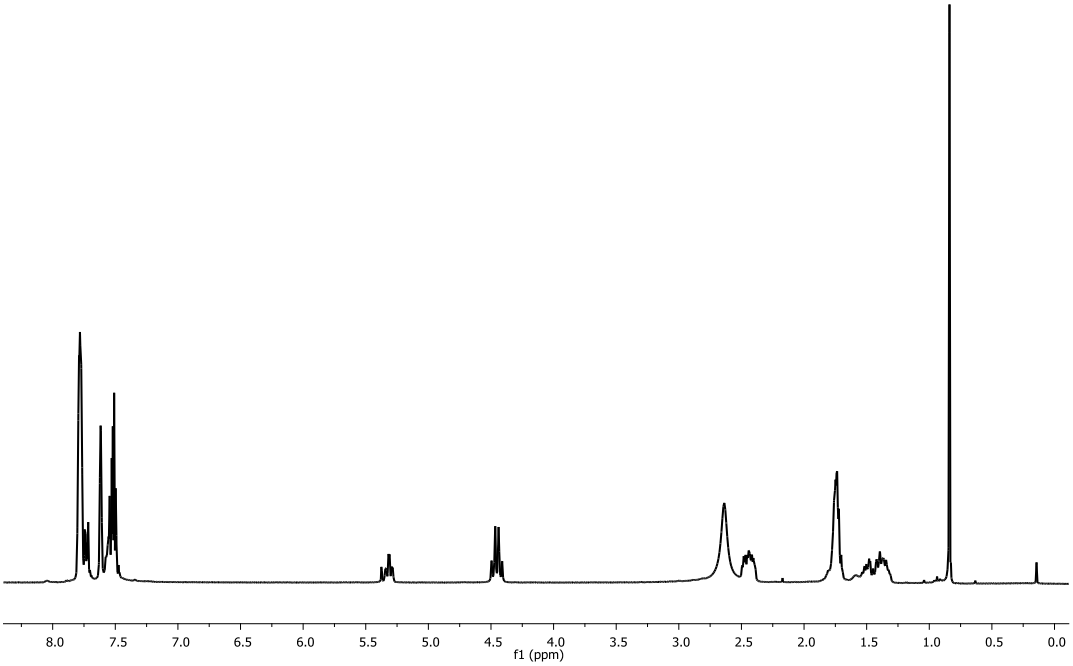

Figure 19. ^{1}H NMR spectrum of compound **4** in CD_2Cl_2.

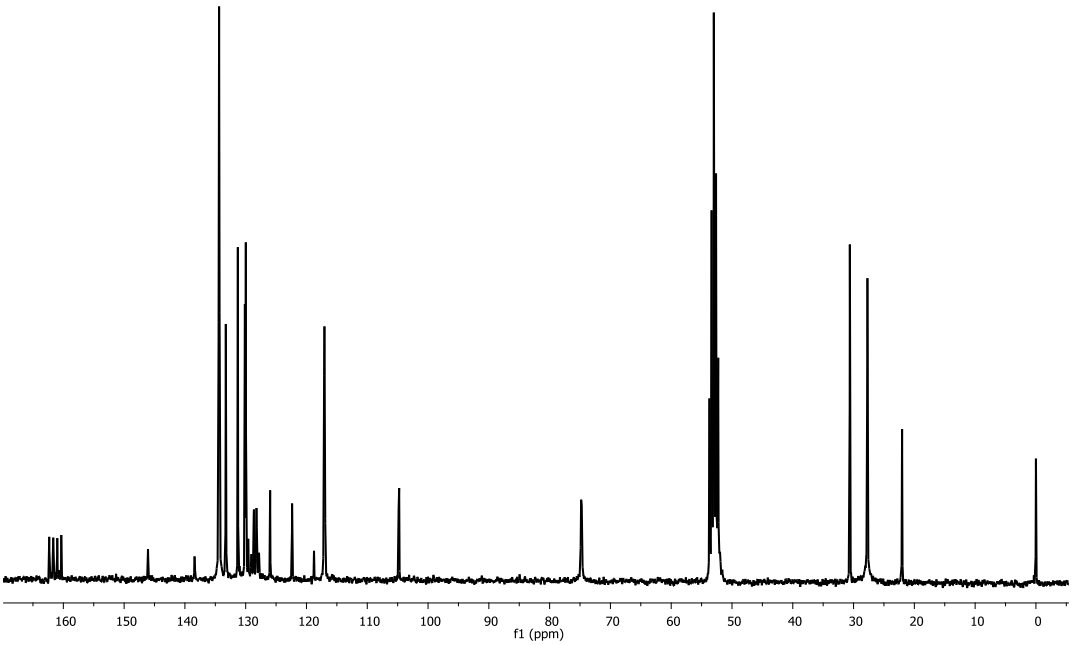

Figure 20. $^{13}C\{^1H\}$ NMR spectrum of compound **4** in CD_2Cl_2.

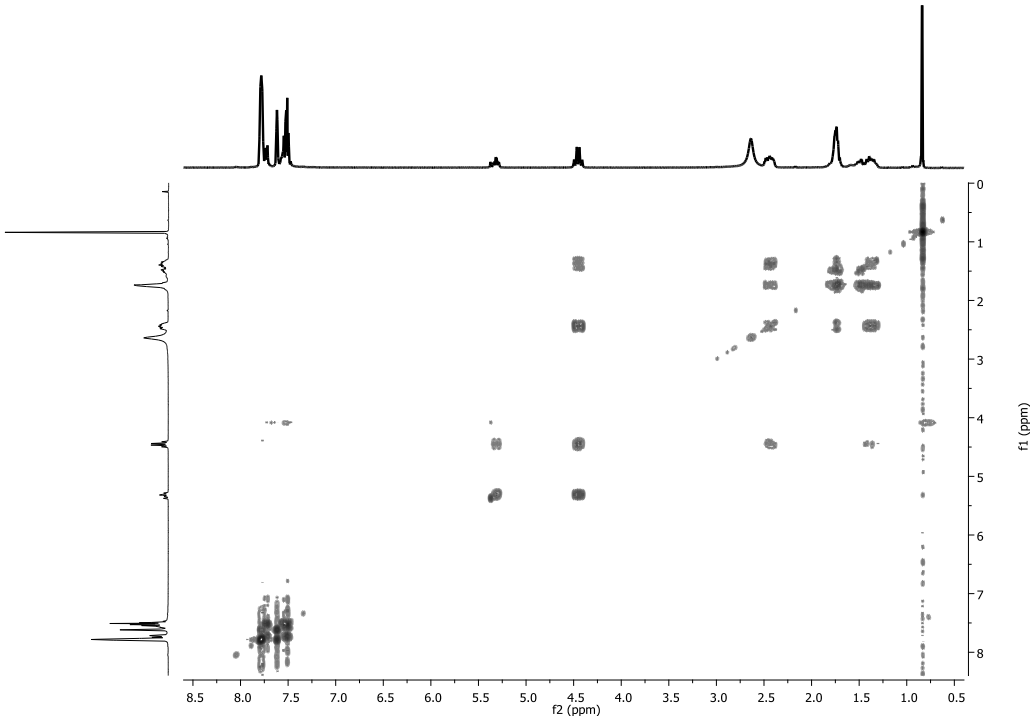

Figure 21. $^{1}H - {}^{1}H$ NMR correlation for compound **4**.

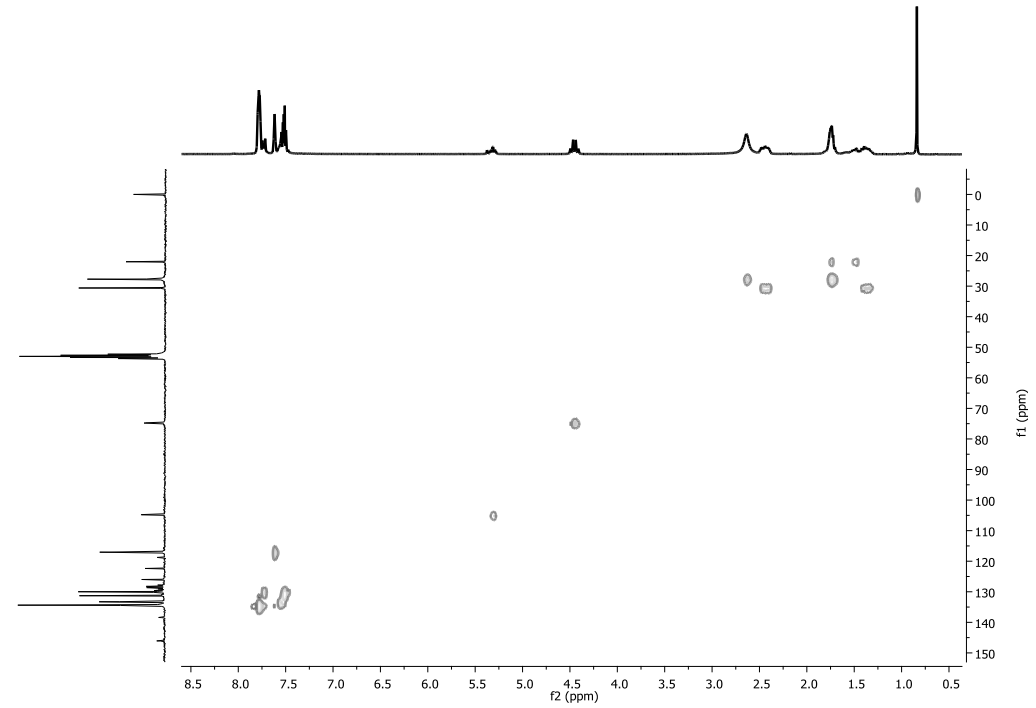

Figure 22. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **4**.

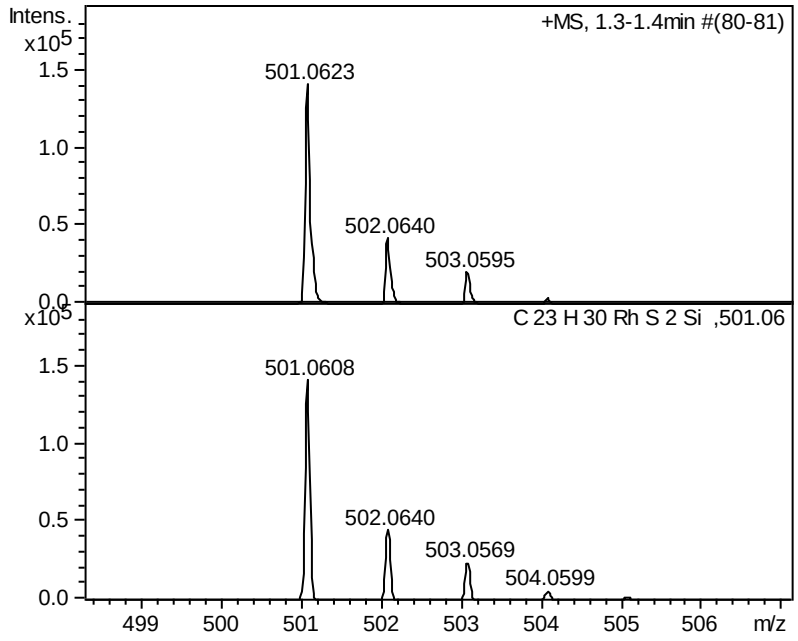

Figure 23. Found (top) and calculated (bottom) ESI-MS of compound **4**.

- **Compound [RhClH(SiMe(*o*-$C_6H_4SMe)_2$)(PPh_3)] (5)**

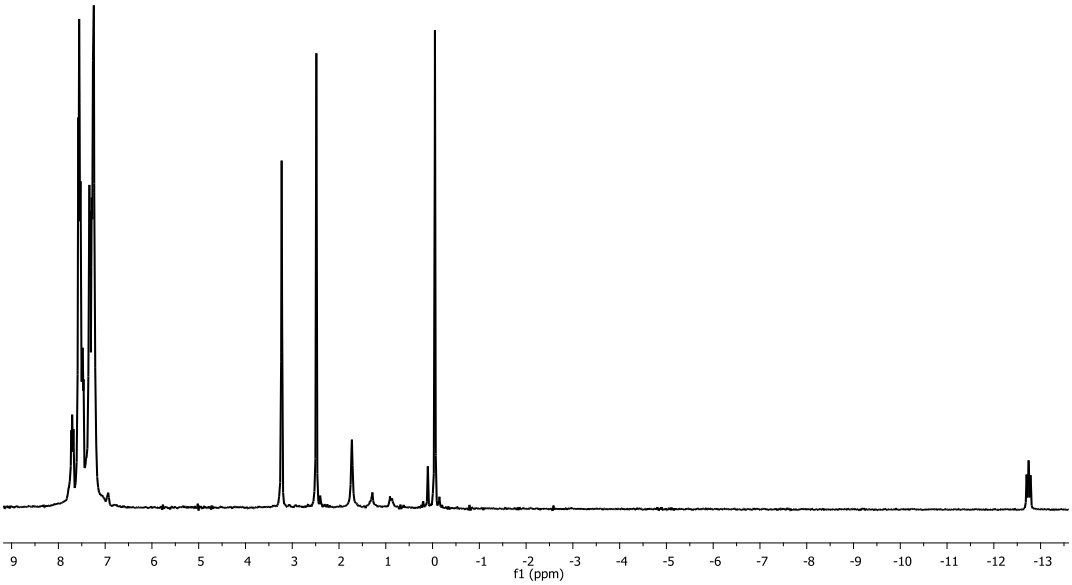

Figure 24. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

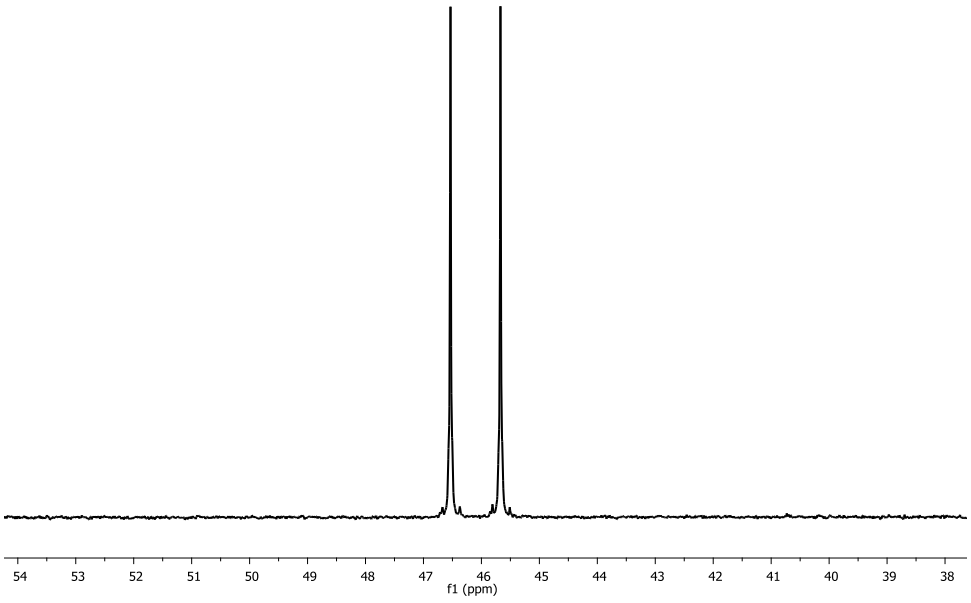

Figure 25. $^{31}P\{^{1}H\}$ NMR spectrum for compound **5** in $CDCl_3$.

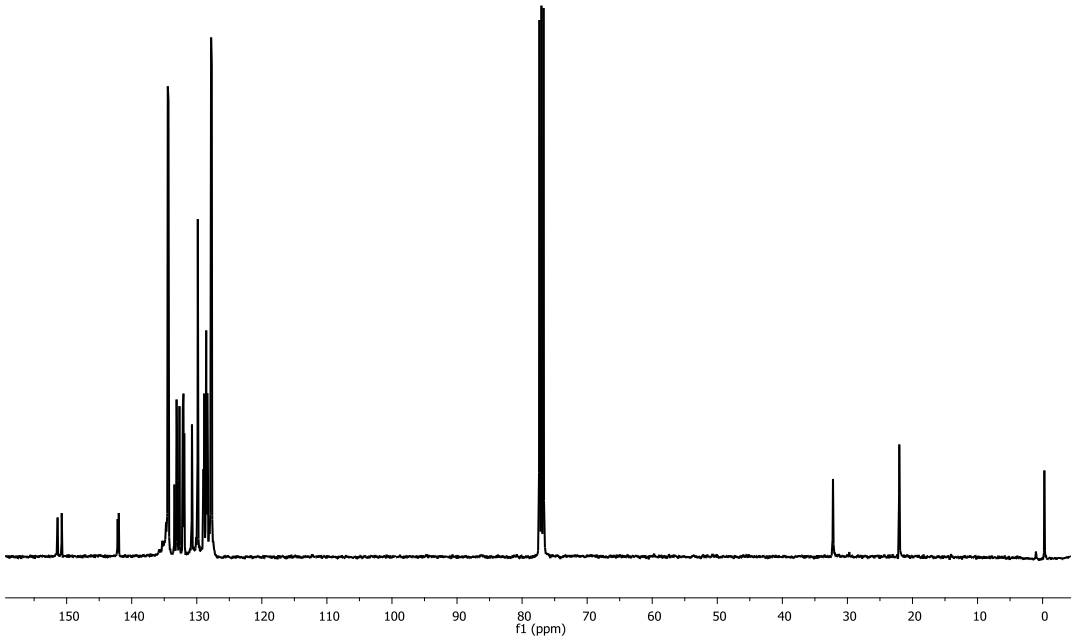

Figure 26. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$.

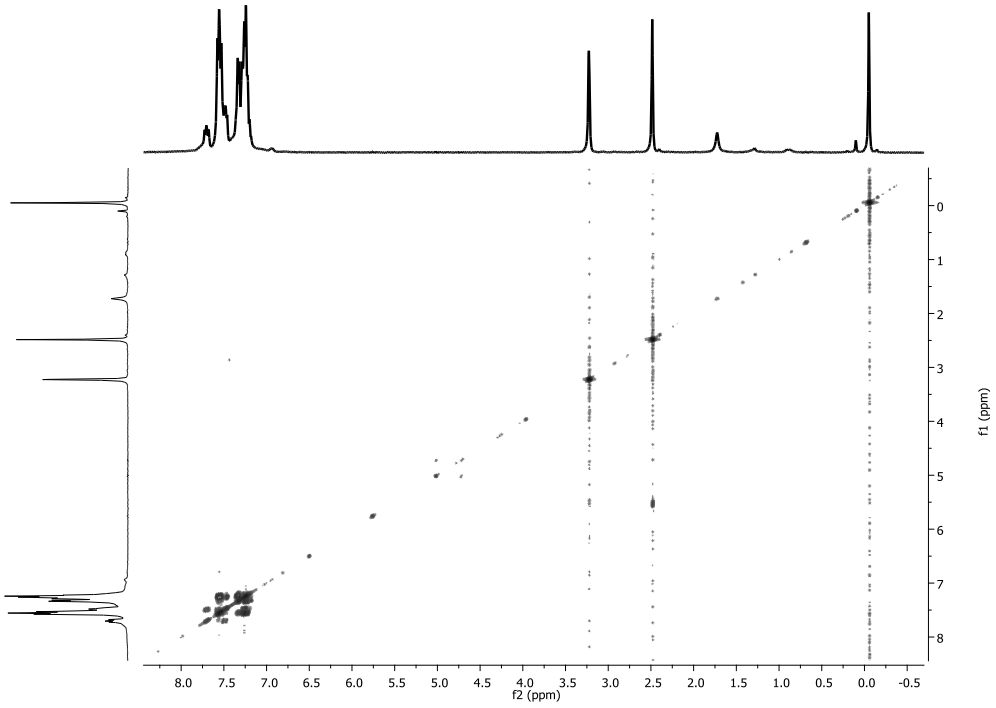

Figure 27. $^{1}H - {}^{1}H$ NMR correlation for compound **5**.

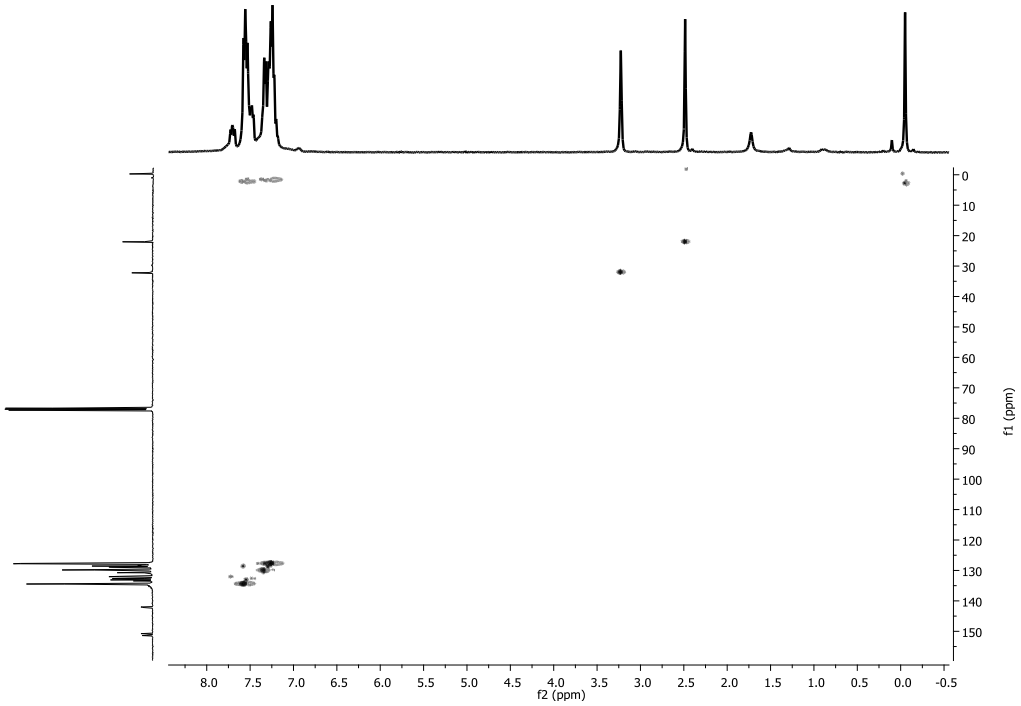

Figure 28. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **5**.

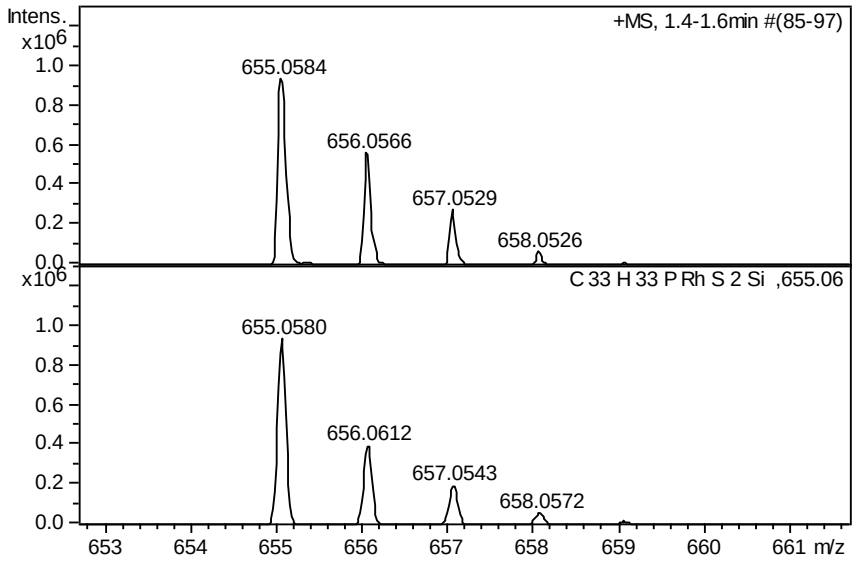

Figure 29. Found (top) and calculated (bottom) ESI-MS of compound **5**.

- **Compound [RhH(SiMe(*o*-$C_6H_4SMe)_2$)(PPh_3)]BAr^F_4 (6)**

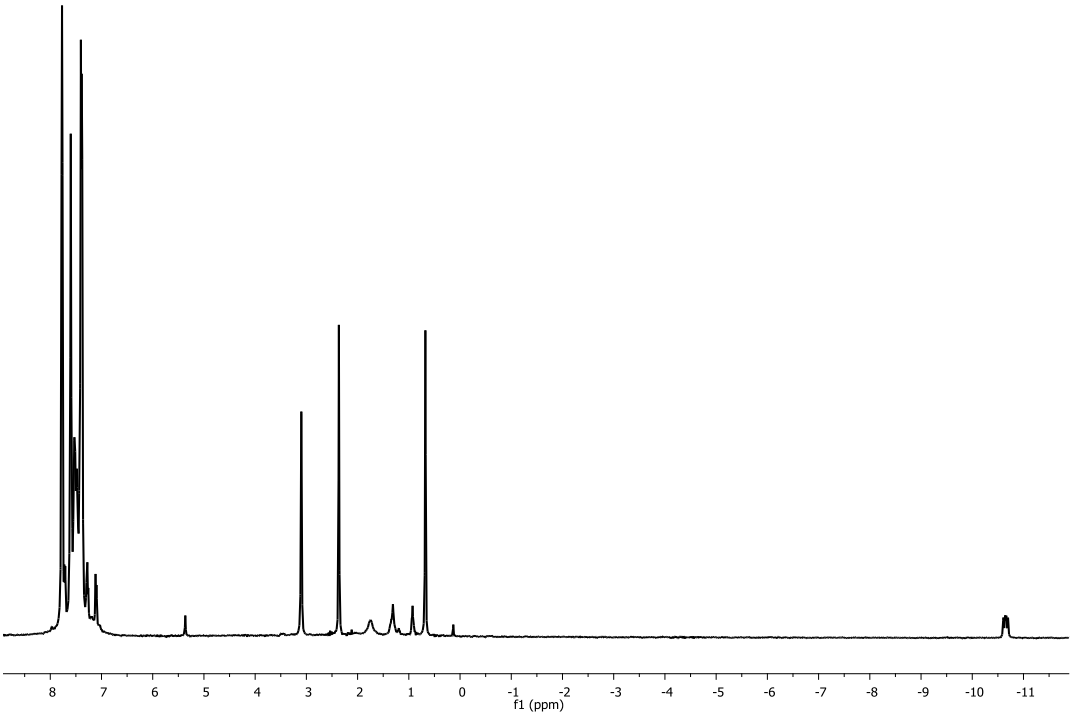

Figure 30. ^1H NMR spectrum of compound **6** in CD_2Cl_2.

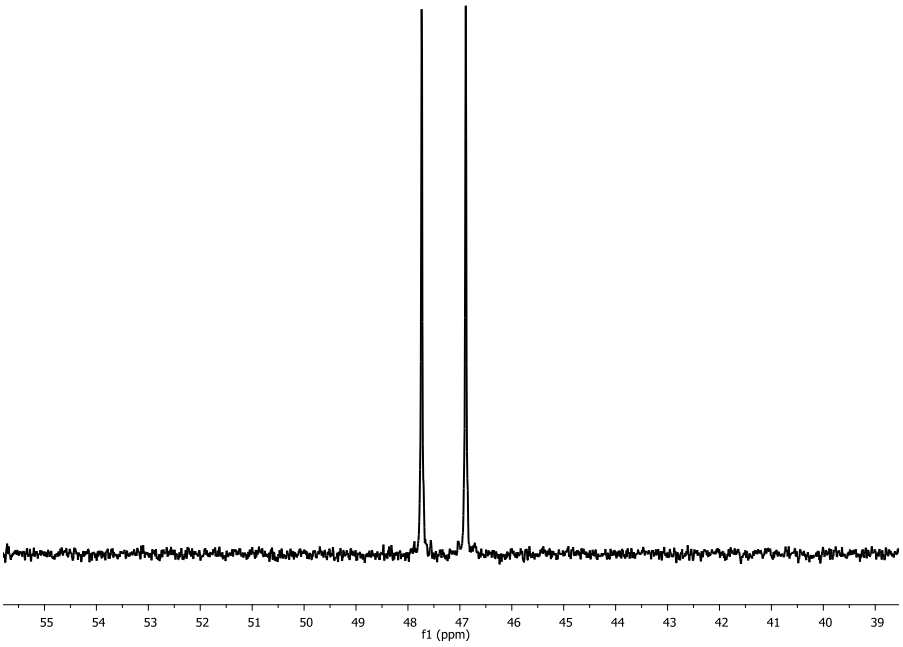

Figure 31. $^{31}P\{^1H\}$ NMR spectrum for compound **6** in CD_2Cl_2.

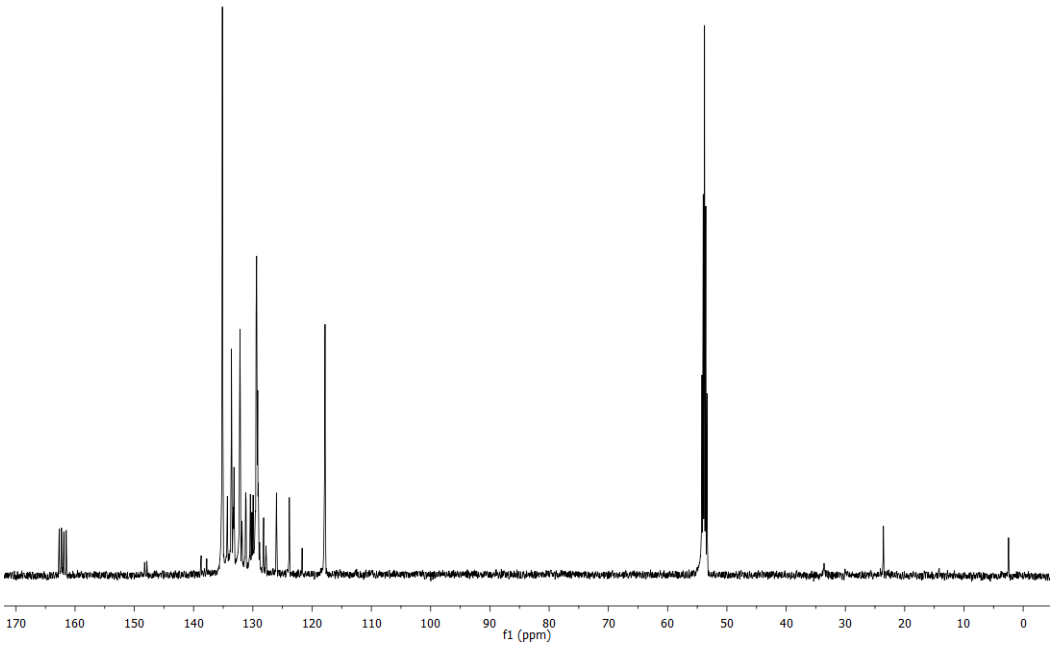

Figure 32. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **6** in CD_2Cl_2.

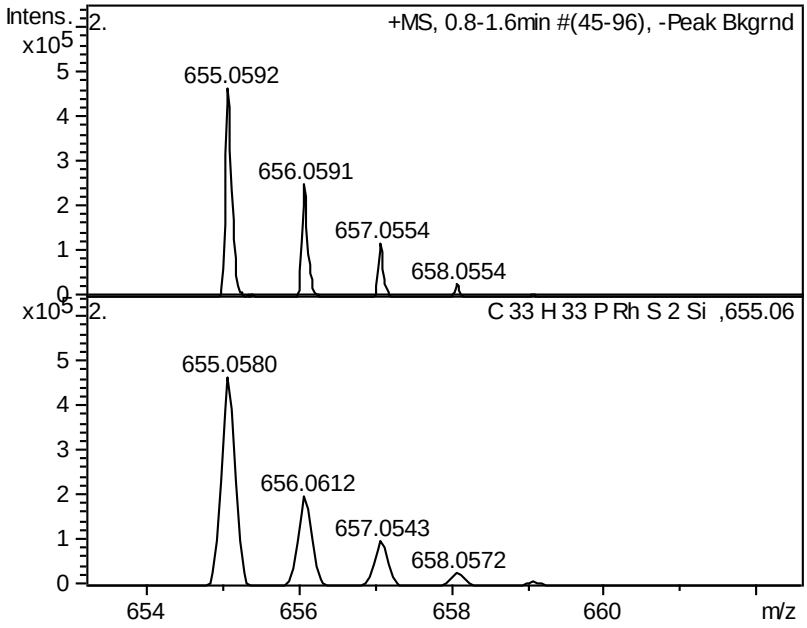

Figure 33. Found (top) and calculated (bottom) ESI-MS of compound **6**.

- **Compound [IrCl(η^3-cyclooctenyl)(SiMe(*o*-$C_6H_4SMe)_2$)] (7)**

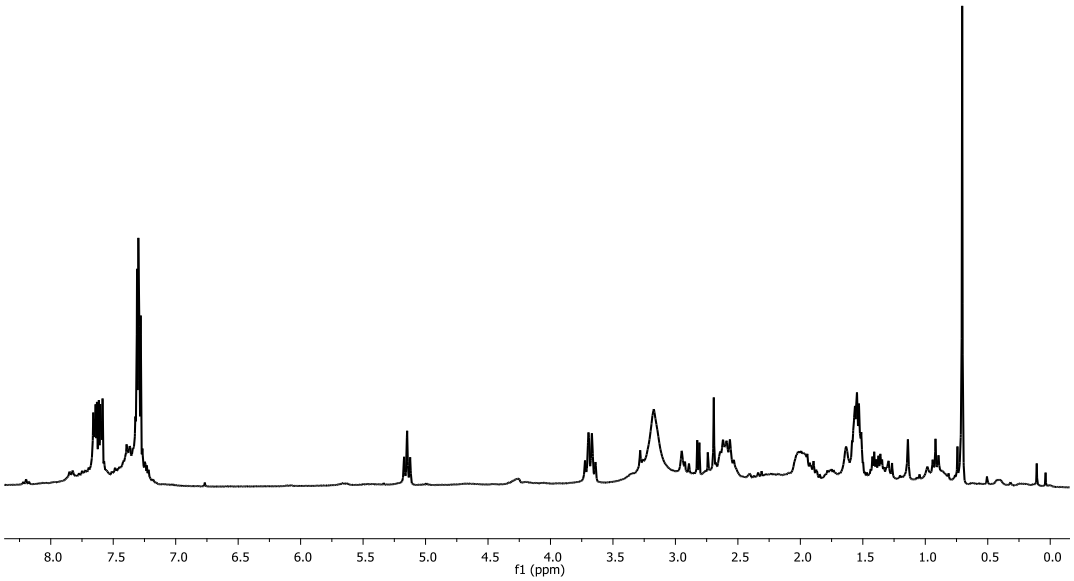

Figure 34. ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

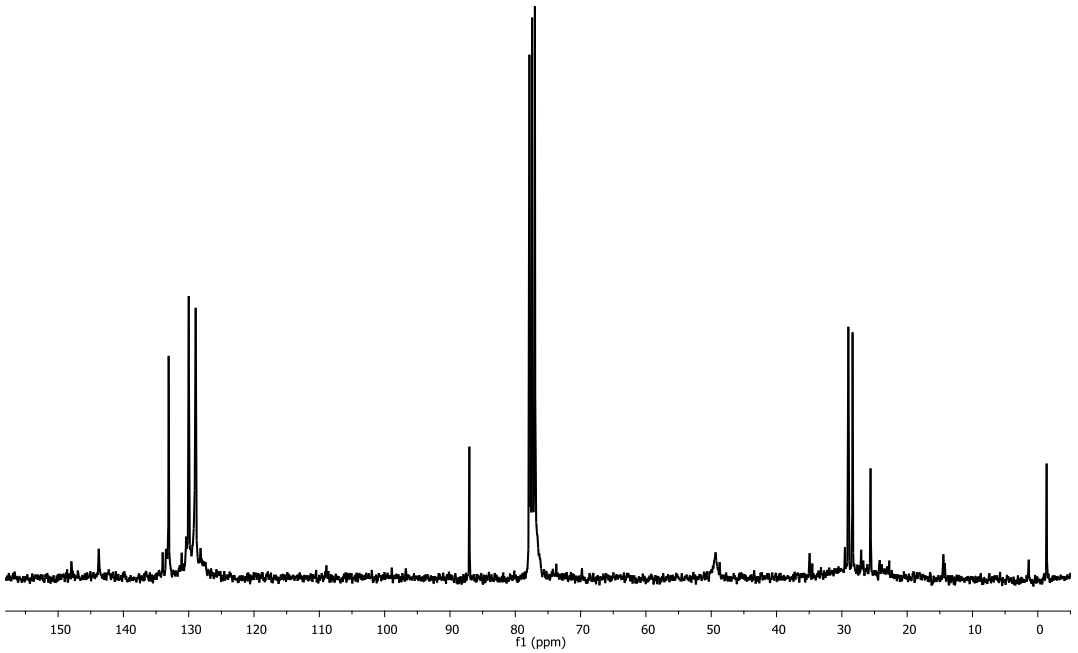

Figure 35. $^{13}C\{^1H\}$ NMR spectrum of compound **7** in $CDCl_3$.

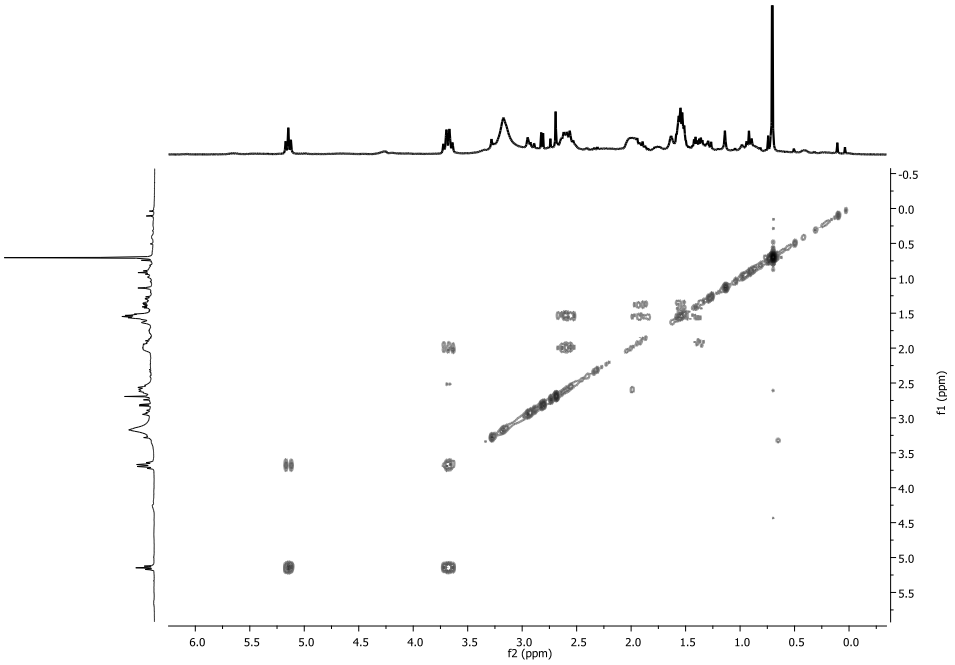

Figure 36. ^{1}H - ^{1}H NMR correlation for compound **7**.

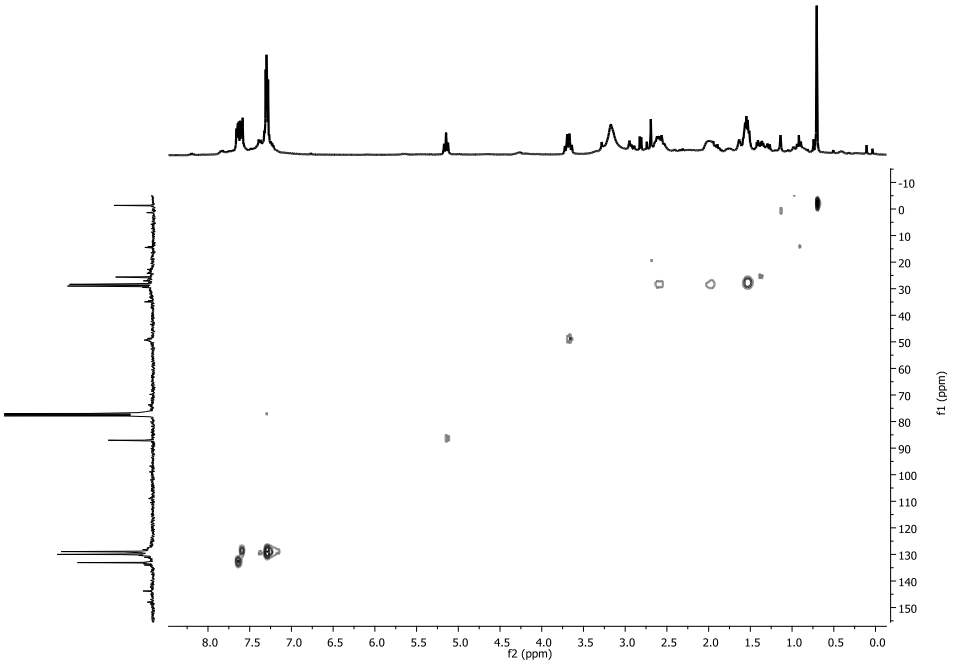

Figure 37. ^{1}H – $^{13}C\{^{1}H\}$ NMR correlation for compound **7**.

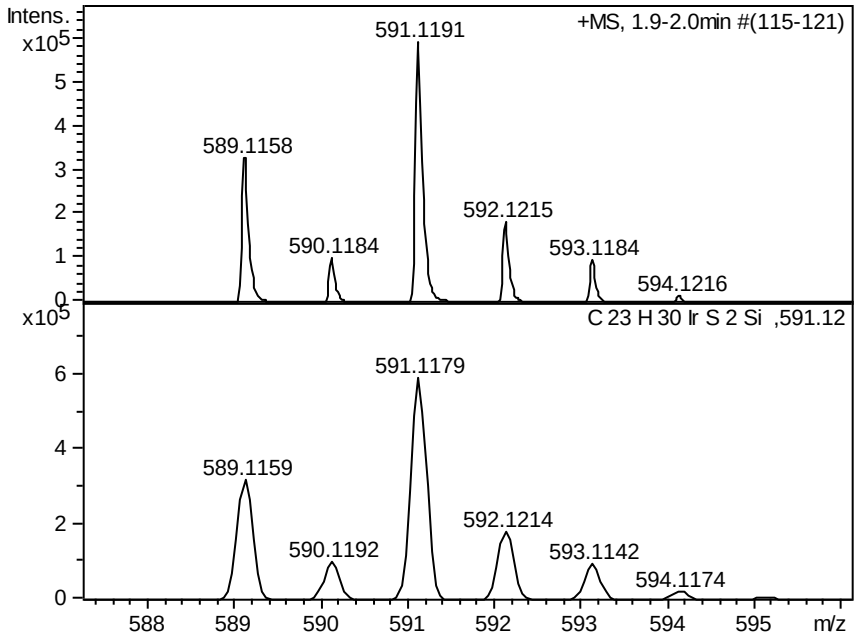

Figure 38. Found (top) and calculated (bottom) ESI-MS of compound **7**.

- **Compound [Ir(η^3-cyclooctenyl)(SiMe(*o*-$C_6H_4SMe)_2$)]BAr^F_4 (8)**

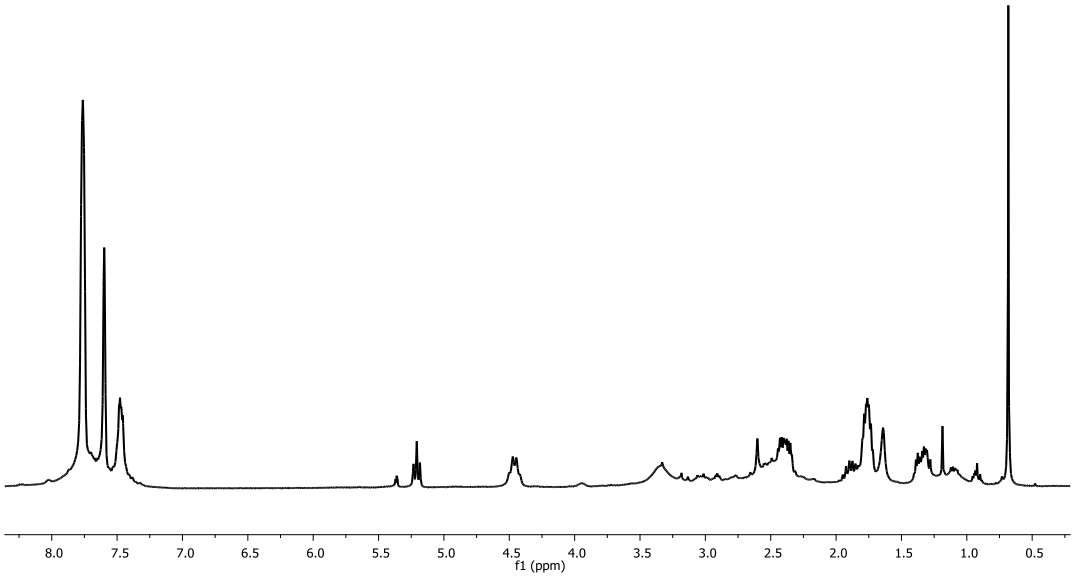

Figure 39. ^1H NMR spectrum of compound **8** in CD_2Cl_2 at room temperature.

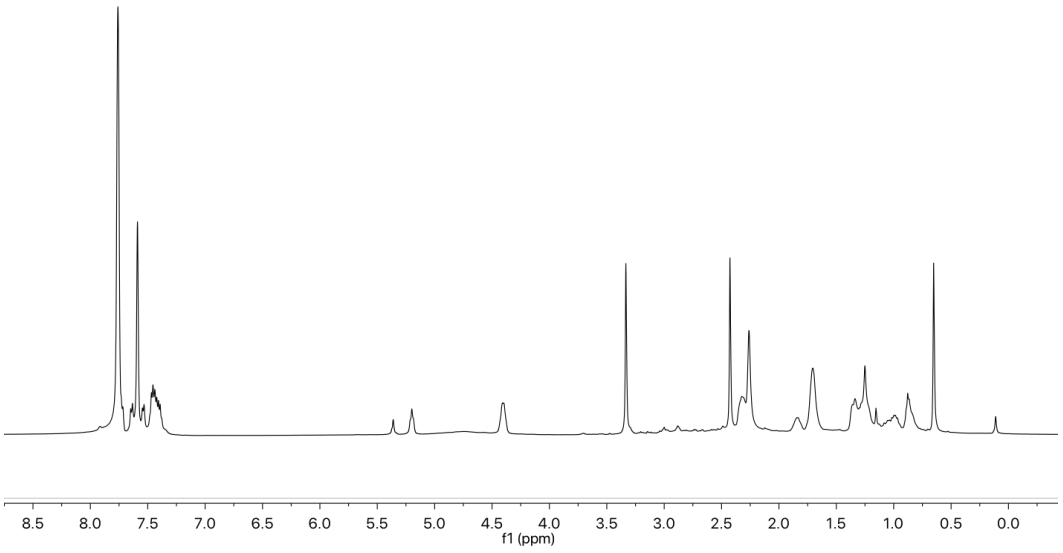

Figure 40. ^1H NMR spectrum of compound **8** in CD_2Cl_2 at 248K.

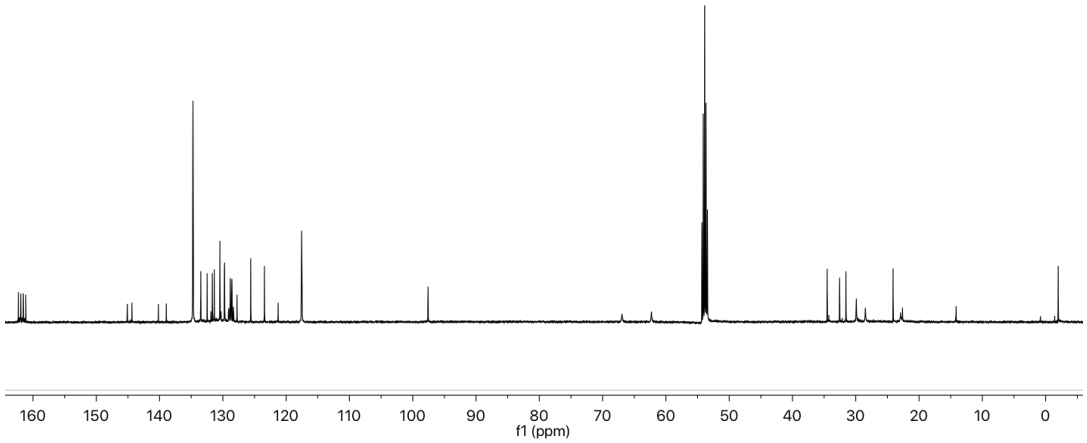

Figure 41. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** in CD_2Cl_2 at 248K.

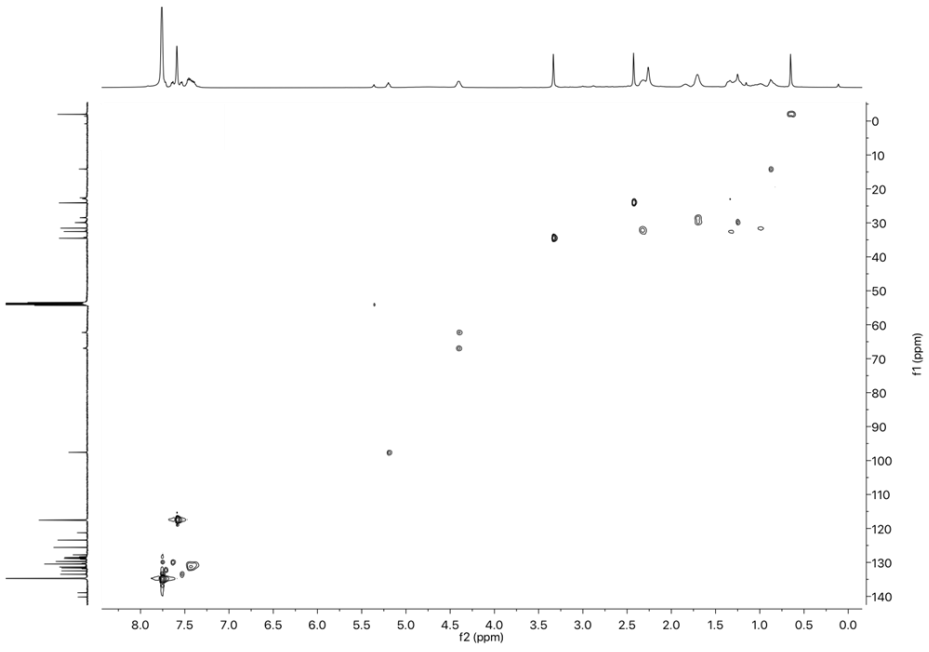

Figure 42. $^{1}H - ^{13}C\{^{1}H\}$ NMR correlation for compound **8** at 248K.

- **Compound [IrH(η^4-cod)(SiMe(*o*-$C_6H_4SMe)_2$)]BAr^F_4 (9)**

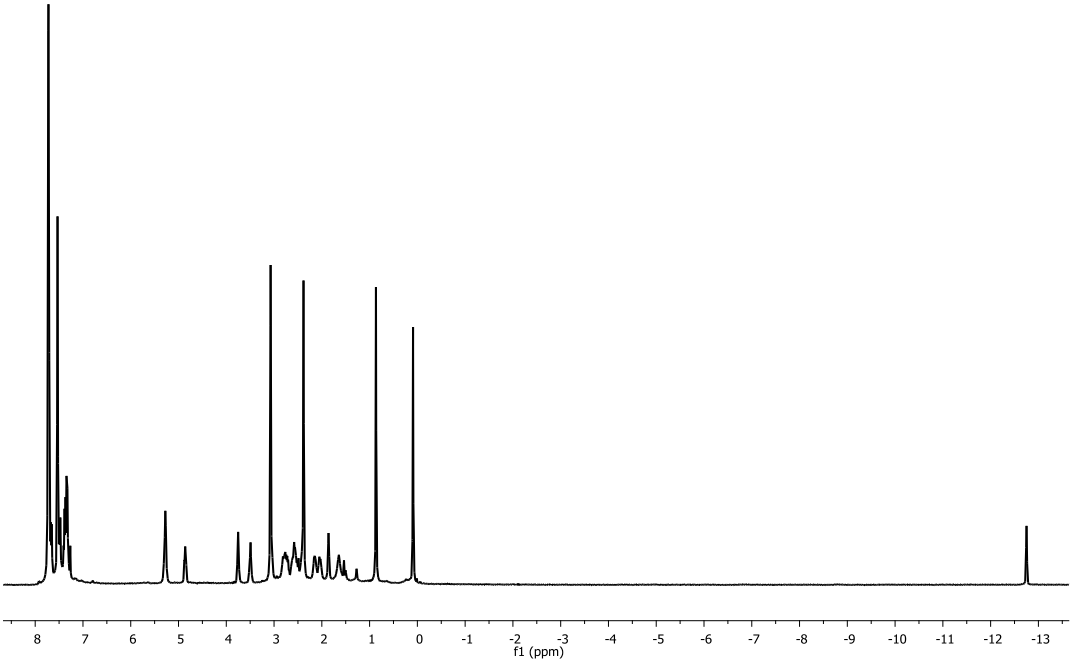

Figure 43. ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

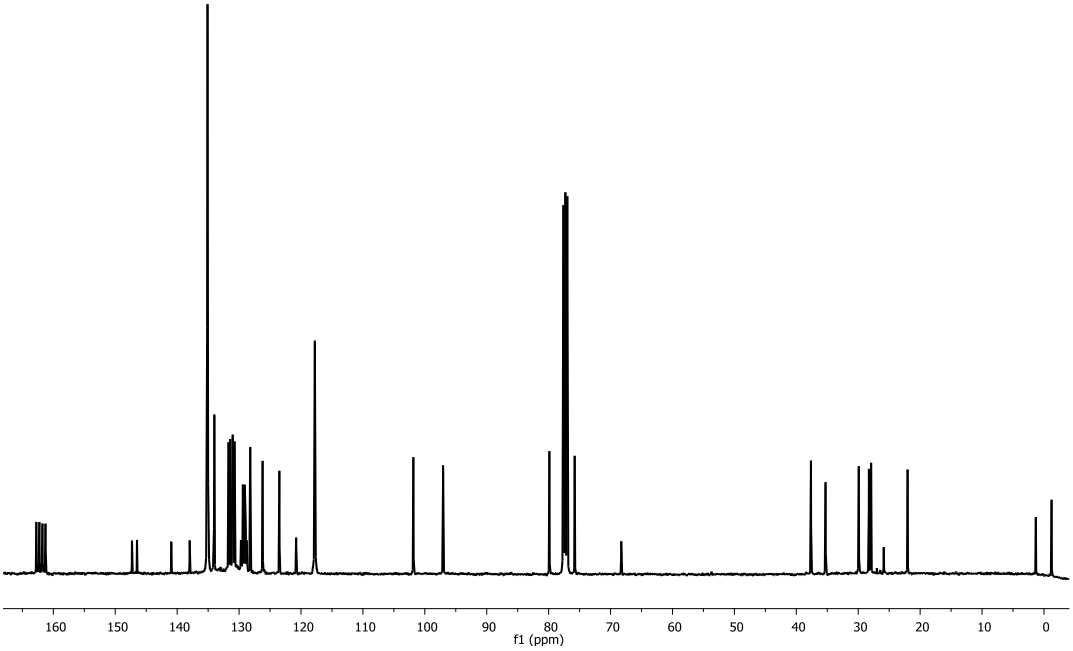

Figure 44. $^{13}C\{^1H\}$ NMR spectrum of compound **9** in $CDCl_3$.

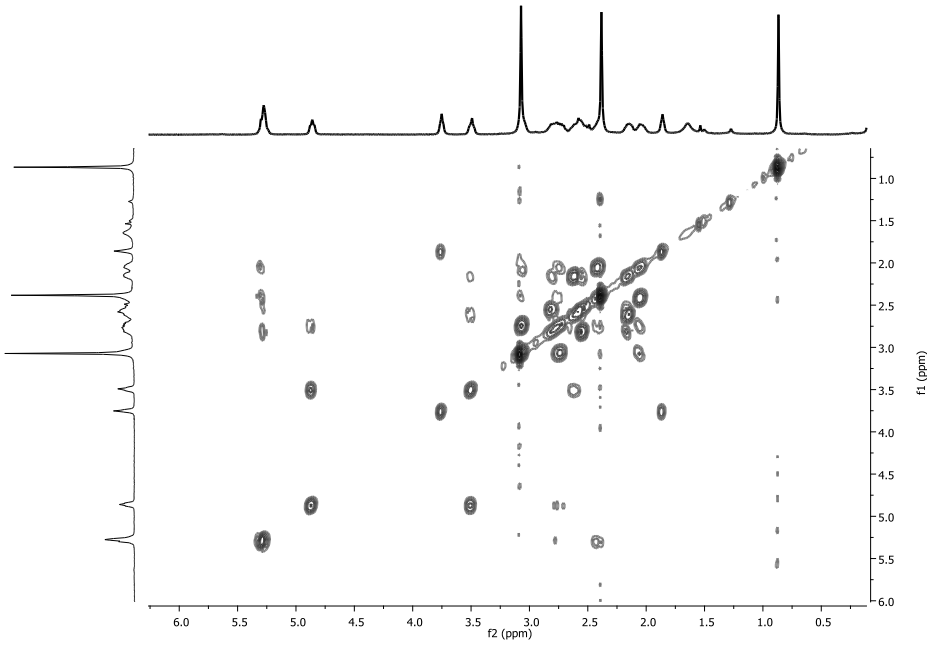

Figure 45. ^{1}H - ^{1}H NMR correlation for compound **9**.

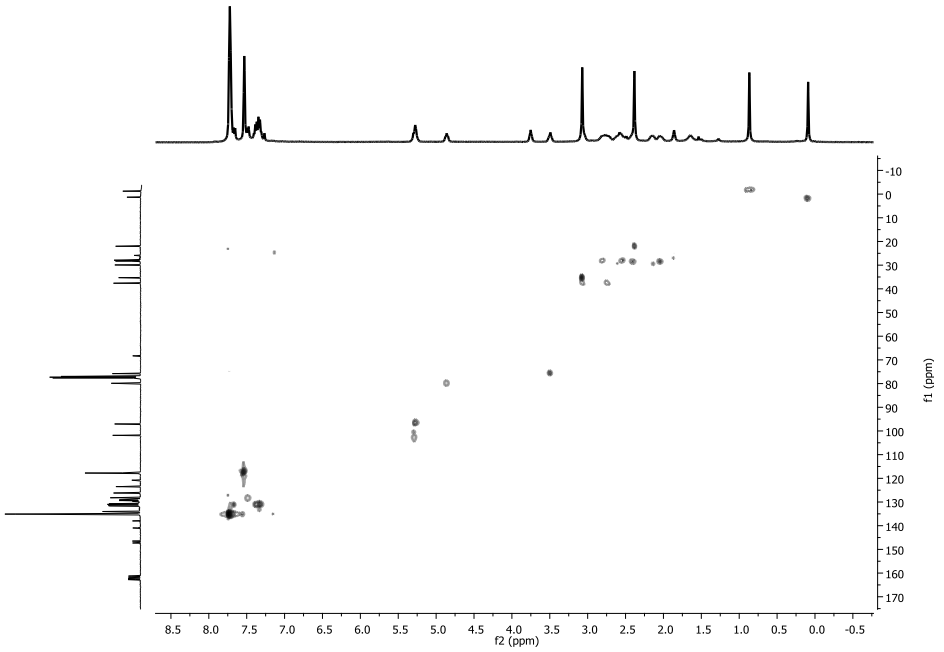

Figure 46. ^{1}H – $^{13}C\{^{1}H\}$ NMR correlation for compound **9**.

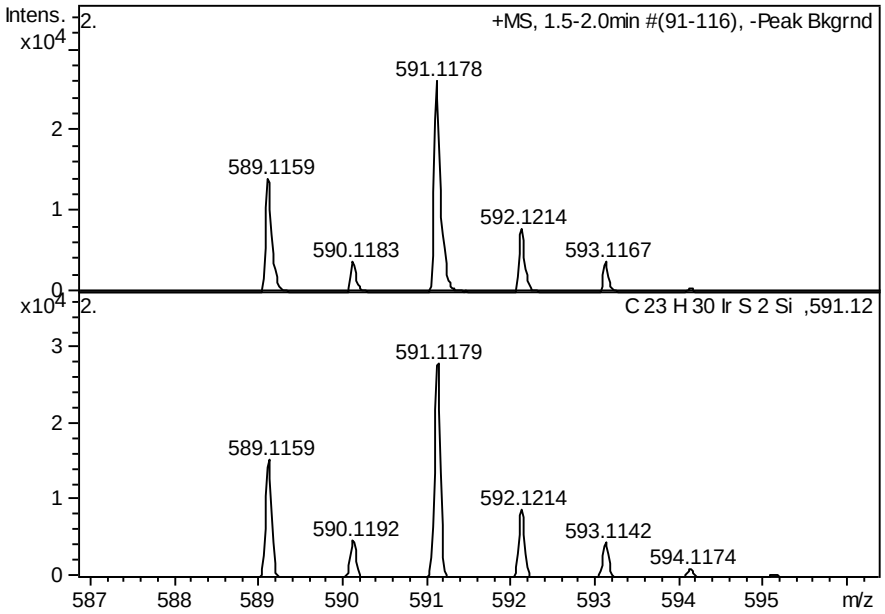

Figure 47. Found (top) and calculated (bottom) ESI-MS of compound **9**.

- **Compound [RhCl(ntyl)(SiMe(*o*-$C_6H_4SMe)_2$)] (10)**

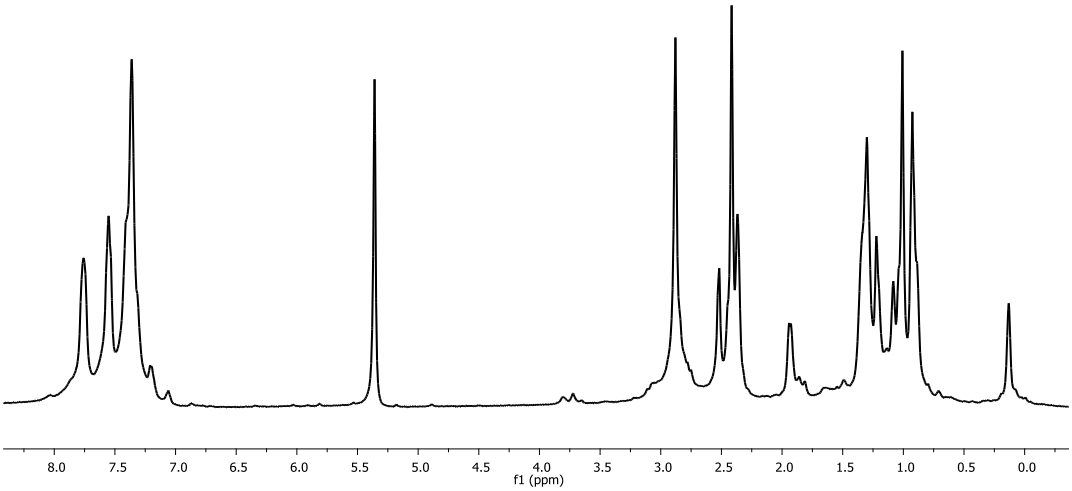

Figure 48. ^{1}H NMR spectrum of compound **10** in CD_2Cl_2.

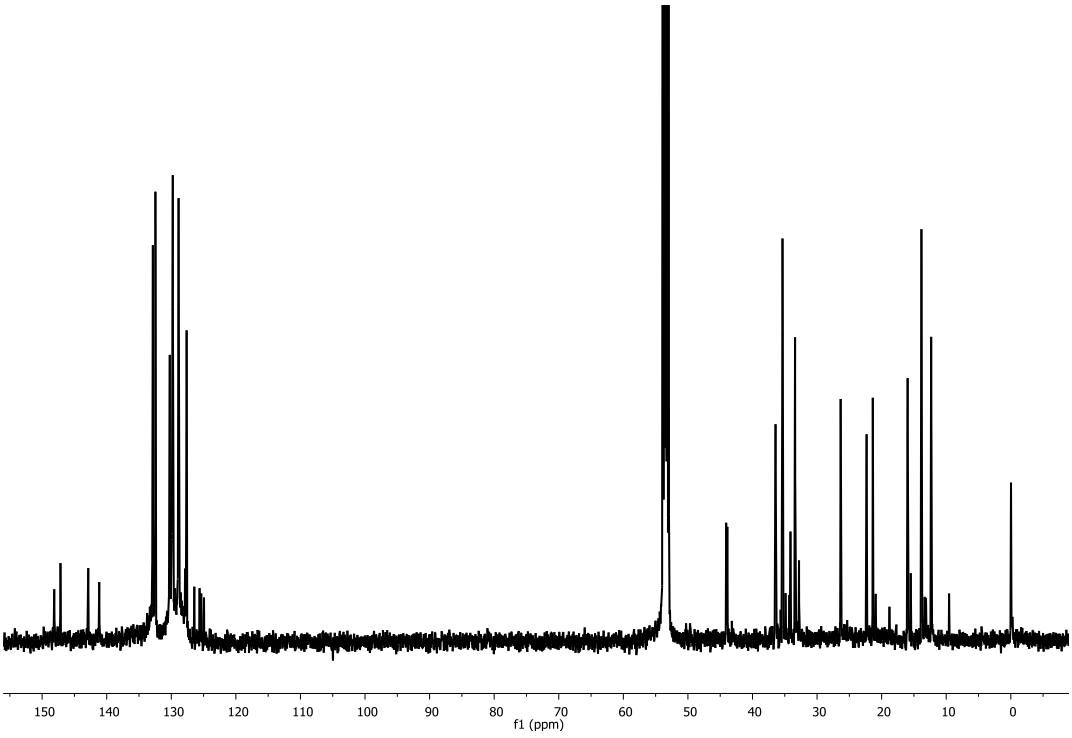

Figure 49. $^{13}C\{^{1}H\}$ NMR spectrum of compound **10** in CD_2Cl_2.

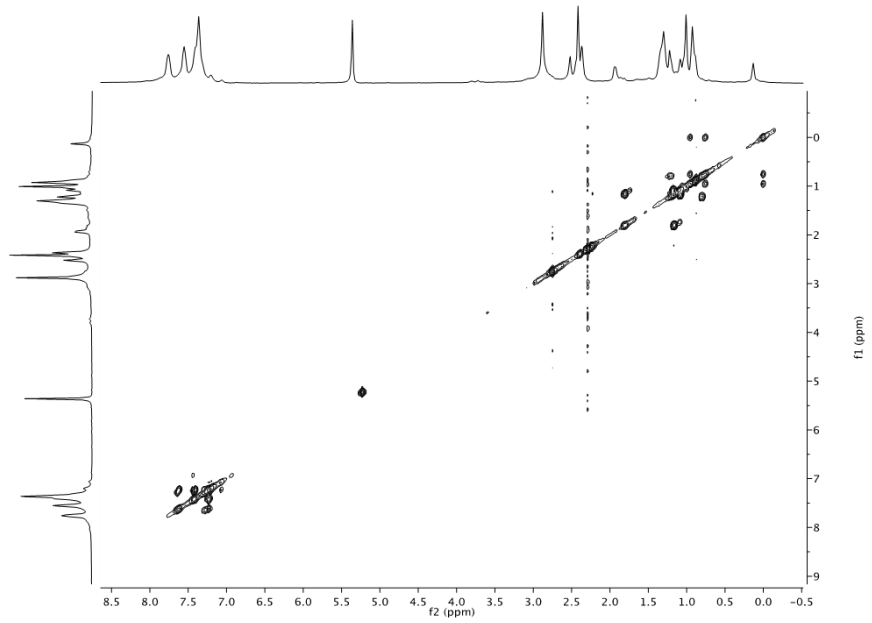

Figure 50. ^{1}H - ^{1}H NMR correlation for compound **10**.

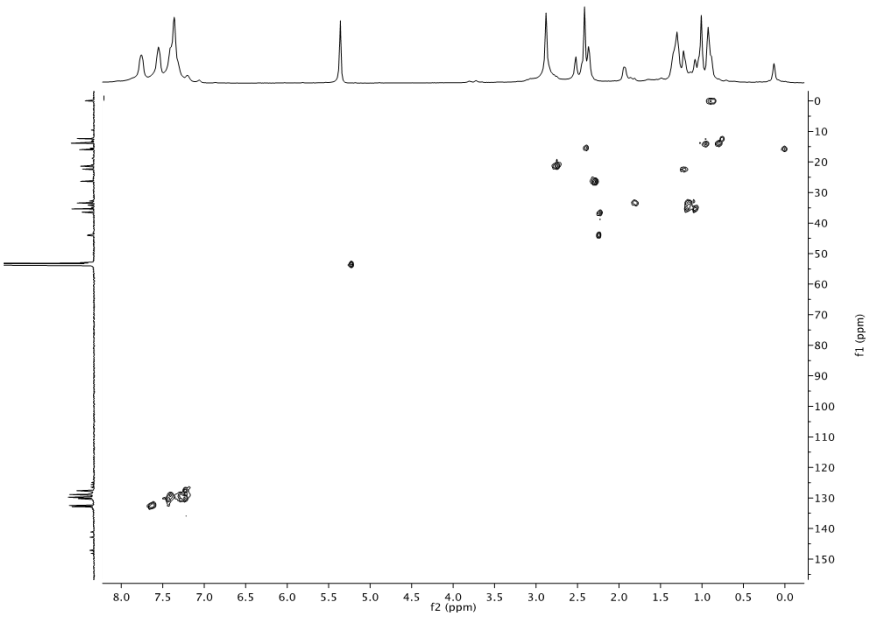

Figure 51. ^{1}H – $^{13}C\{^{1}H\}$ NMR correlation for compound **10**.

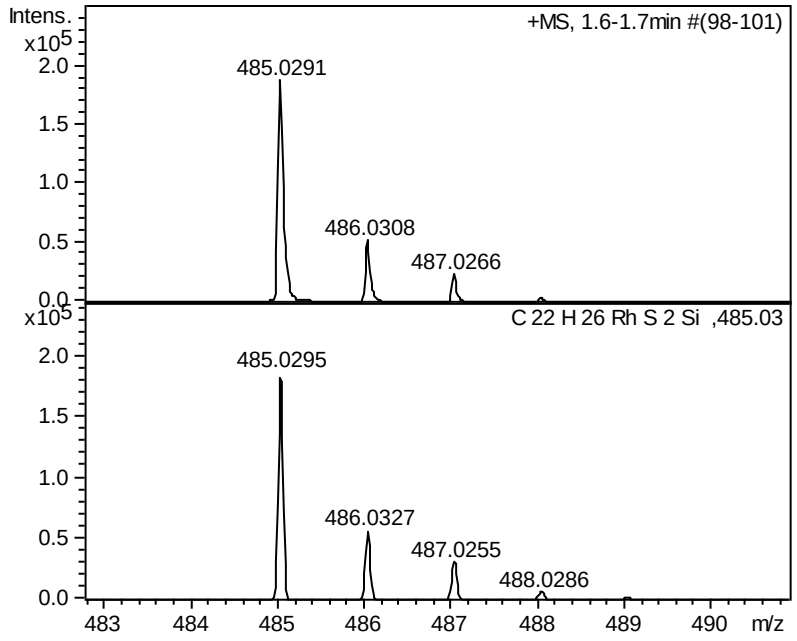

Figure 52. Found (top) and calculated (bottom) ESI-MS of compound **10**.

- **Compound [Rh(σ,π-nbyl)(SiMe(*o*-$C_6H_4SMe)_2$)]BAr^F_4 (11)**

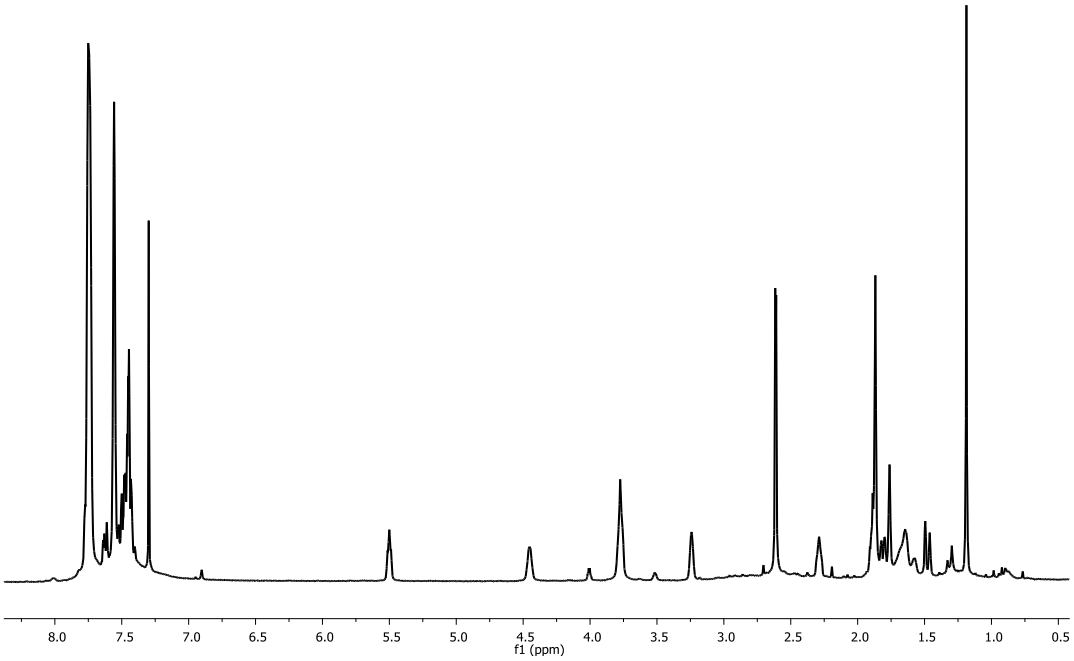

Figure 53. ^{1}H NMR spectrum of compound **11** in $CDCl_3$.

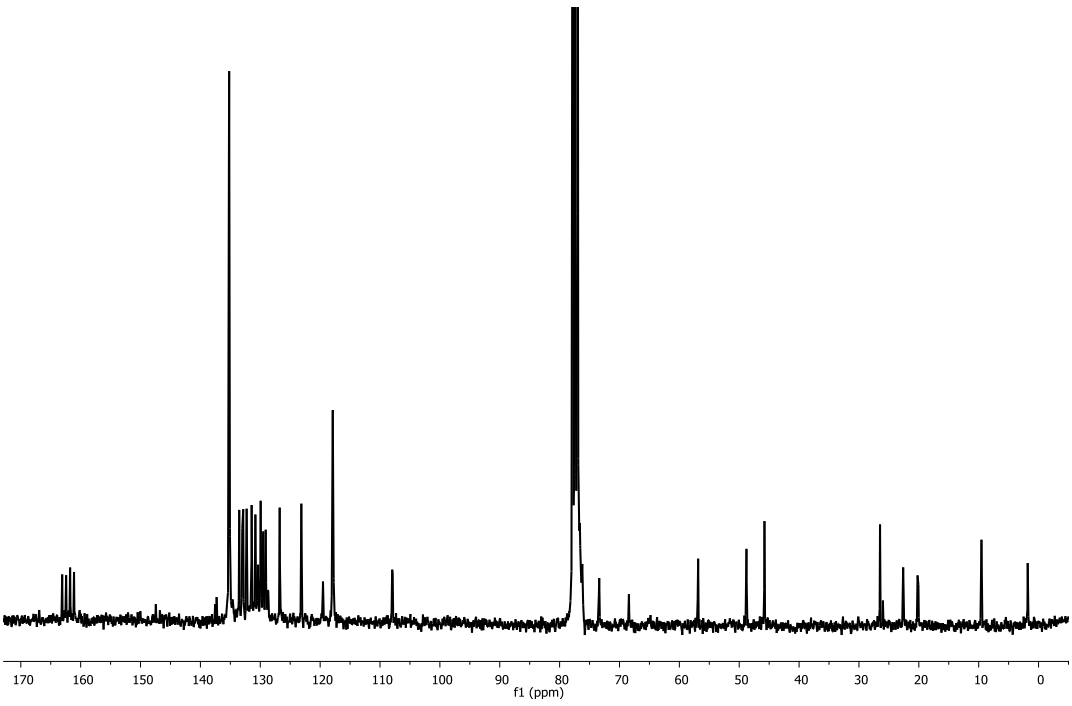

Figure 54. $^{13}C\{^1H\}$ NMR spectrum of compound **11** in $CDCl_3$.

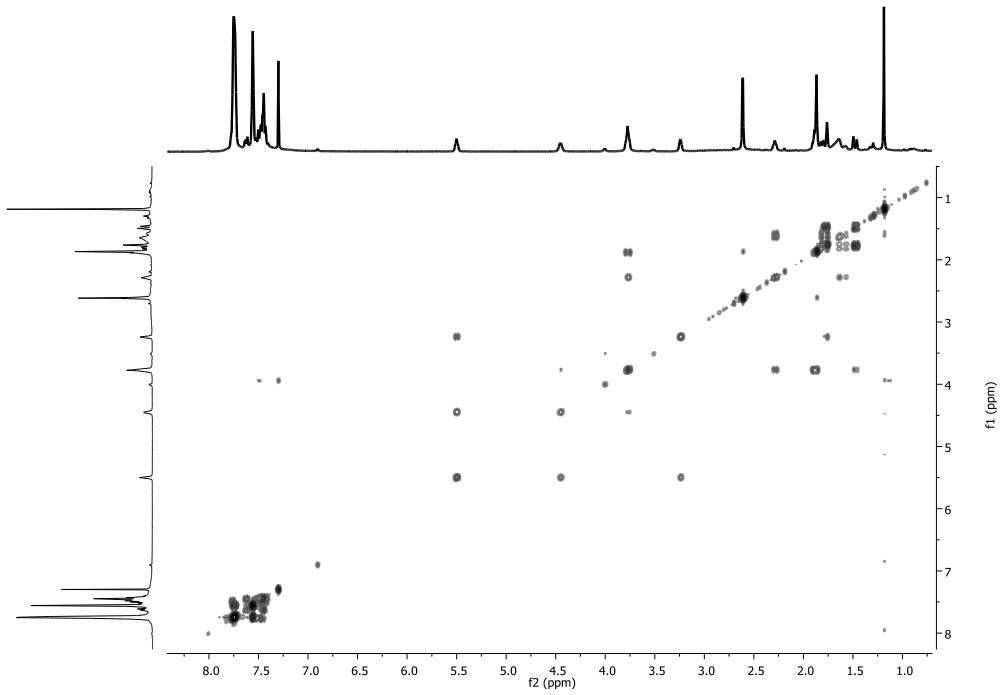

Figure 55. ^{1}H - ^{1}H NMR correlation for compound **11**.

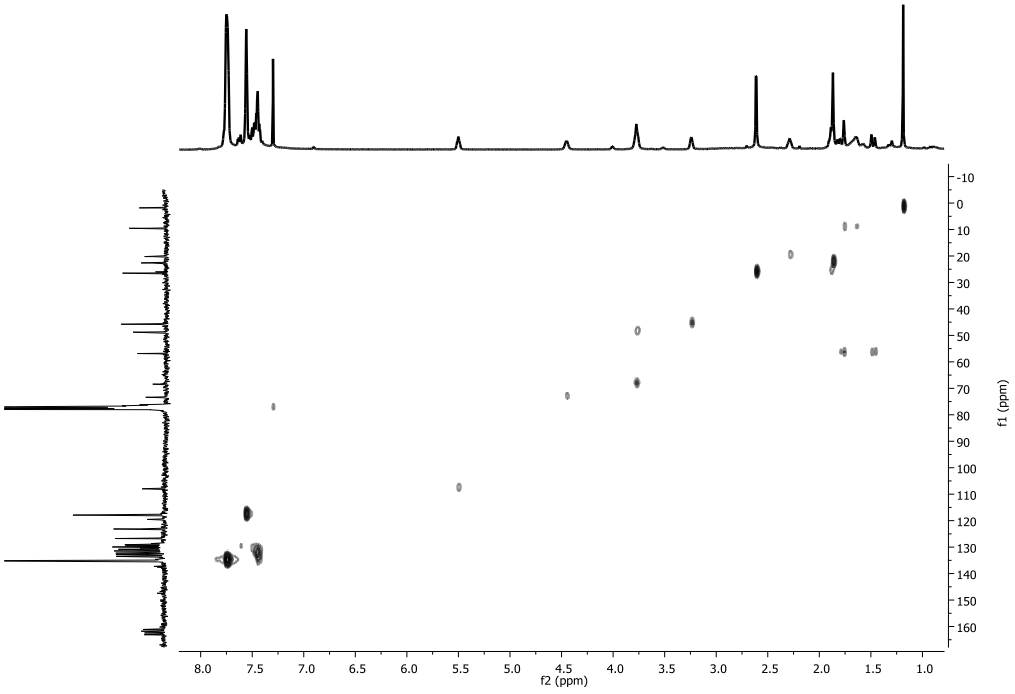

Figure 56. ^{1}H – $^{13}C\{^{1}H\}$ NMR correlation for compound **11**.

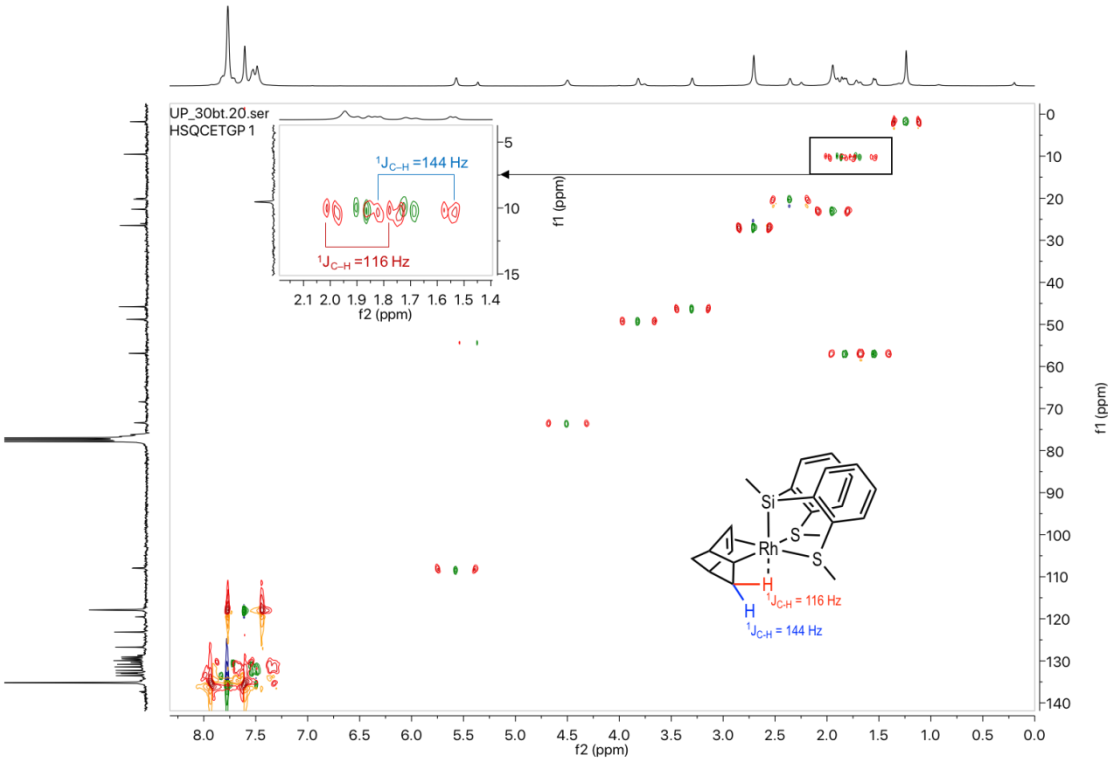

Figure 57. Overlapped ^{1}H-^{13}C HSQC (green) and ^{1}H-^{13}C HSQC coupled (red) spectra of **11** in CD_2Cl_2.

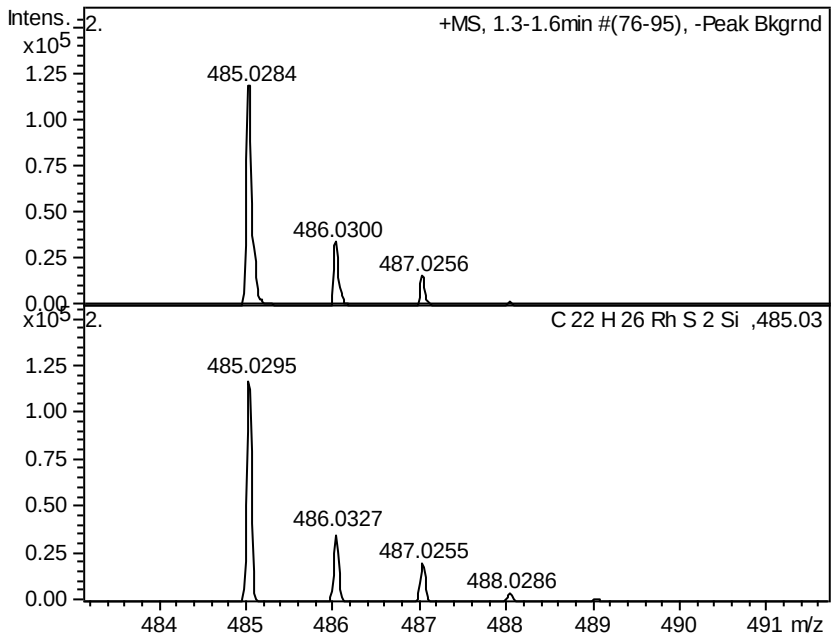

Figure 58. Found (top) and calculated (bottom) ESI-MS of compound **11**.

- **Compound [Rh(cod)(SiMe$_2$(*o*-C$_6$H$_4$SMe)$_2$)]BAr$^F_4$ (12)**

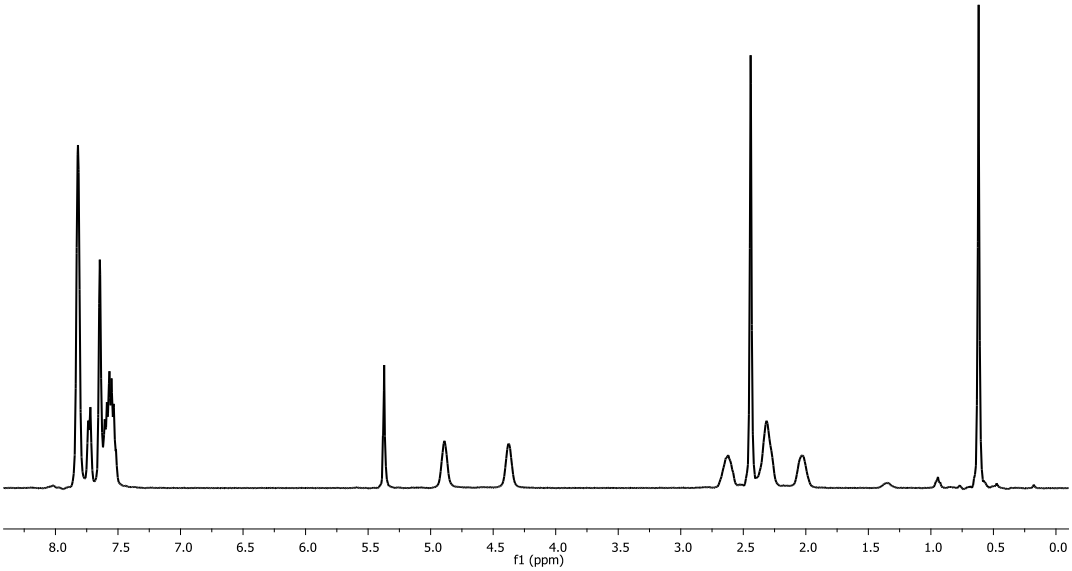

Figure 59. ^{1}H NMR spectrum of compound **12** in CD_2Cl_2.

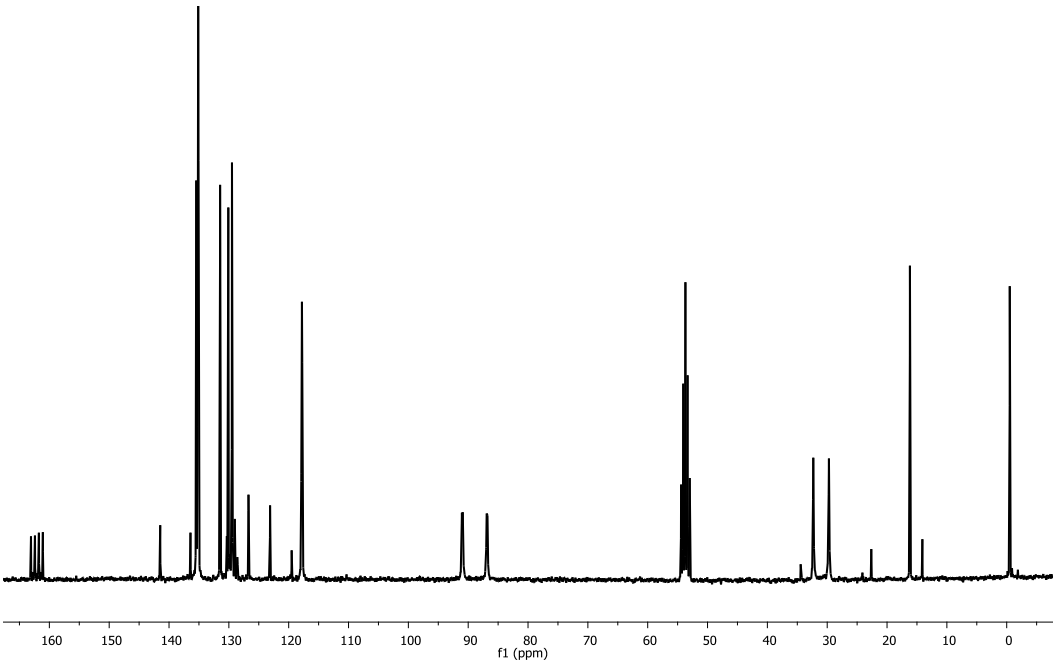

Figure 60. $^{13}C\{^1H\}$ NMR spectrum of compound **12** in CD_2Cl_2.

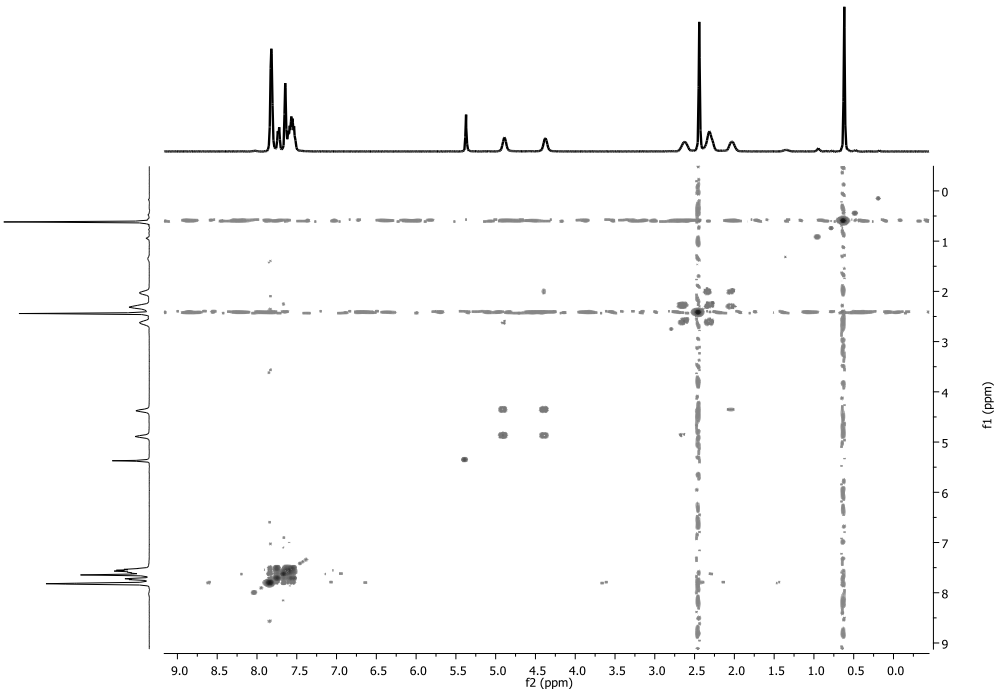

Figure 61. ^{1}H - ^{1}H NMR correlation for compound **12**.

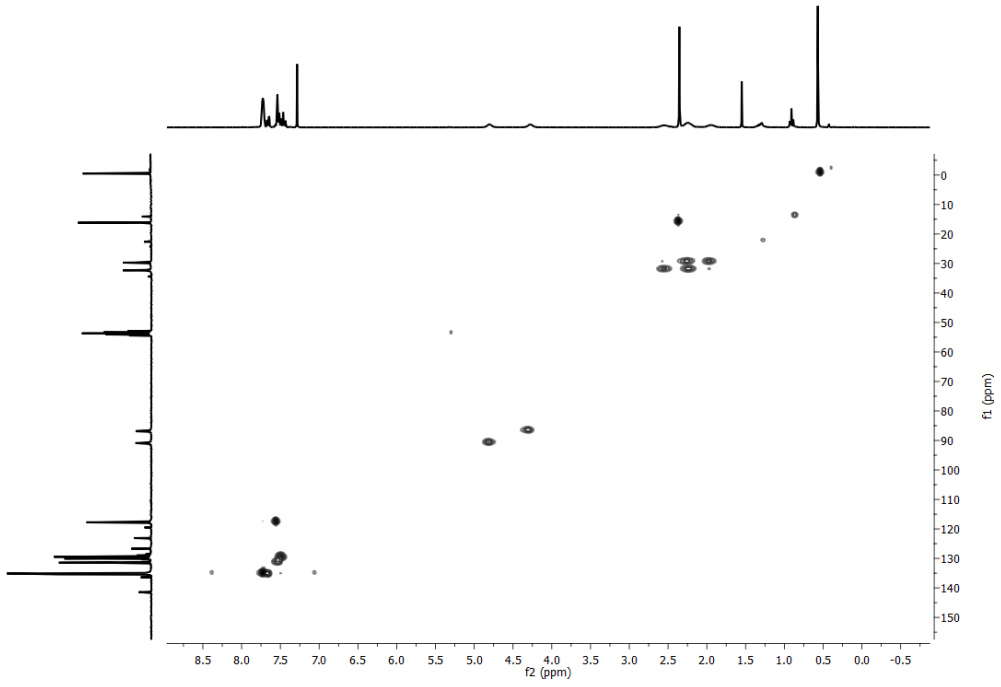

Figure 62. ^{1}H – $^{13}C\{^{1}H\}$ NMR correlation for compound **12**.

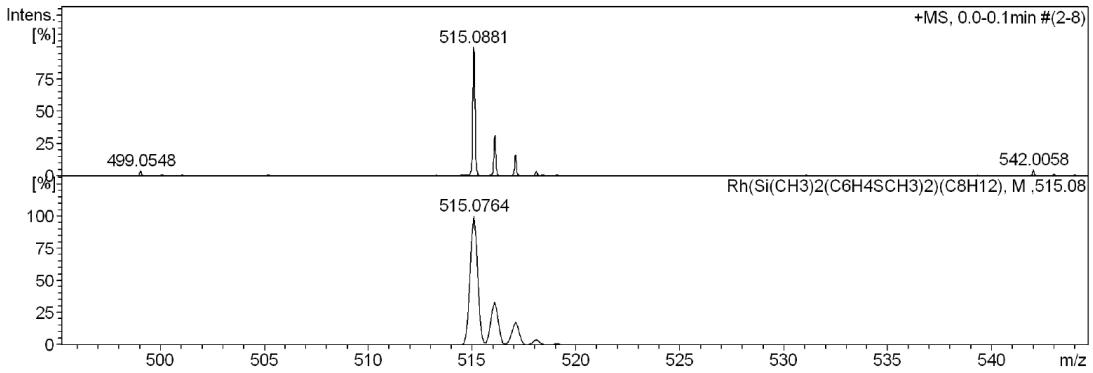

Figure 63. Found (top) and calculated (bottom) ESI-MS of compound **12**.

- **Compound [Rh(nbd)(SiMe$_2$(*o*-C$_6$H$_4$SMe)$_2$)]BAr$^F_4$ (13)**

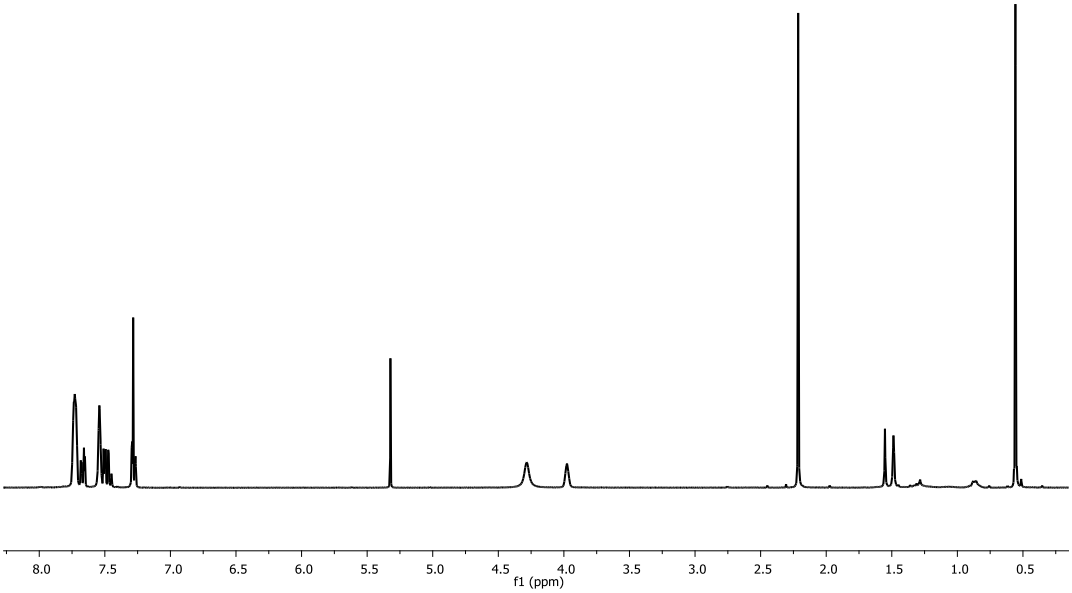

Figure 64. ^{1}H NMR spectrum of compound **13** in CD_2Cl_2.

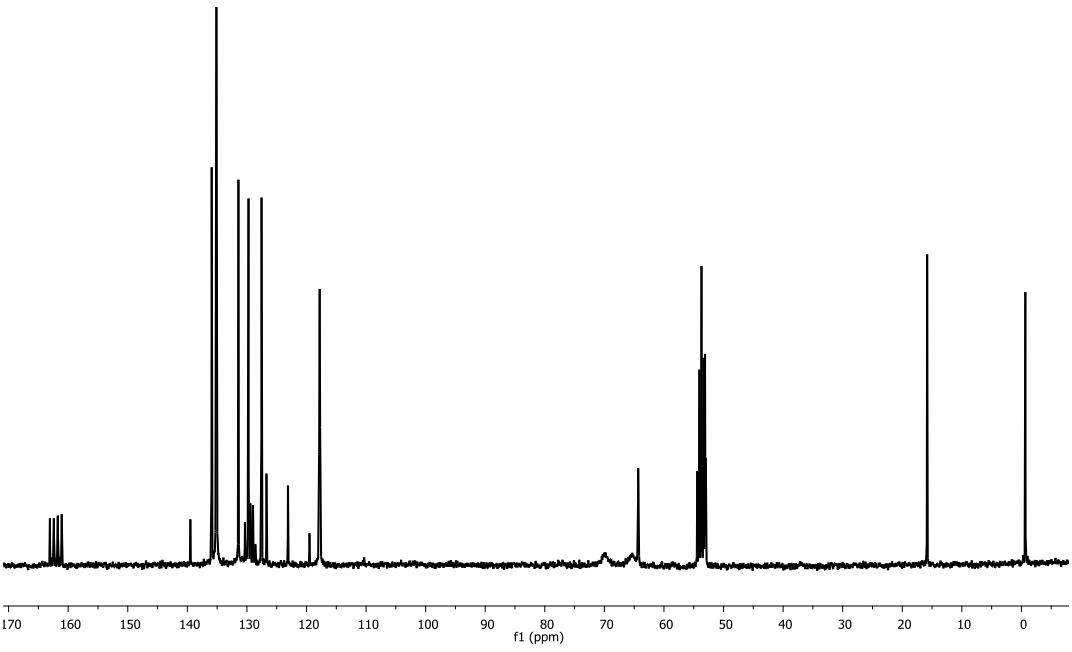

Figure 65. $^{13}C\{^1H\}$ NMR spectrum of compound **13** in CD_2Cl_2.

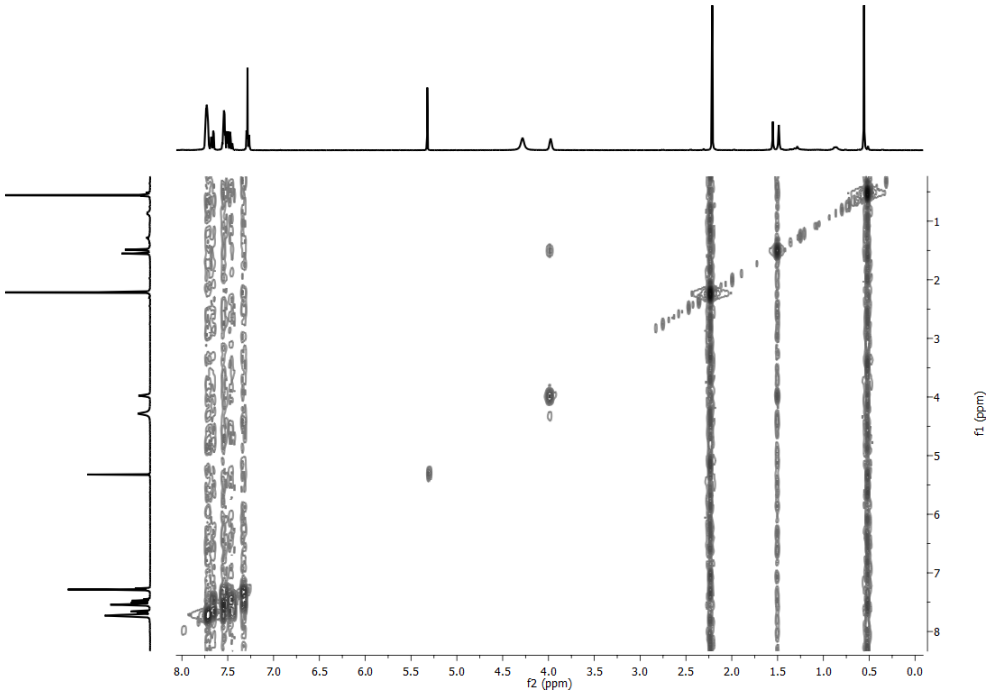

Figure 66. $^{1}H - {}^{1}H$ NMR correlation for compound **13**.

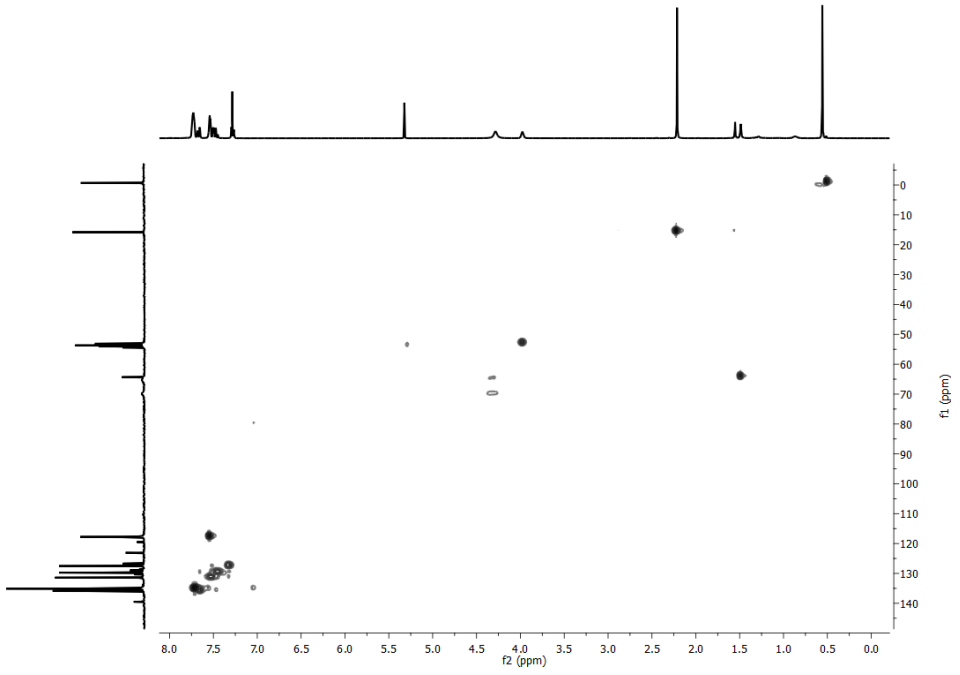

Figure 67. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **13**.

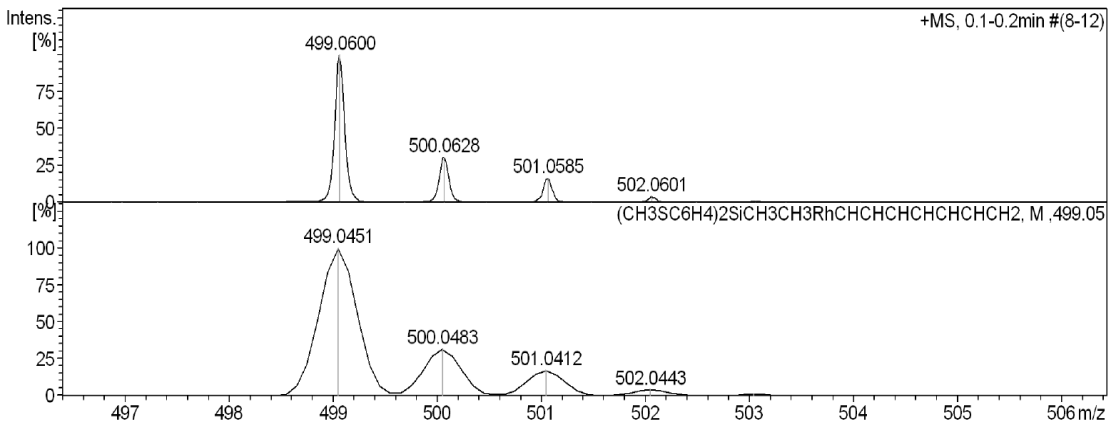

Figure 68. Found (top) and calculated (bottom) ESI-MS of compound **13**.

- **Compound [Ir(cod)($SiMe_2$(*o*-$C_6H_4SMe)_2$)]BAr^F_4 (14)**

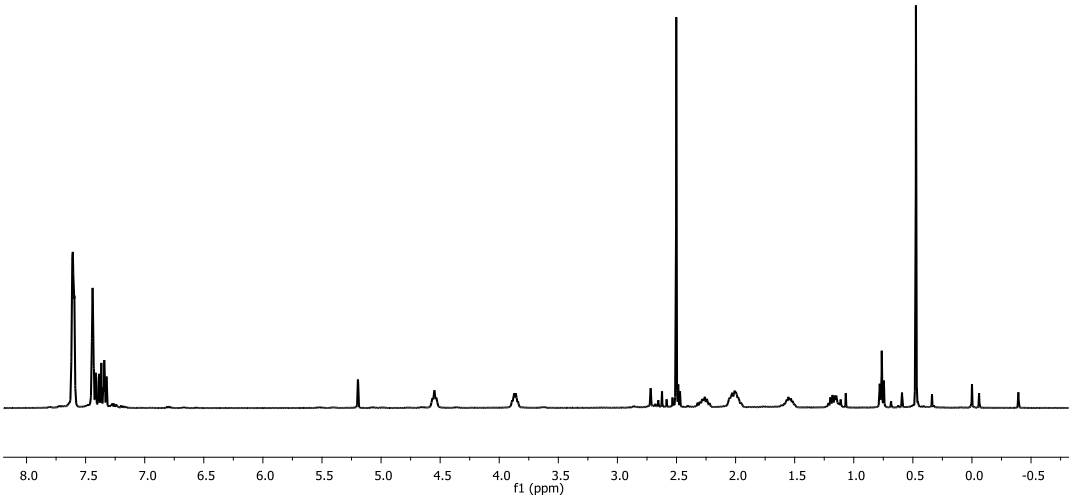

Figure 69. ^{1}H NMR spectrum of compound **14** in CD_2Cl_2.

- **Compound [RhCl(SiMe$_2$(*o*-C$_6$H$_4$SMe)$_2$)(DMSO)] (15)**

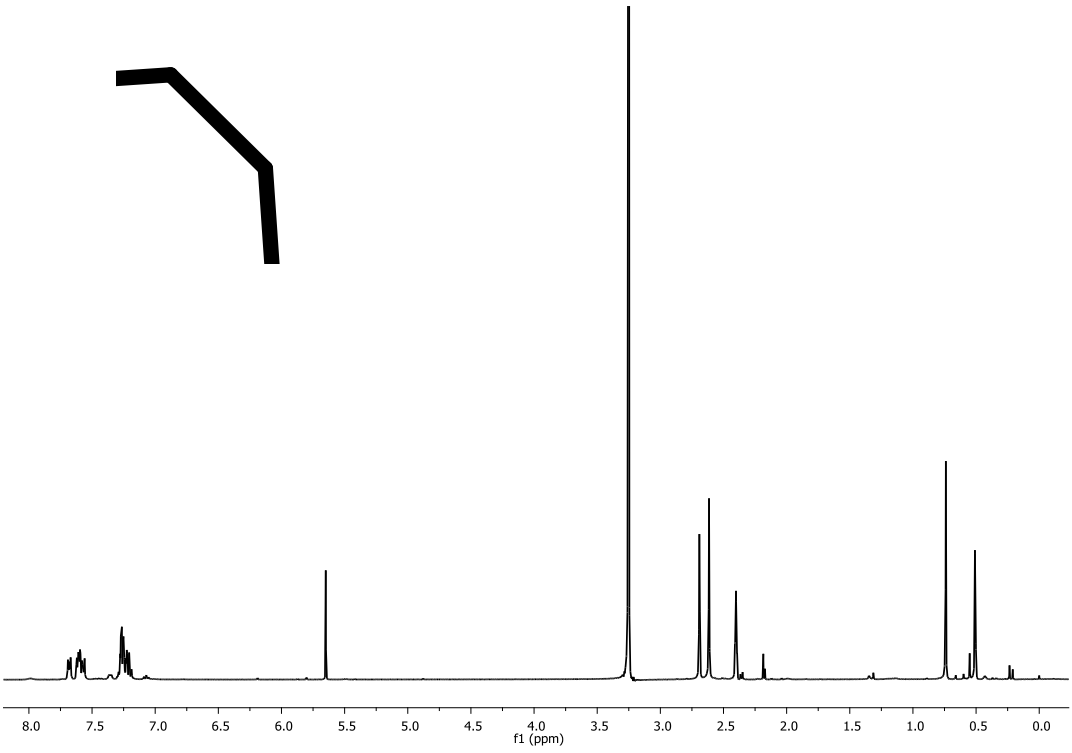

Figure 70. ^{1}H NMR spectrum of compound **15** in DMSO-d$_6$.

- **Compound [Rh(Me)(SiMe(*o*-$C_6H_4SMe)_2$)$(MeCN)_2$]BAr^F_4 (16)**

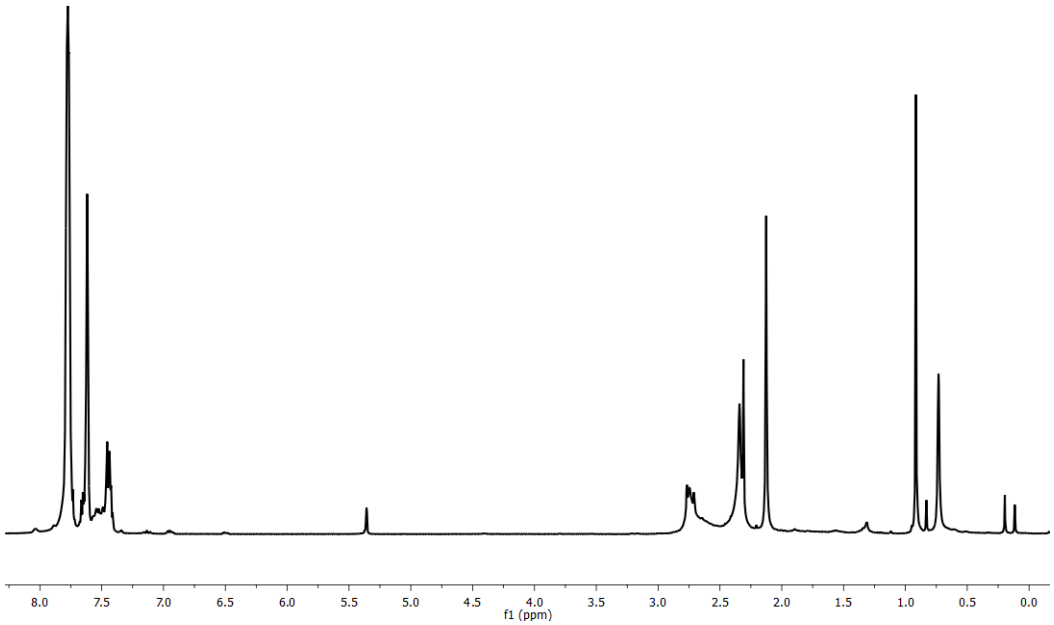

Figure 71. ^1H NMR spectrum of compound **16** in CD_2Cl_2.

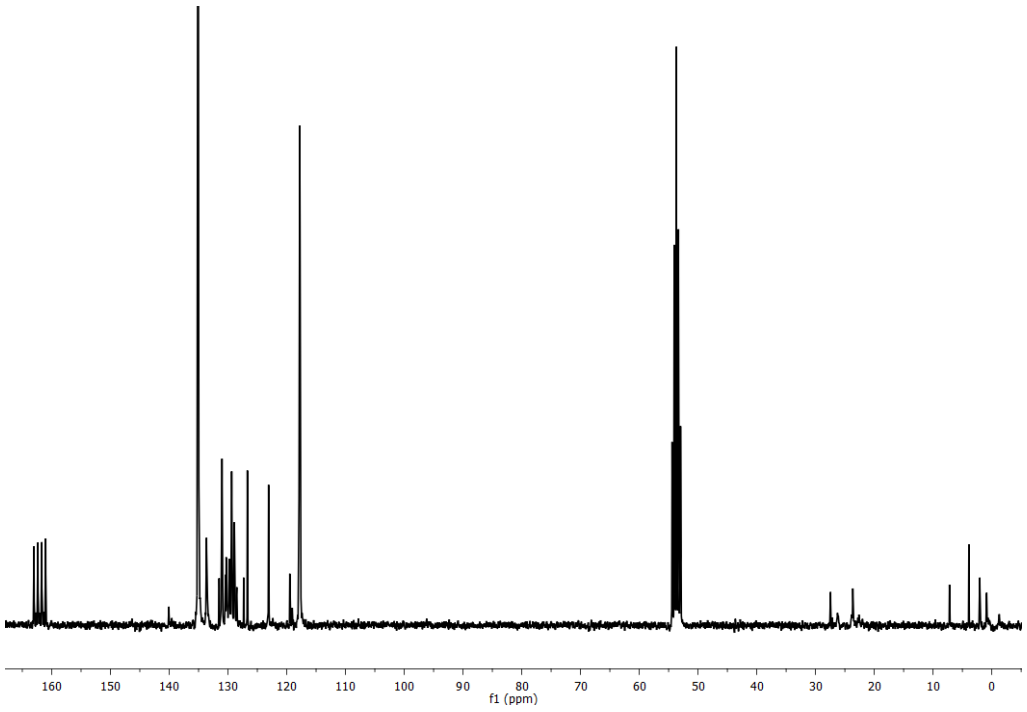

Figure 72. $^{13}C\{^1H\}$ NMR spectrum of compound **16** in CD_2Cl_2.

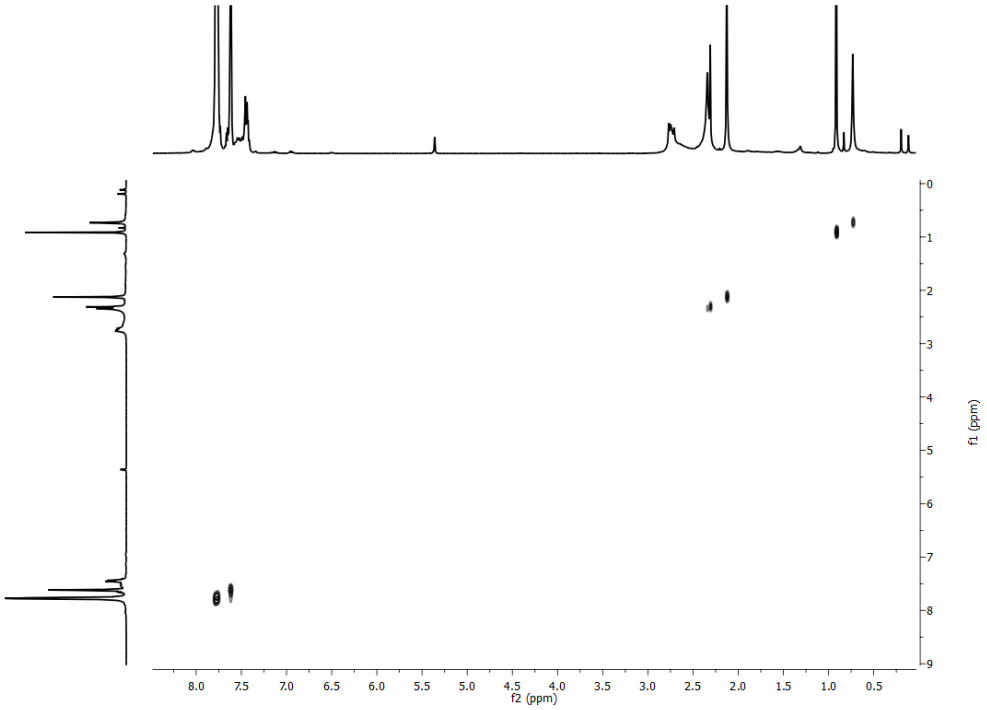

Figure 73. $^{1}H - {}^{1}H$ NMR correlation for compound **16**.

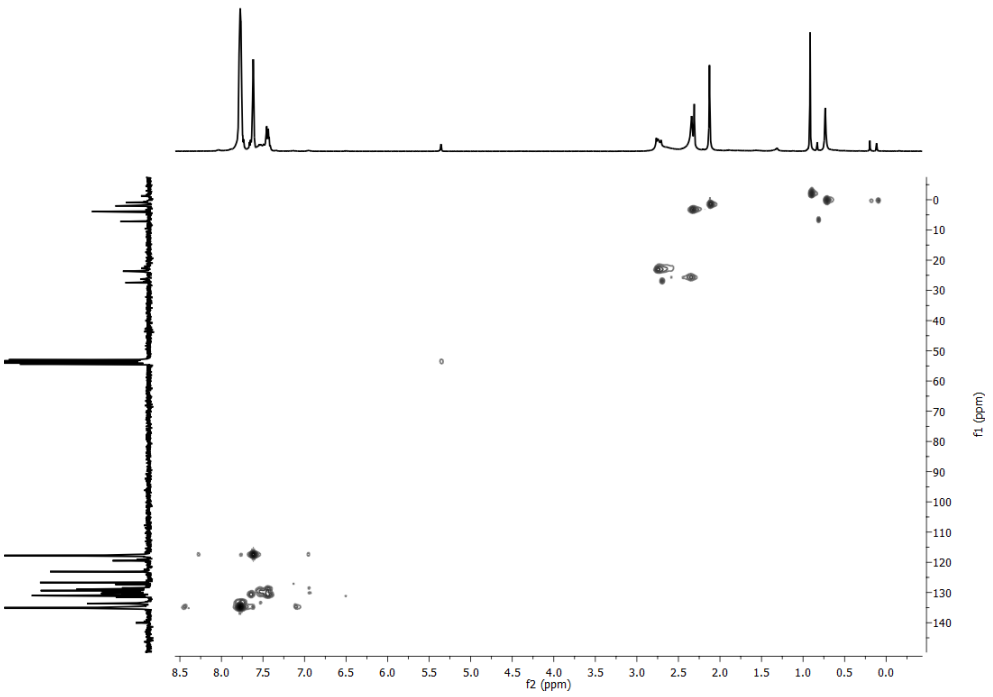

Figure 74. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **16**.

- **Compound [RhH(SiMe$_2$(*o*-C$_6$H$_4$SMe))(PPh$_3$)$_2$]BAr$^F_4$ (17)**

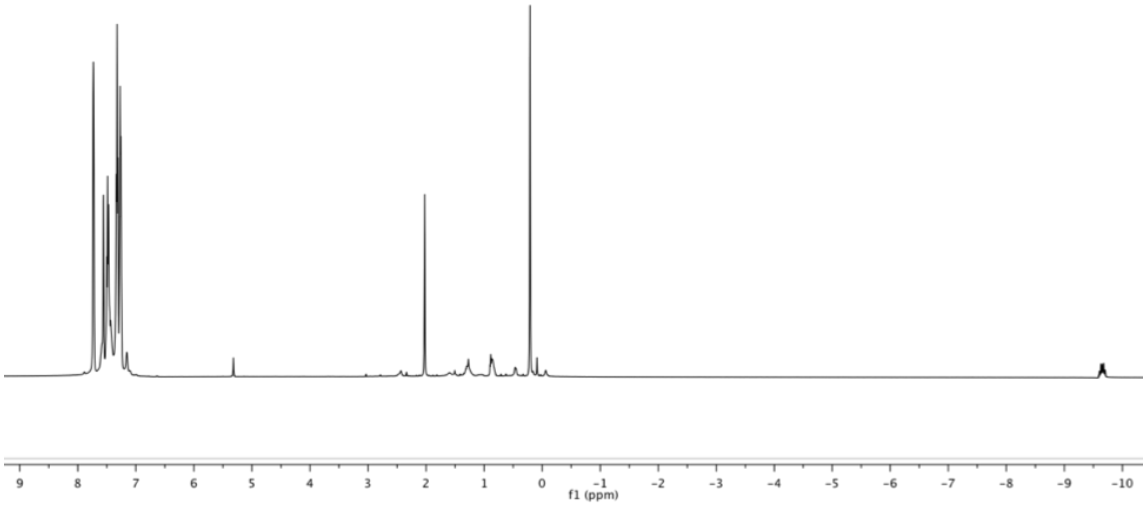

Figure 75. ^{1}H NMR spectrum of compound **17** in CD_2Cl_2.

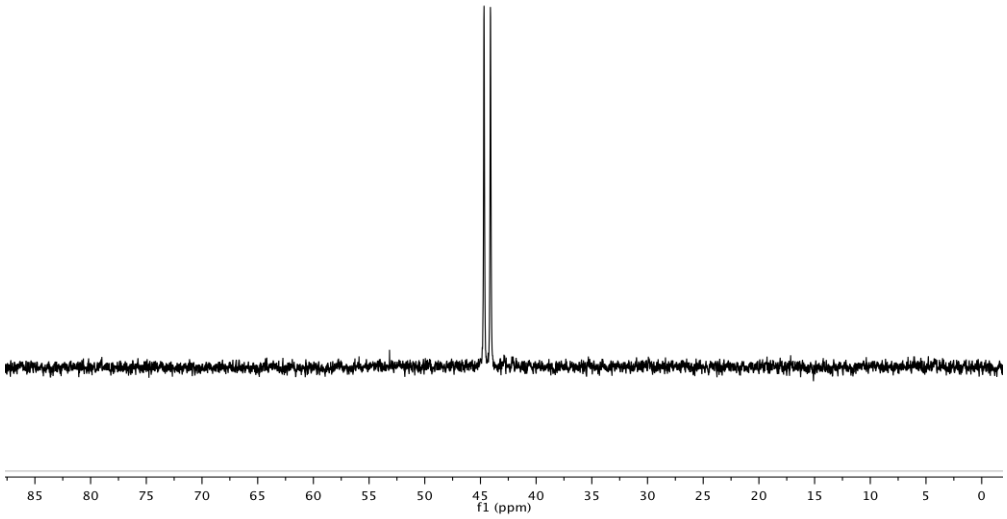

Figure 76. $^{31}P\{^1H\}$ NMR spectrum of compound **17** in CD_2Cl_2.

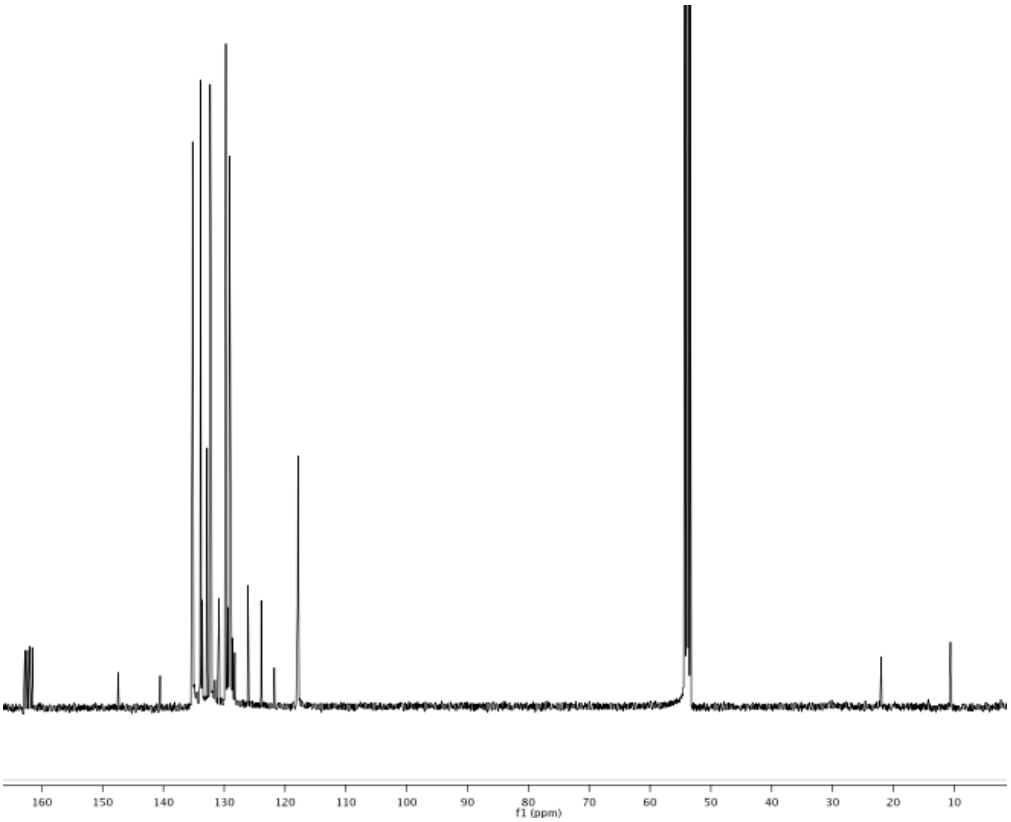

Figure 77. $^{13}C\{^{1}H\}$ NMR spectrum of compound **17** in CD_2Cl_2.

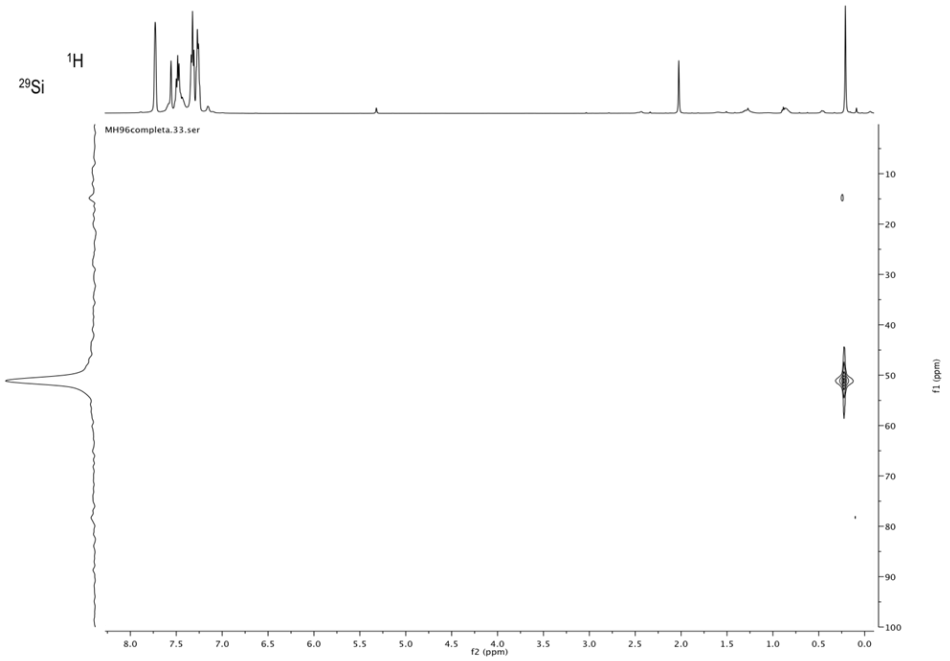

Figure 78. ^{1}H – ^{29}Si NMR correlation for compound **17**.

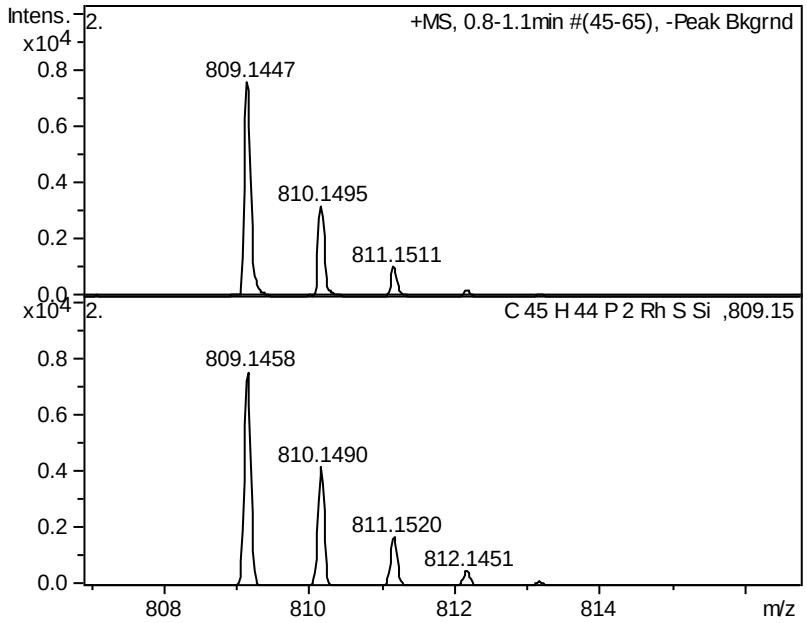

Figure 79. Found (top) and calculated (bottom) ESI-MS of compound **17**.

- **Compound [IrClH(SiMe(*o*-$C_6H_4SMe)_2$)(PPh_3)] (18)**

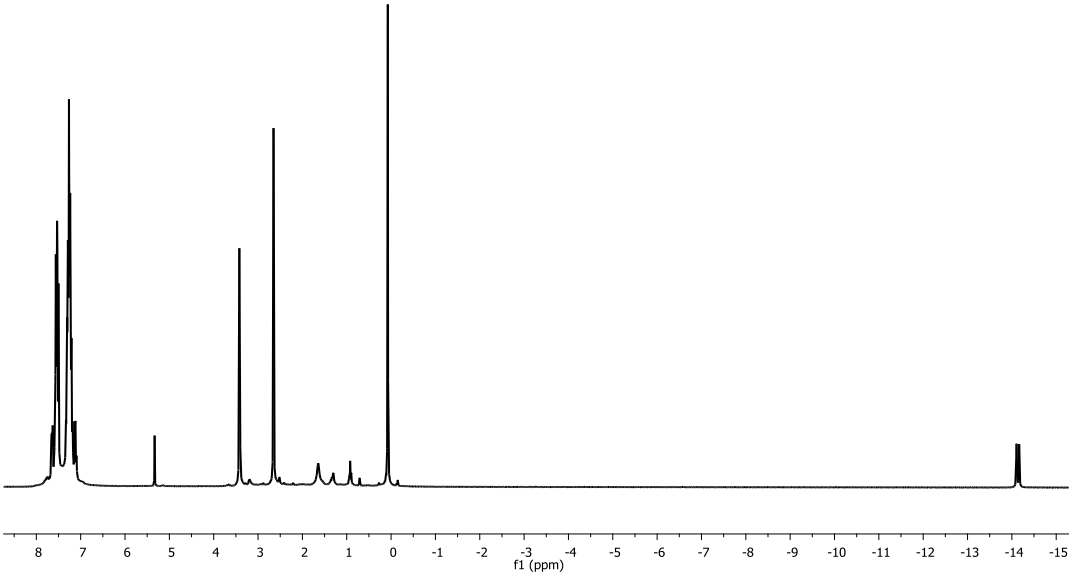

Figure 80. ^{1}H NMR spectrum of compound **18** in $CDCl_3$.

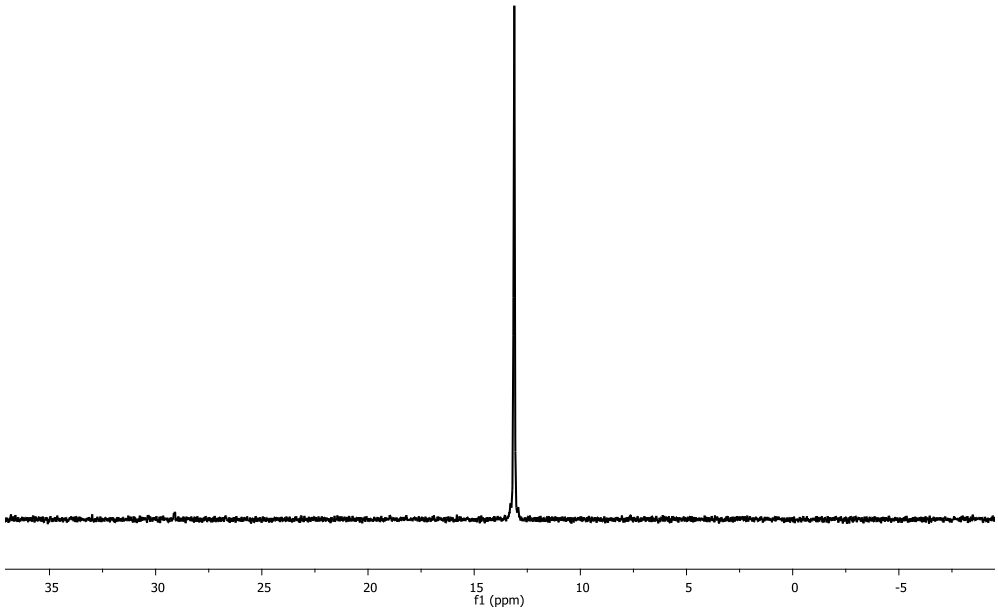

Figure 81. $^{31}P\{^{1}H\}$ NMR spectrum for compound **18** in $CDCl_3$.

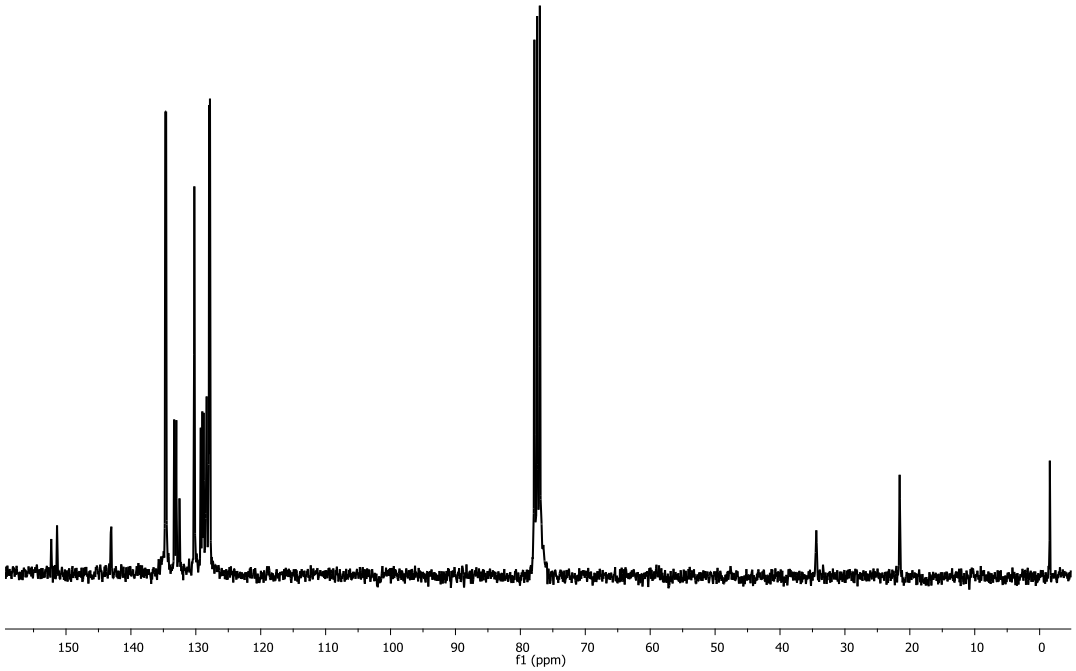

Figure 82. $^{13}C\{^{1}H\}$ NMR spectrum for compound **18** in $CDCl_3$.

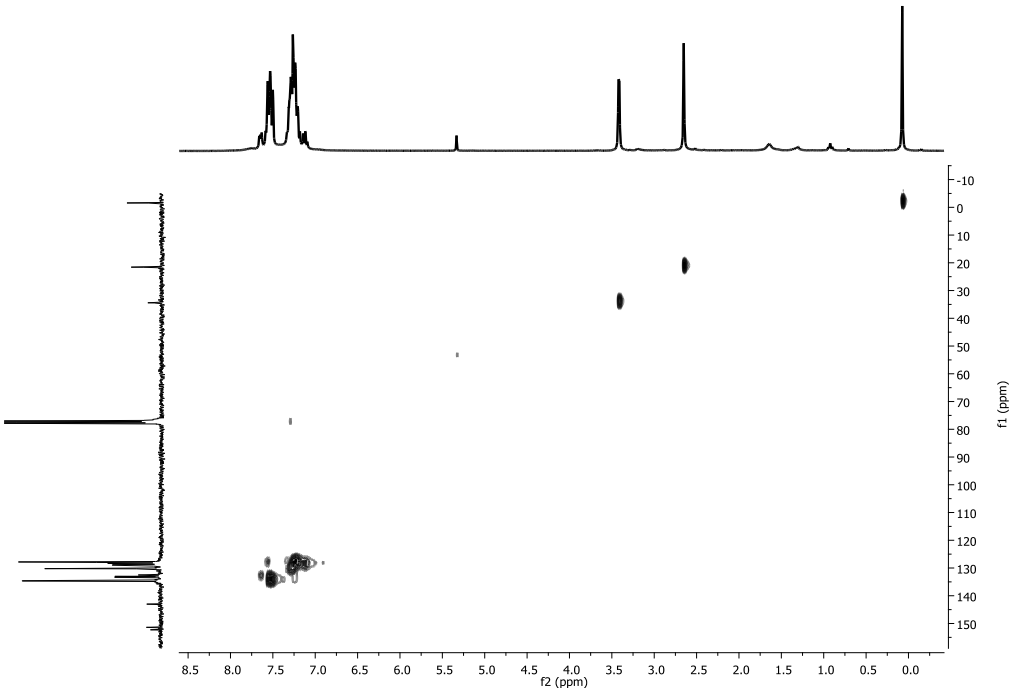

Figure 83. $^{1}H - ^{13}C\{^{1}H\}$ NMR correlation for compound **18**.

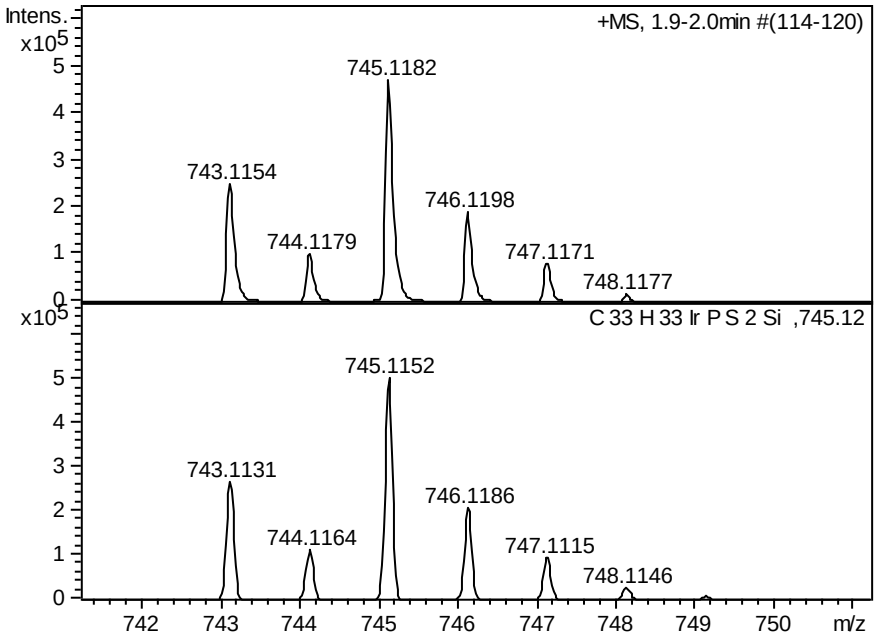

Figure 84. Found (top) and calculated (bottom) ESI-MS of compound **18**.

- **Compound [IrH_2(SiMe(*o*-$C_6H_4SMe)_2$)(PPh_3)] (19)**

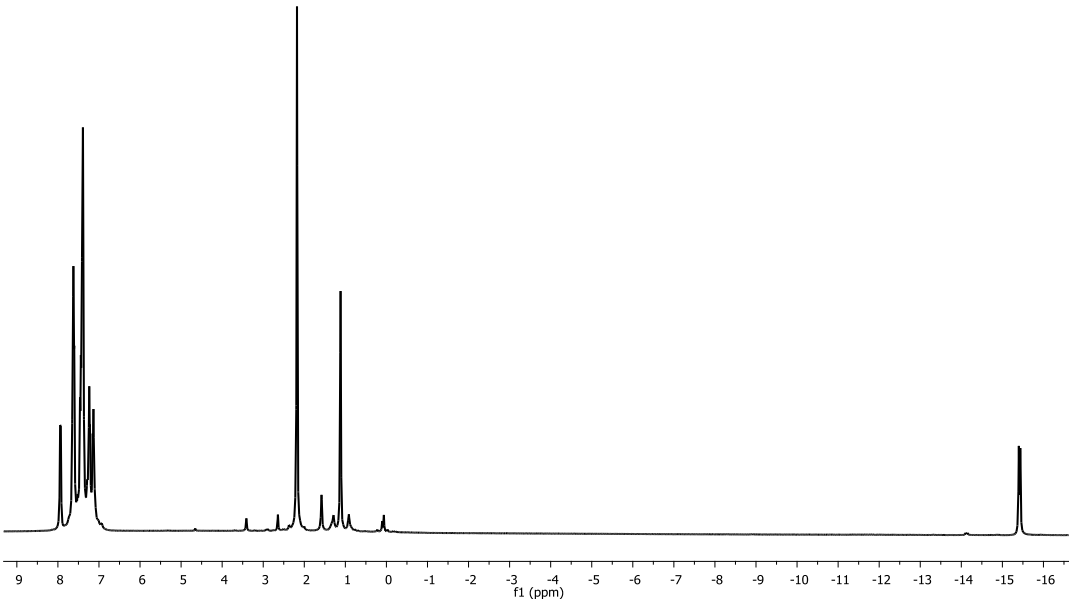

Figure 85. ^{1}H NMR spectrum of compound **19** in $CDCl_3$.

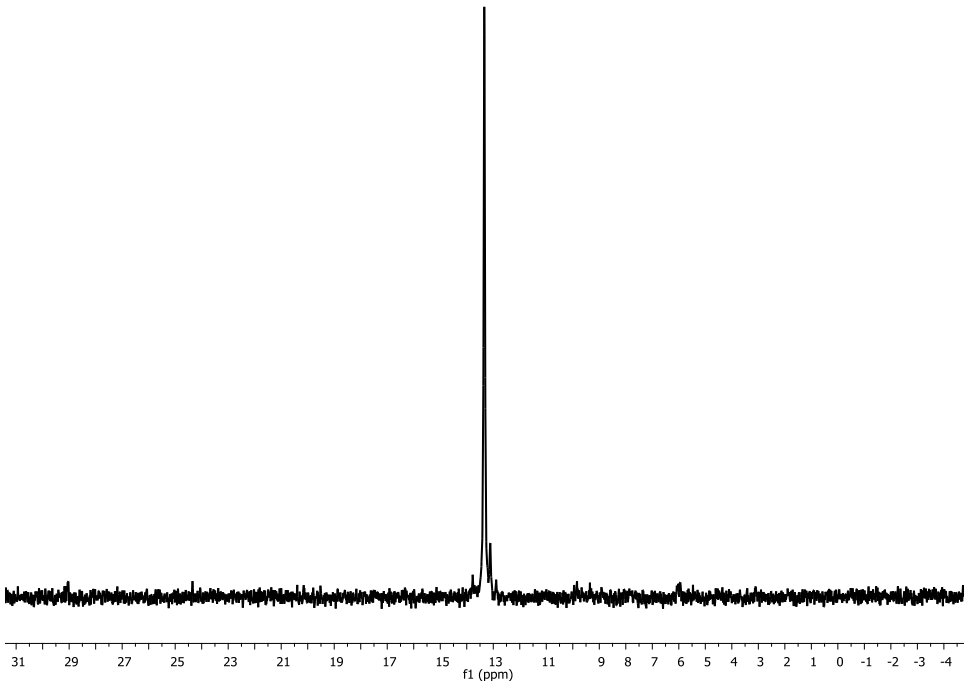

Figure 86. $^{31}P\{^{1}H\}$ NMR spectrum for compound **19** in $CDCl_3$.

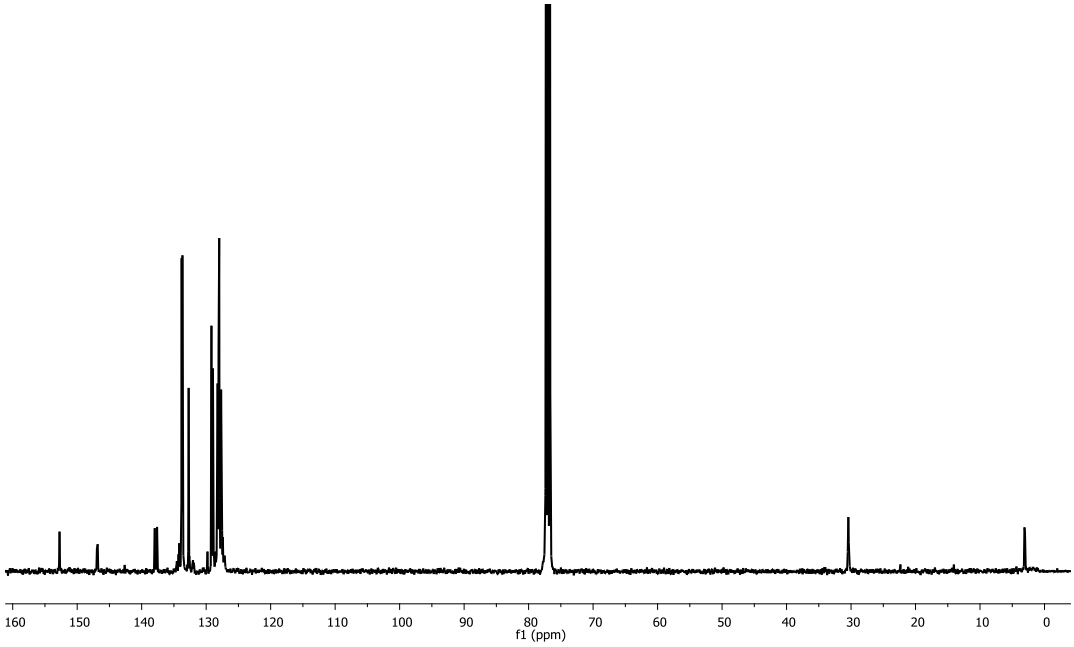

Figure 87. $^{13}C\{^{1}H\}$ NMR spectrum of compound **19** in $CDCl_3$.

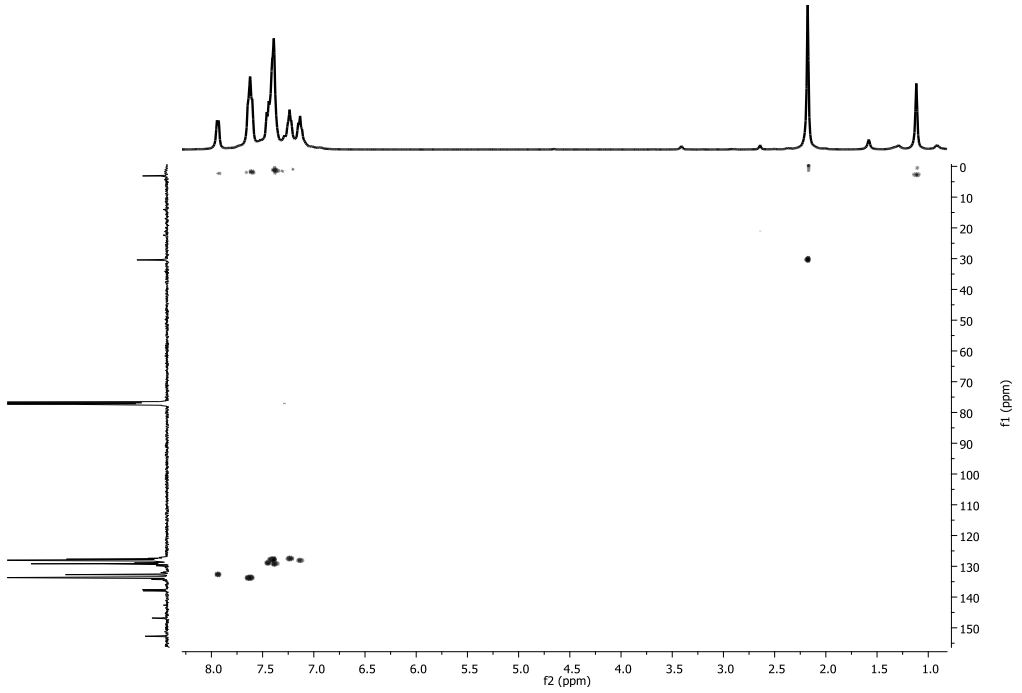

Figure 88. $^{1}H - ^{13}C\{^{1}H\}$ NMR correlation for compound **19**.

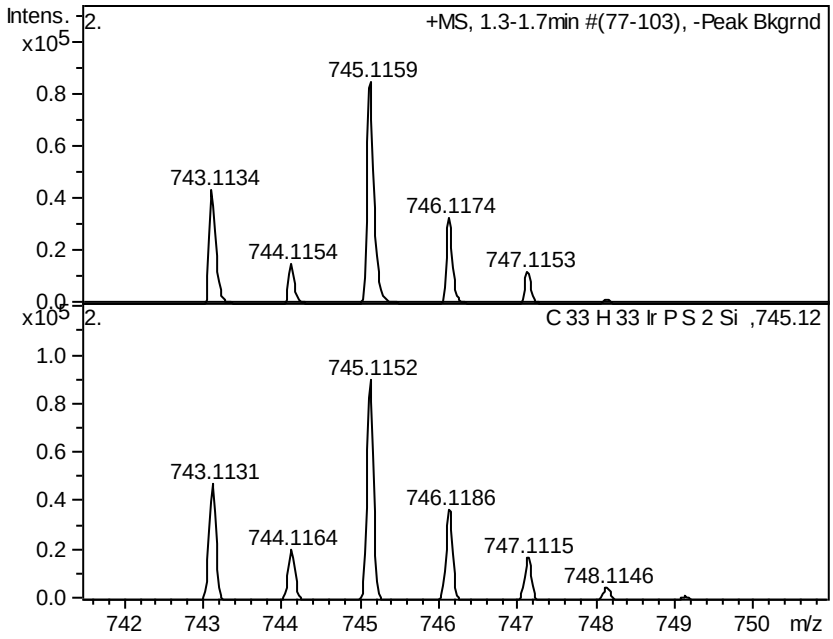

Figure 89. Found (top) and calculated (bottom) ESI-MS of compound **19**.

- **Compound [IrH(SiMe(*o*-$C_6H_4SMe)_2$)(PPh_3)(THF)]BAr^F_4 (20)**

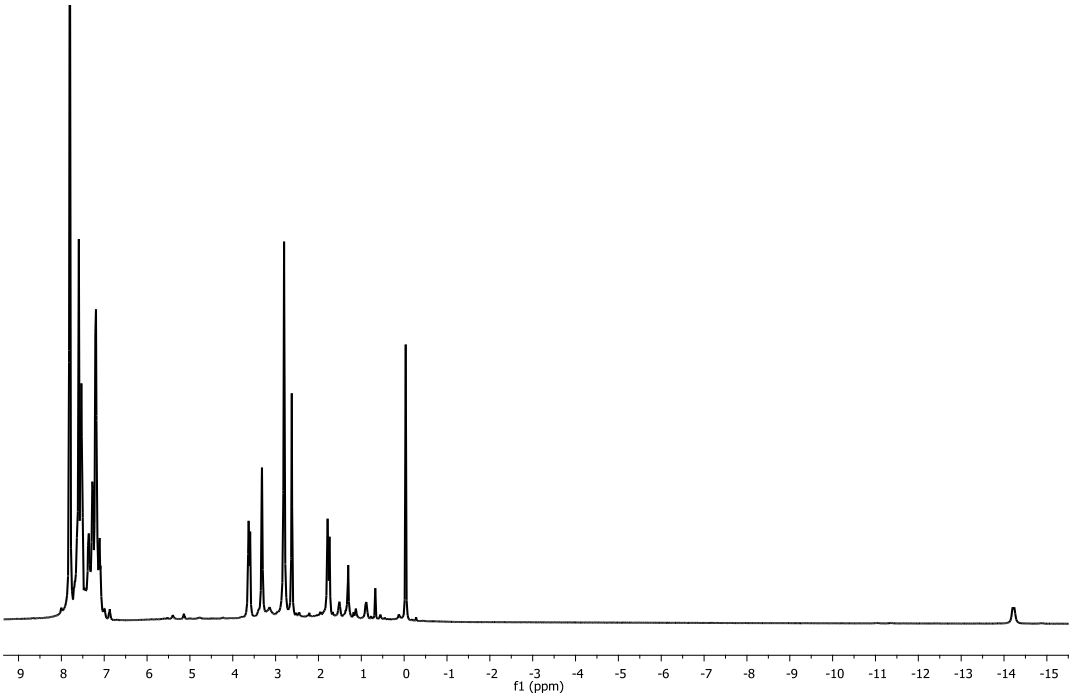

Figure 90. ^{1}H NMR spectrum of compound **20** in THF-d_8.

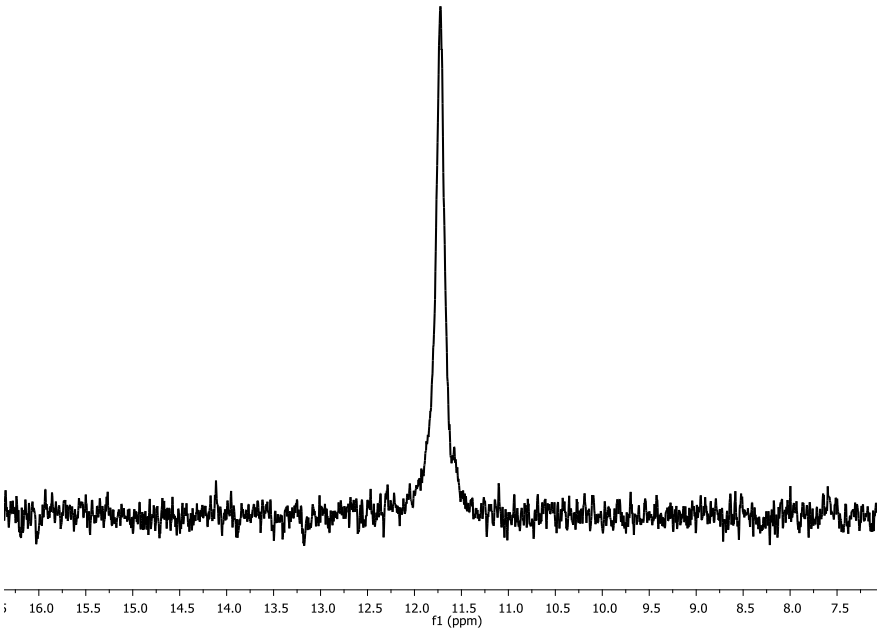

Figure 91. $^{31}P\{^1H\}$ NMR spectrum of compound **20** in THF-d_8.

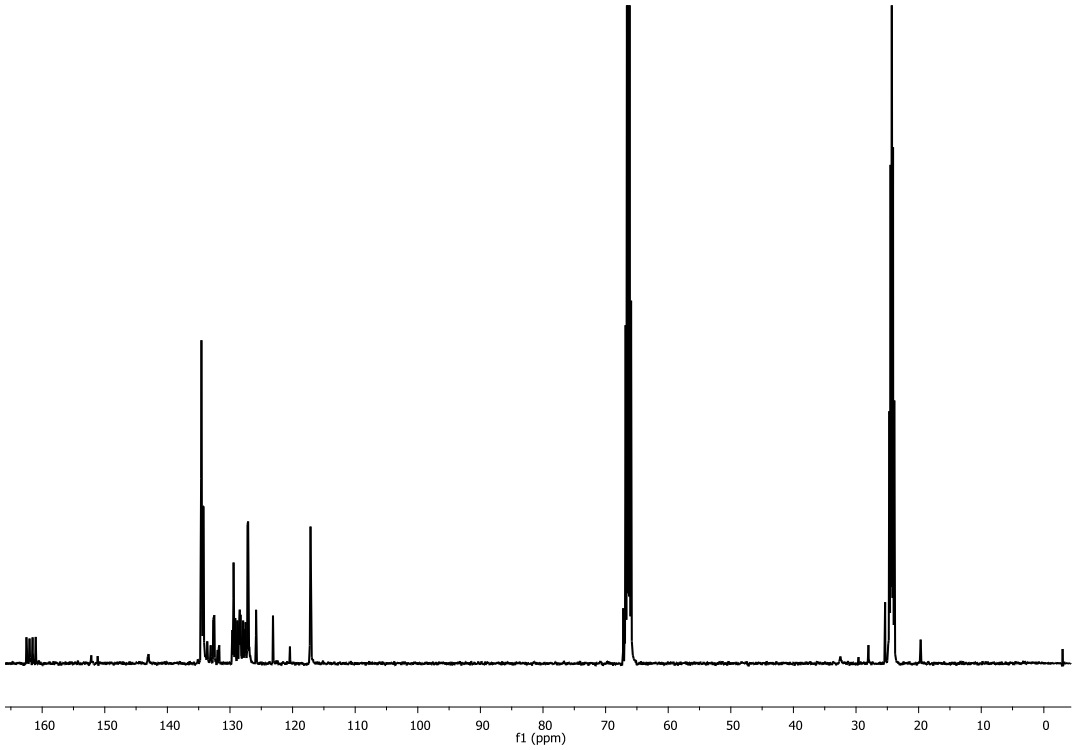

Figure 92. $^{13}C\{^{1}H\}$ NMR spectrum of compound **20** in THF-d_8.

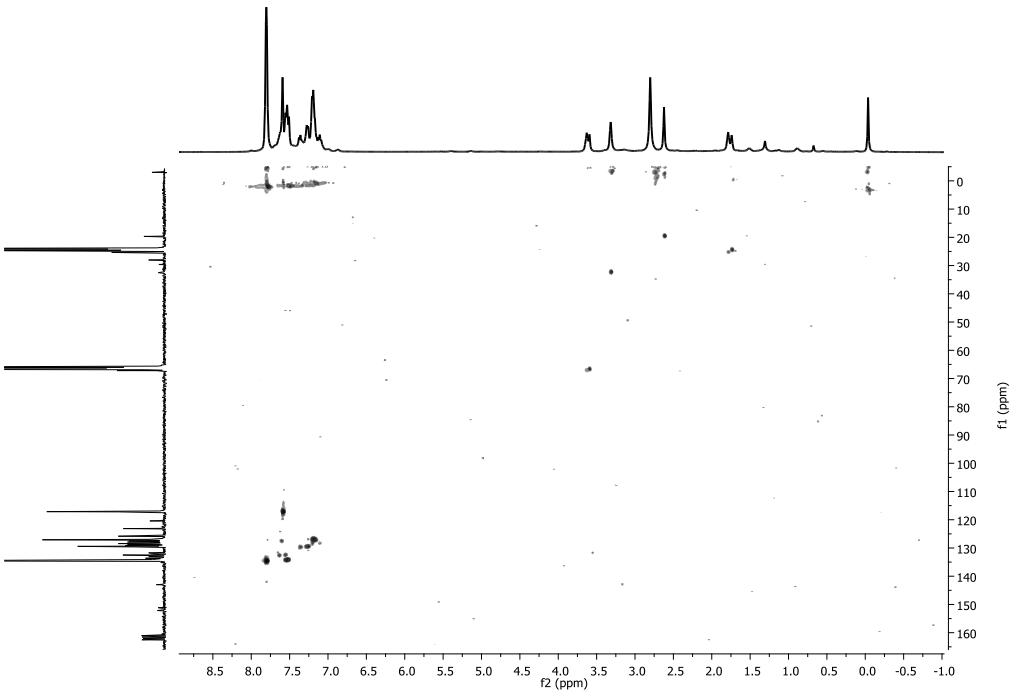

Figure 93. $^{1}H - ^{13}C\{^{1}H\}$ NMR correlation for compound **20**.

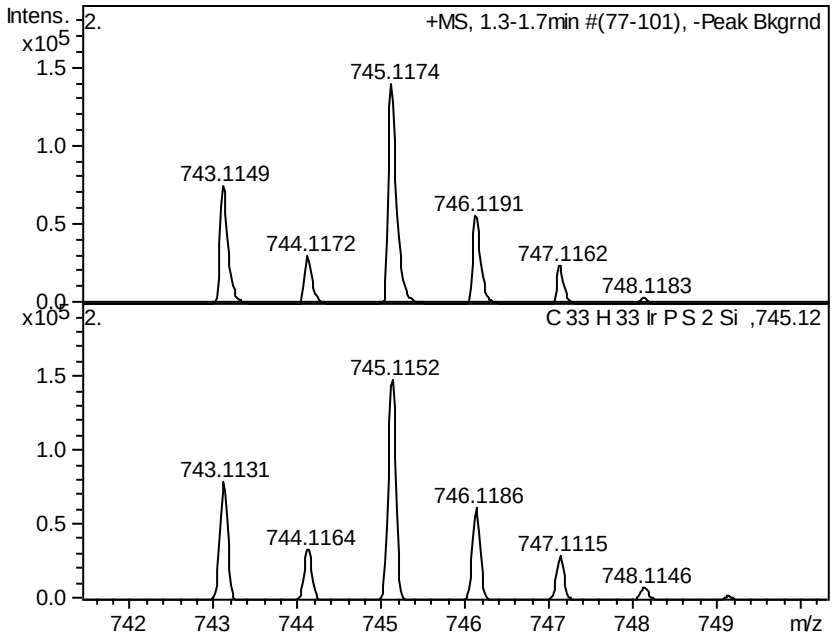

Figure 94. Found (top) and calculated (bottom) ESI-MS of compound **20**.

- **Compound [Rh(SiMe(*o*-$C_6H_4SMe)_2)_2$]BAr^F_4 (21)**

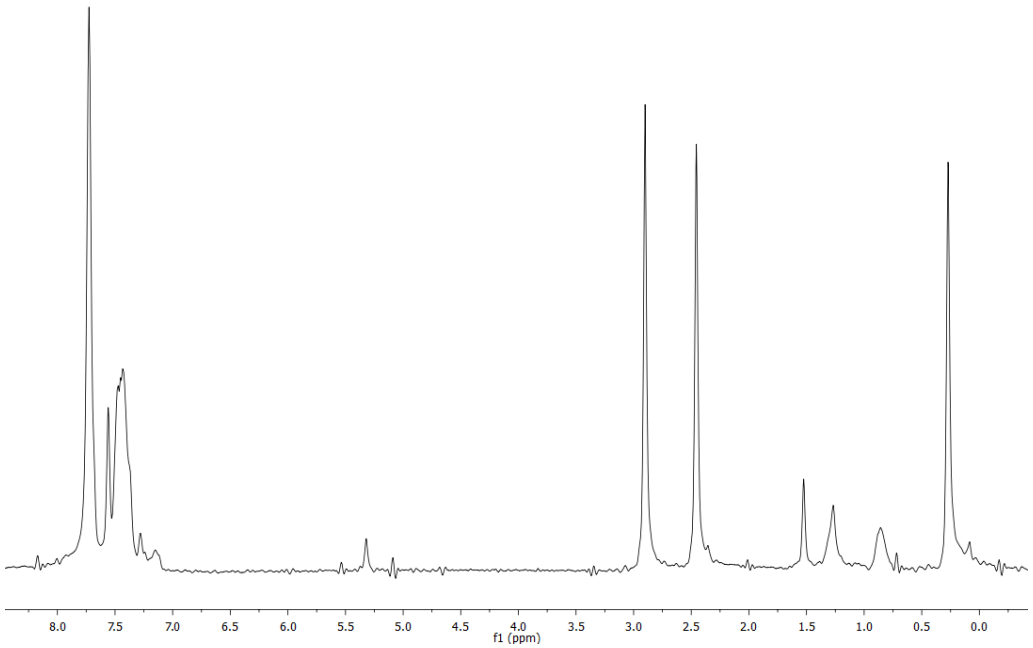

Figure 95. ^{1}H NMR spectrum of compound **21** in $CDCl_3$.

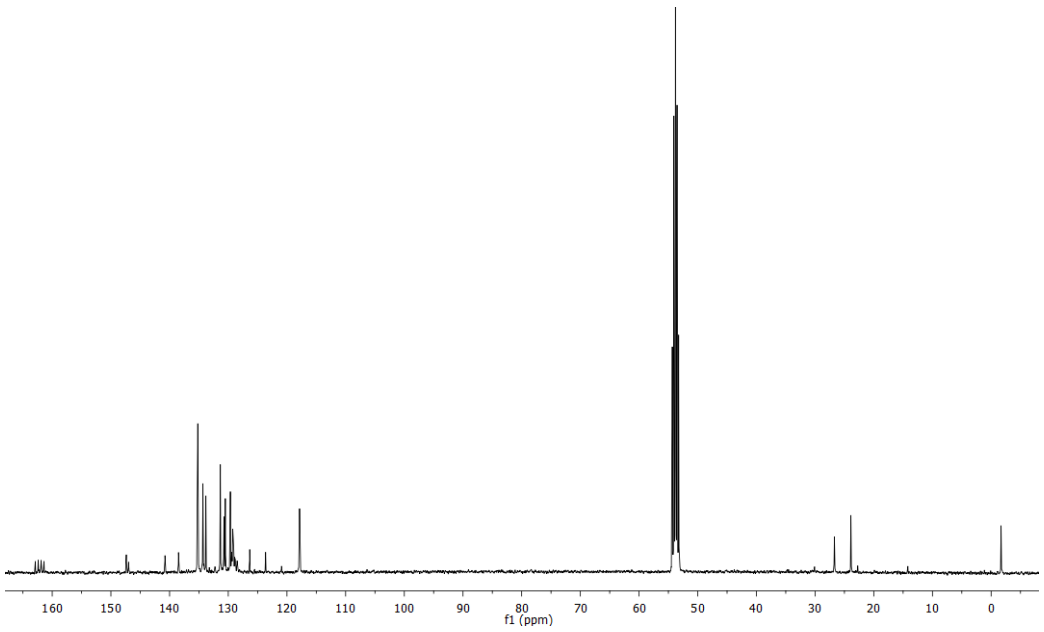

Figure 96. $^{13}C\{^1H\}$ NMR spectrum of compound **21** in $CDCl_3$.

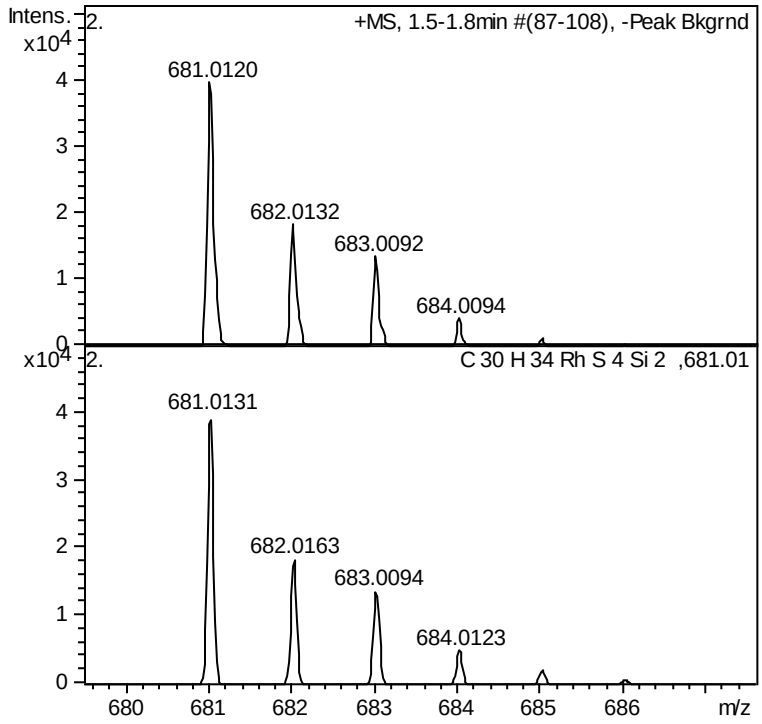

Figure 97. Found (top) and calculated (bottom) ESI-MS of compound **21**.

- **Compound [RhClH($PPh_2CH(Ph)CH_2CO$)$(py)_2$] (22)**

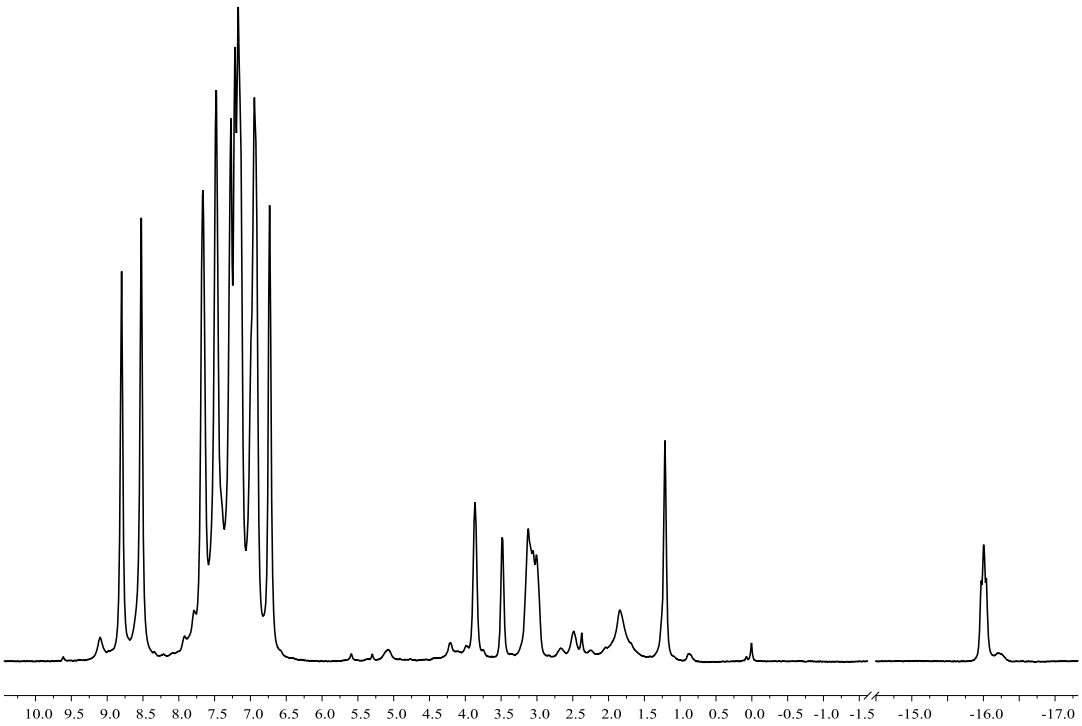

Figure 98. ^{1}H NMR spectrum of compound **22** in $CDCl_3$.

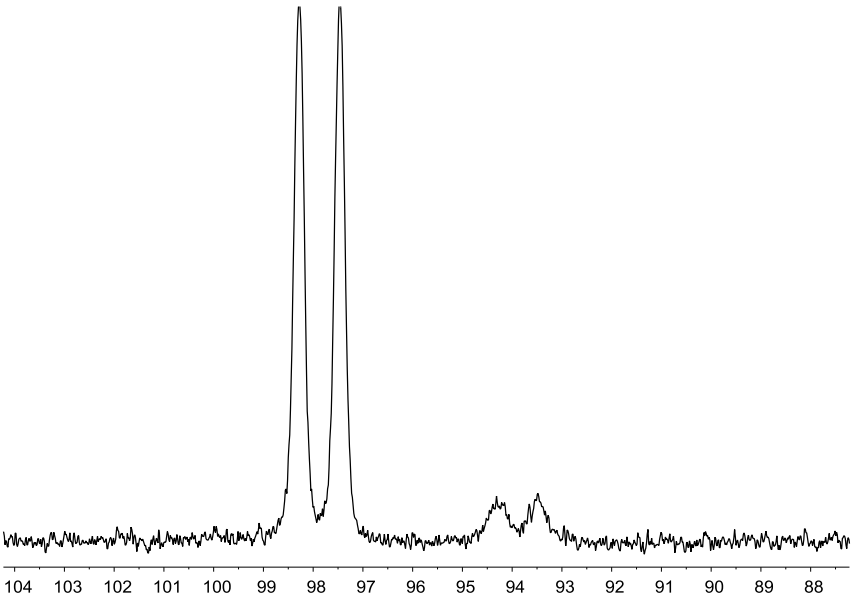

Figure 99. $^{31}P\{^{1}H\}$ NMR spectrum for compound **22** in $CDCl_3$.

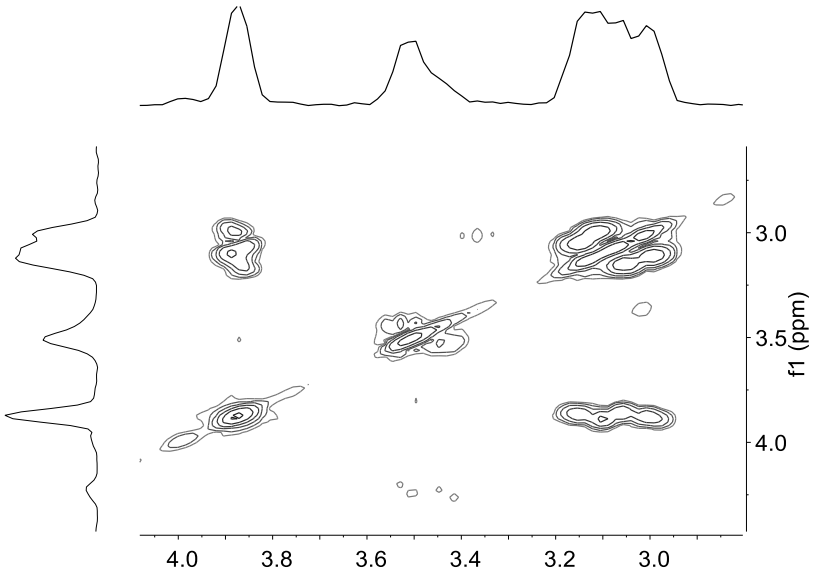

Figure 100. $^{1}H - {}^{1}H$ NMR correlation for compound **22**.

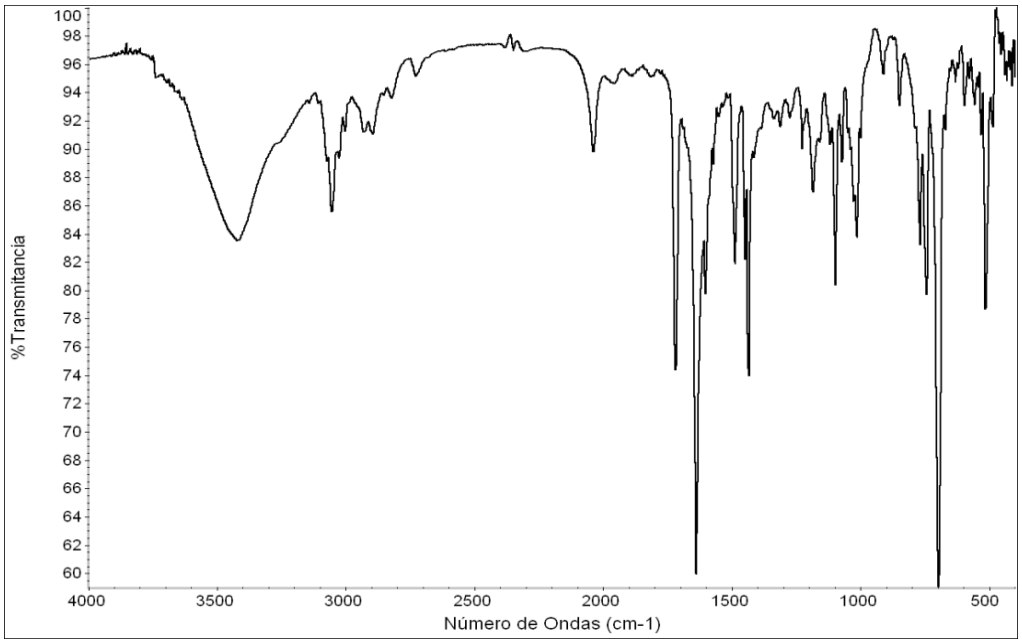

Figure 101. IR spectrum of compound **22**.

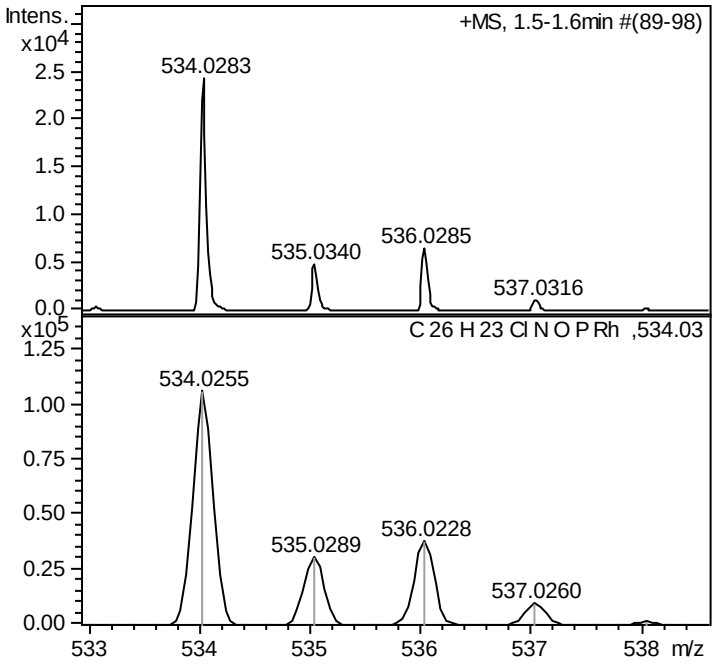

Figure 102. Found (top) and calculated (bottom) ESI-MS of compound **22**.

- **Compound $[RhCl_2(PPh_2CH(Ph)CH_2CO)(py)_2]$ (23)**

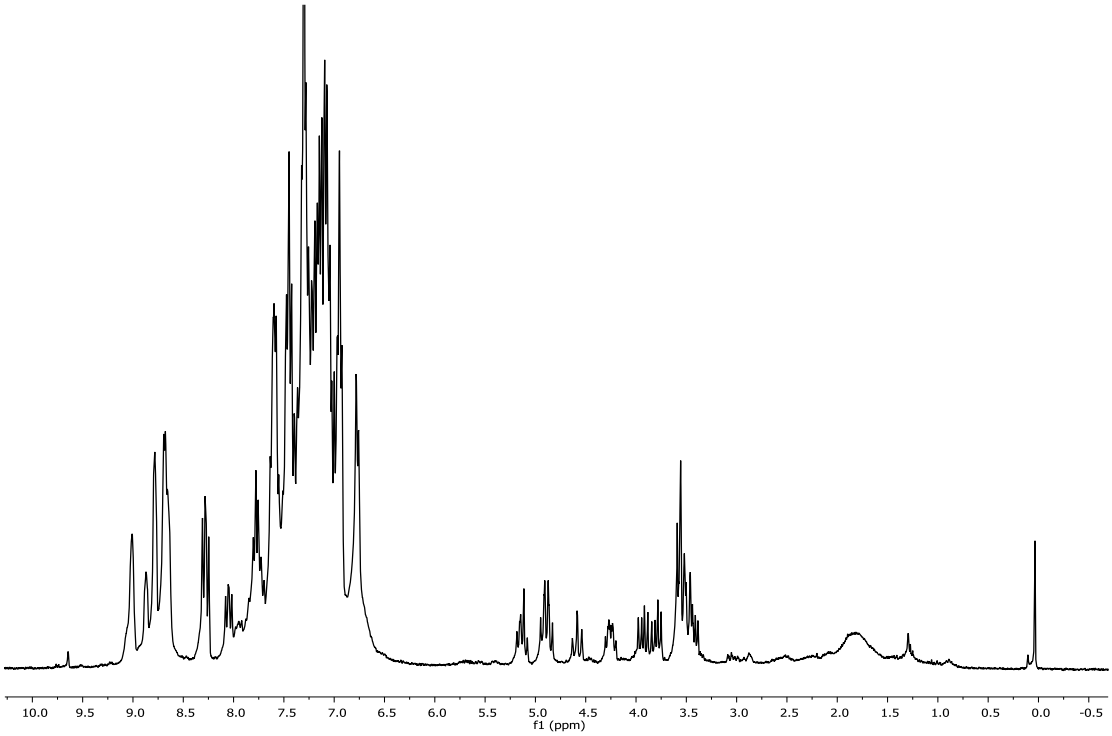

Figure 103. ^{1}H NMR spectrum of compound **23** in $CDCl_3$.

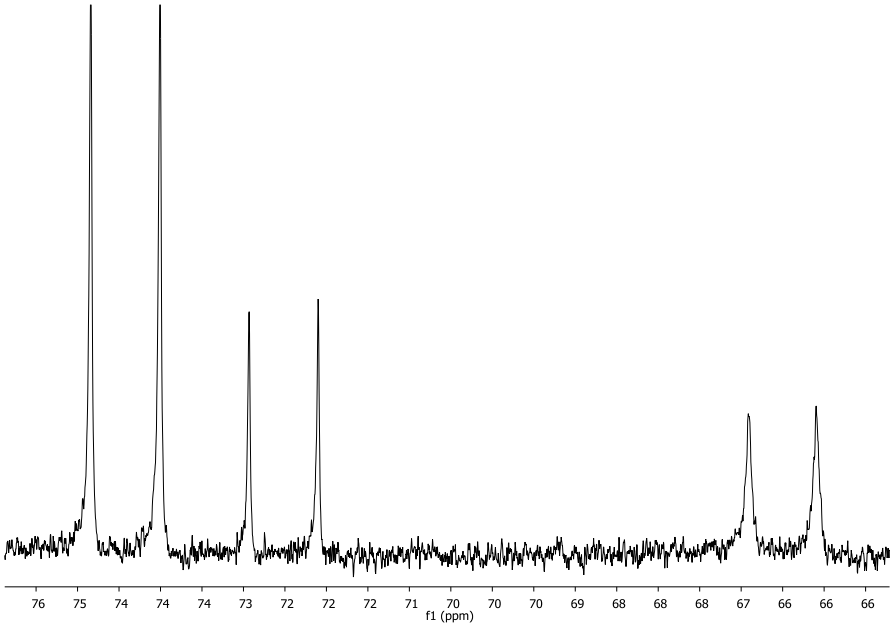

Figure 104. $^{31}P\{^{1}H\}$ NMR spectrum for compound **23** in $CDCl_3$.

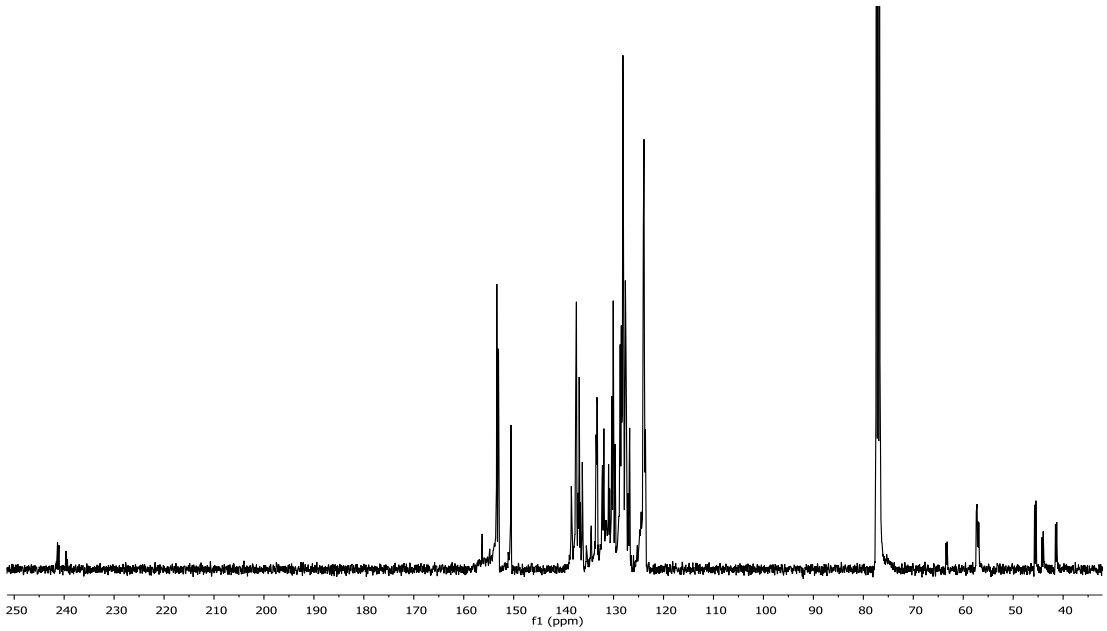

Figure 105. $^{13}C\{^{1}H\}$ NMR spectrum of compound **23** in $CDCl_3$.

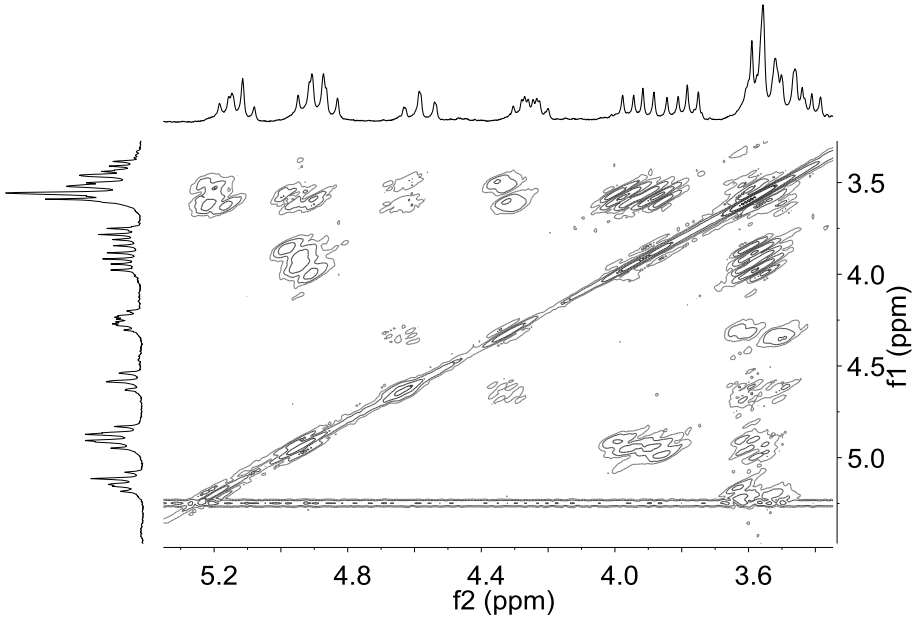

Figure 106. $^{1}H - {}^{1}H$ NMR correlation for compound **23** in $CDCl_3$.

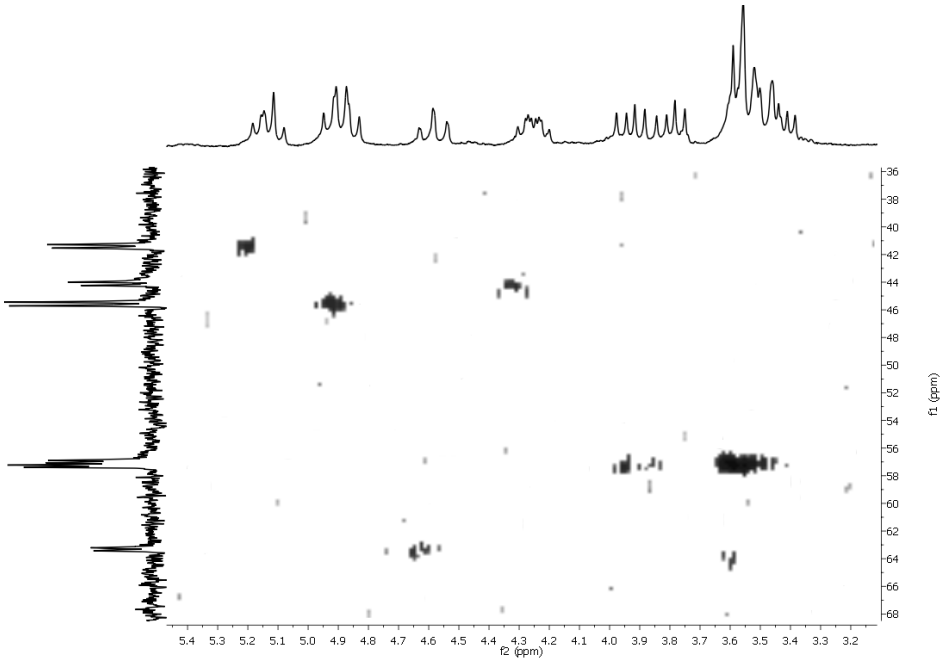

Figure 107. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **23**.

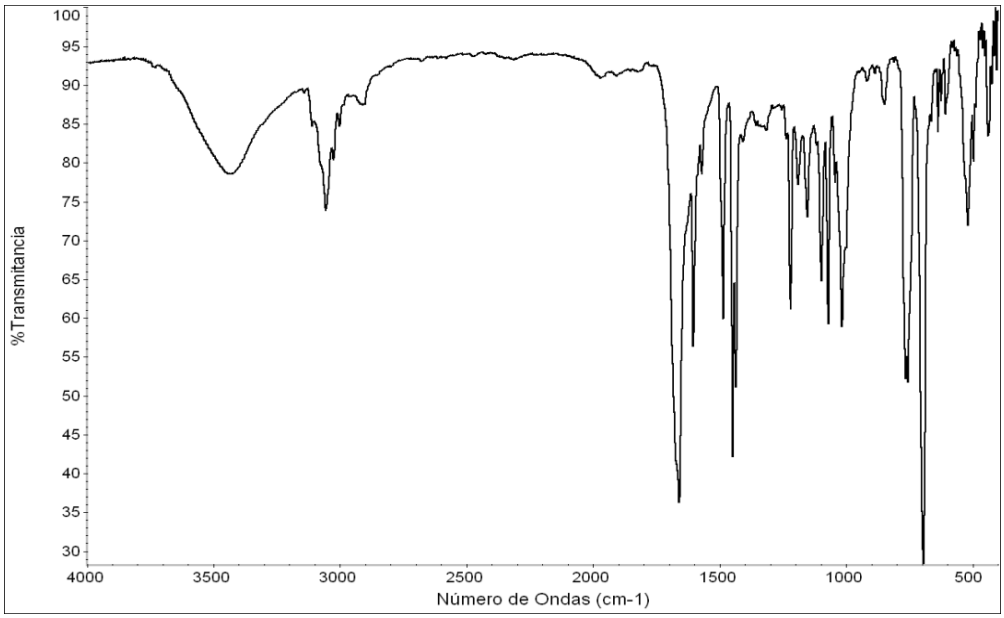

Figure 108. IR spectrum of compound **23**.

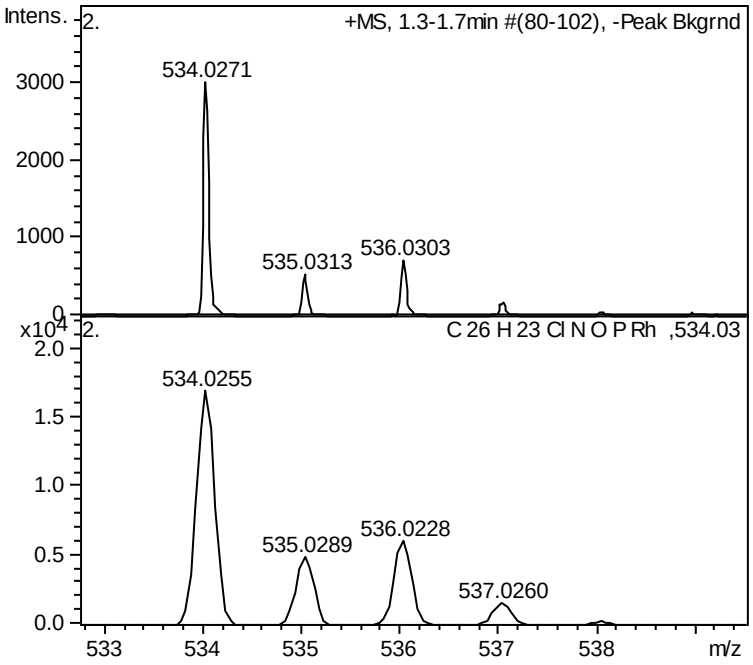

Figure 109. Found (top) and calculated (bottom) ESI-MS of compound **23**.

- **Compound [RhClH($PPh_2CH(Ph)CH_2CO$)($PPh_2CH(Ph)CH_2CHO$)(py)] (24)**

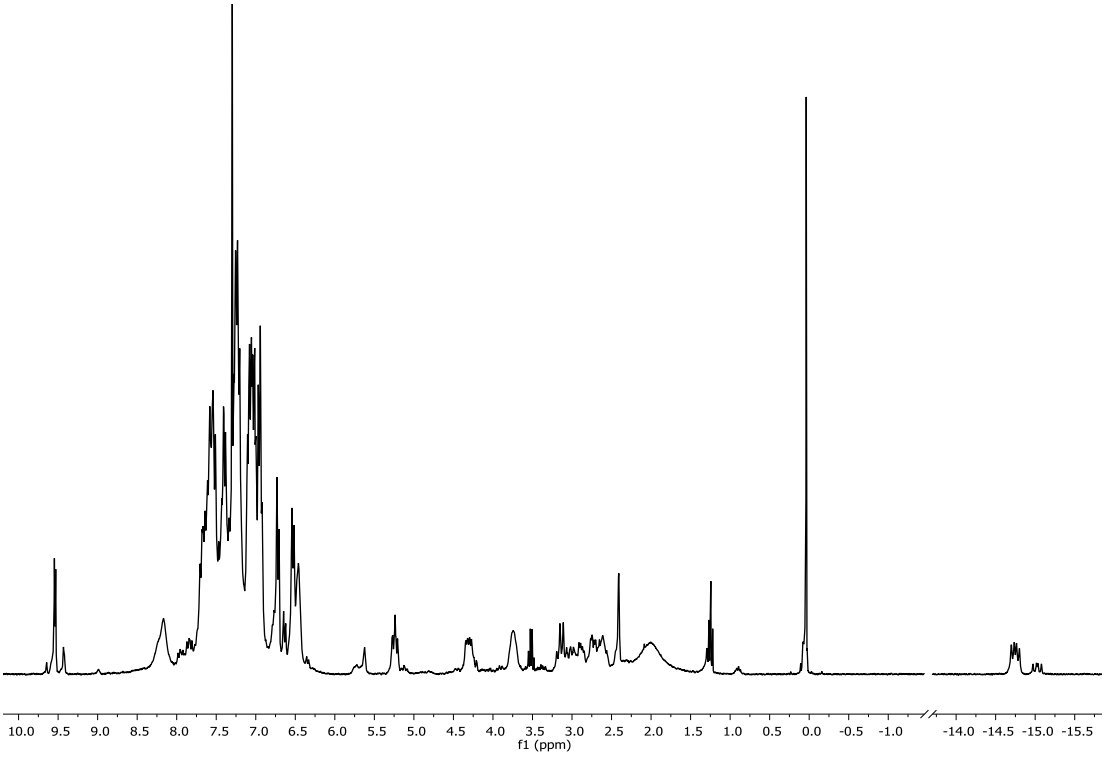

Figure 110. ^{1}H NMR spectrum of compound **24** in $CDCl_3$.

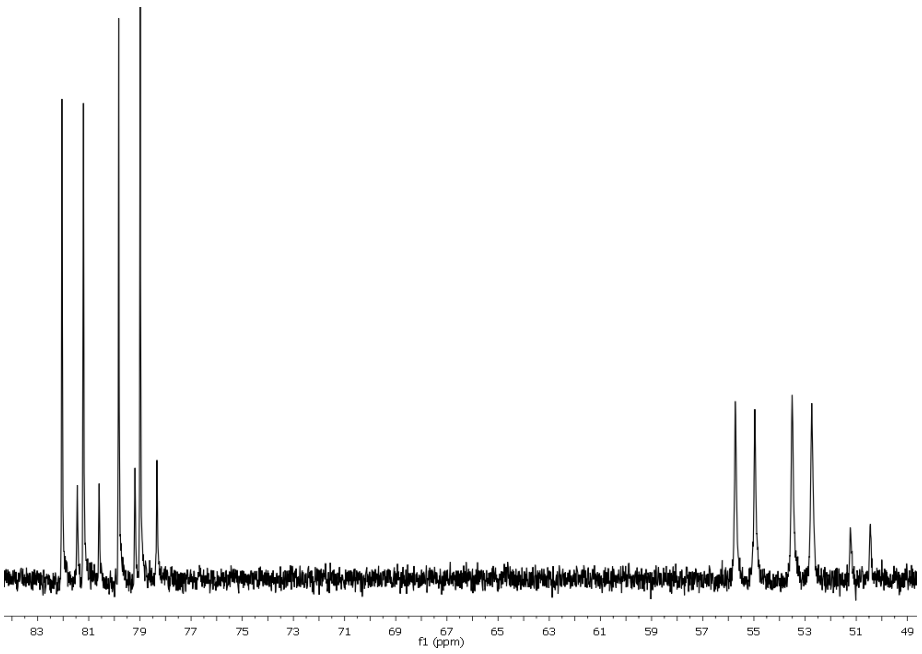

Figure 111. $^{31}P\{^{1}H\}$ NMR spectrum for compound **24** in $CDCl_3$.

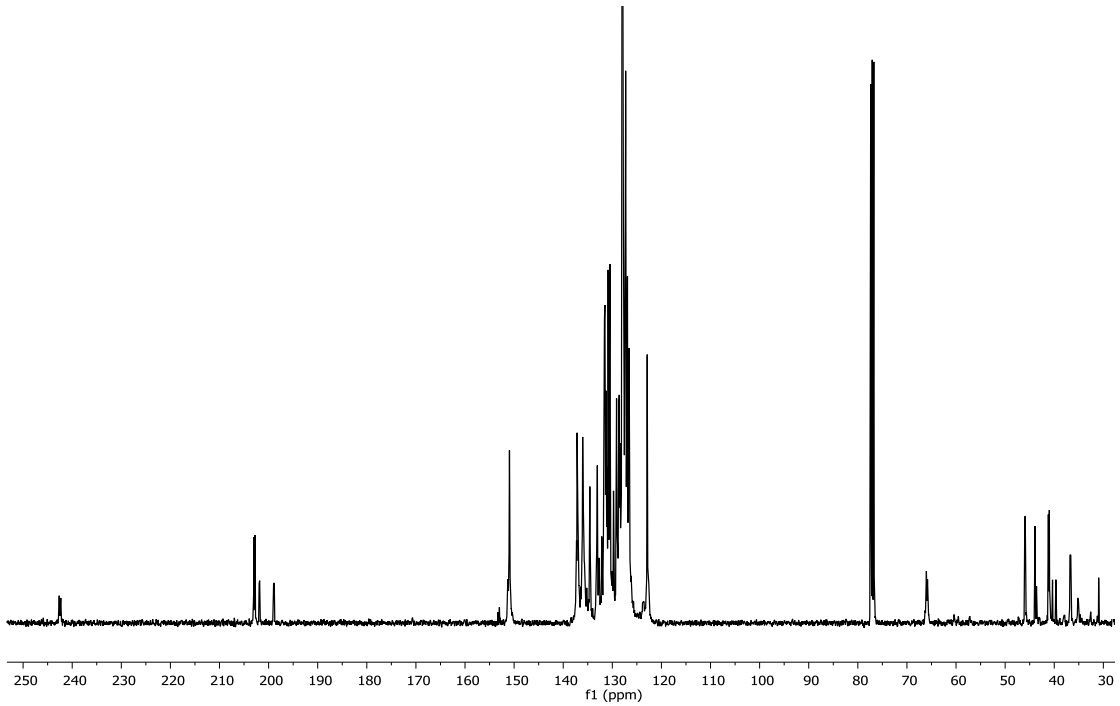

Figure 112. $^{13}C\{^{1}H\}$ NMR spectrum of compound **24** in $CDCl_3$.

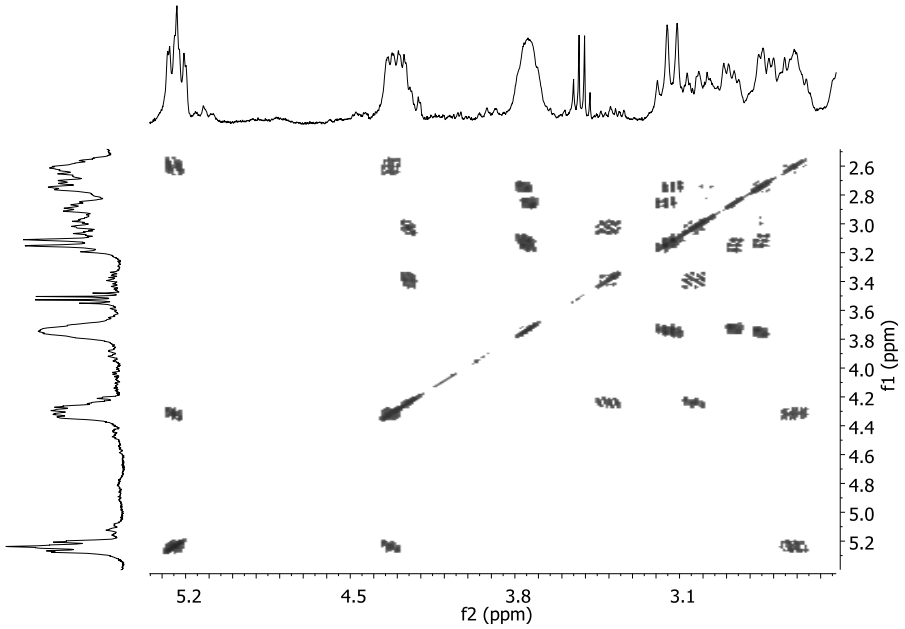

Figure 113. $^{1}H - {}^{1}H$ NMR correlation for compound **24**.

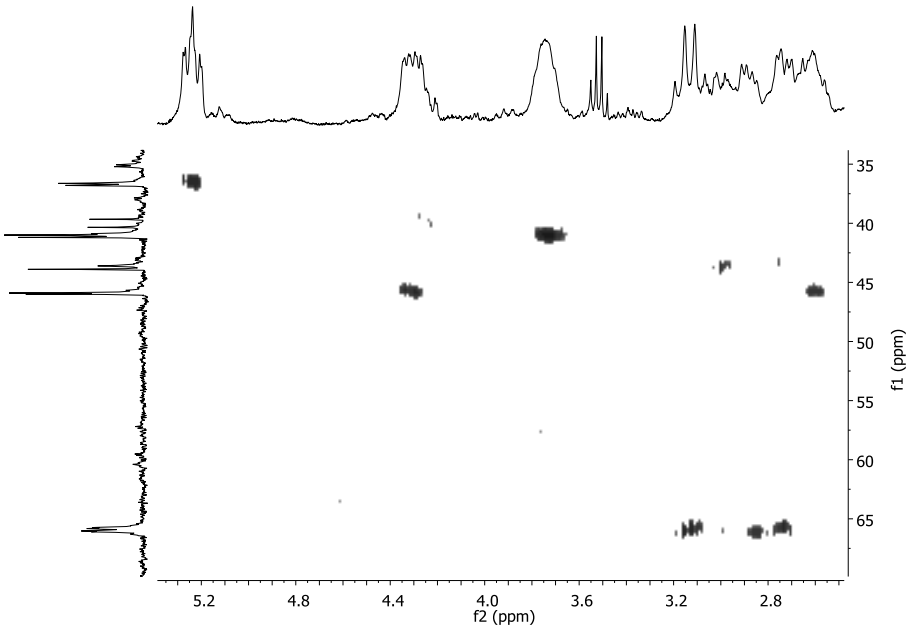

Figure 114. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **24**.

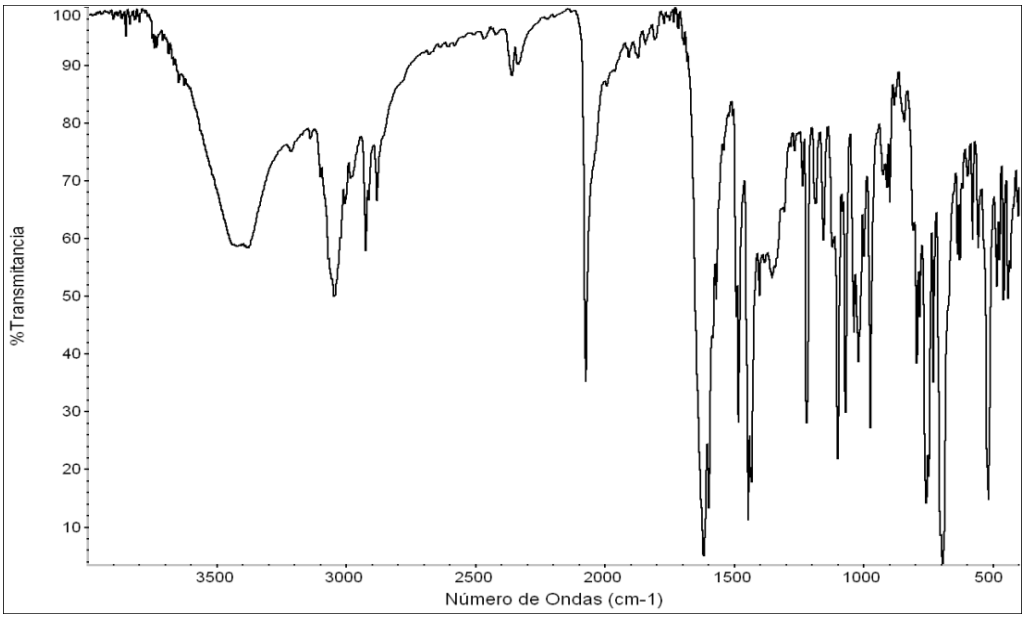

Figure 115. IR spectrum of compound **24**.

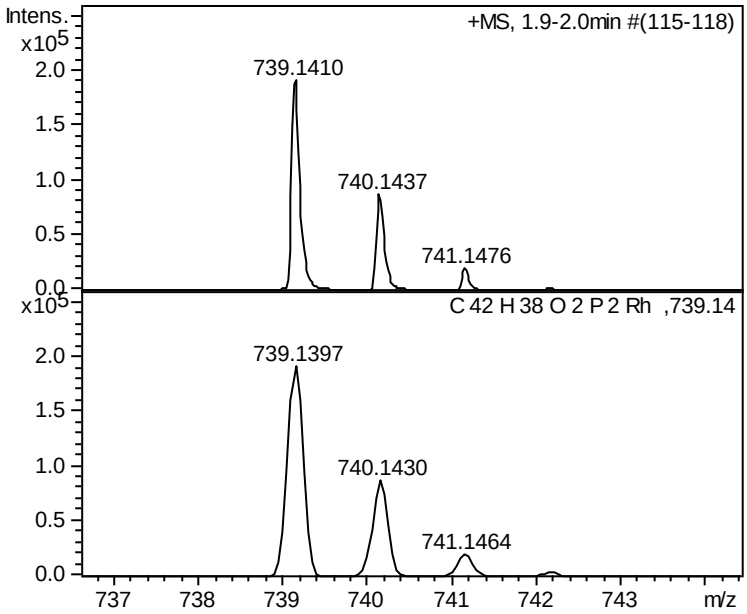

Figure 116. Found (top) and calculated (bottom) ESI-MS of compound **24**.

- **Compound [RhClH(PPh_2(*o*-C_6H_4CO))(κ^1-PPh_2(CH(Ph)CH_2CHO))(py)] (25)**

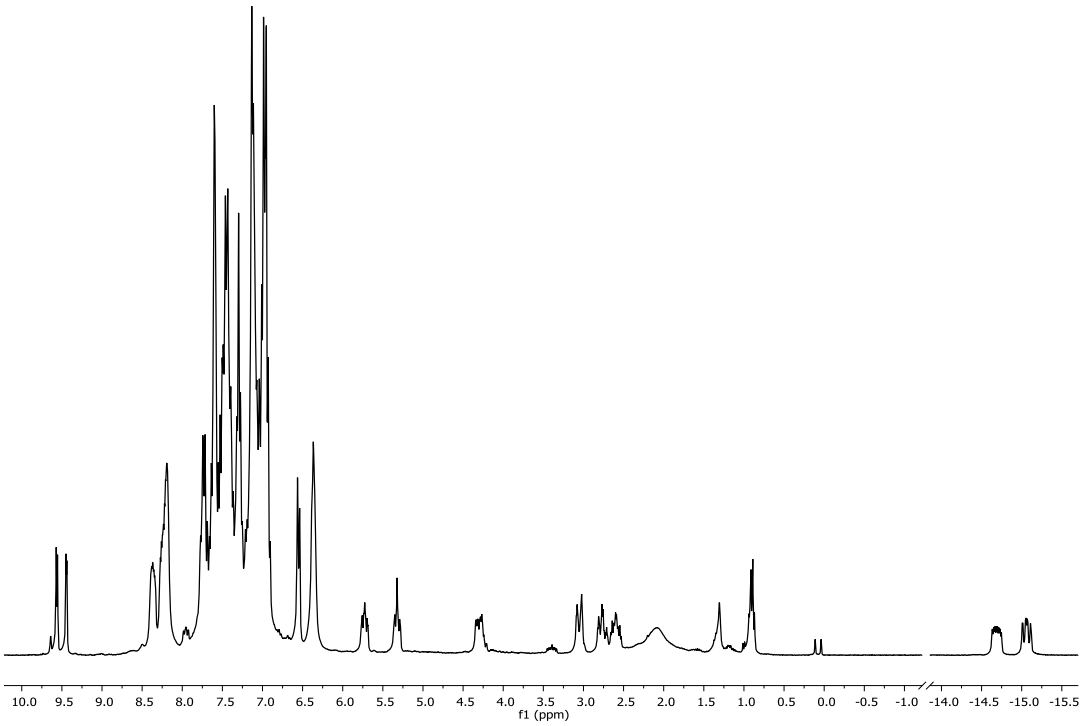

Figure 117. ^{1}H NMR spectrum of compound **25** in $CDCl_3$.

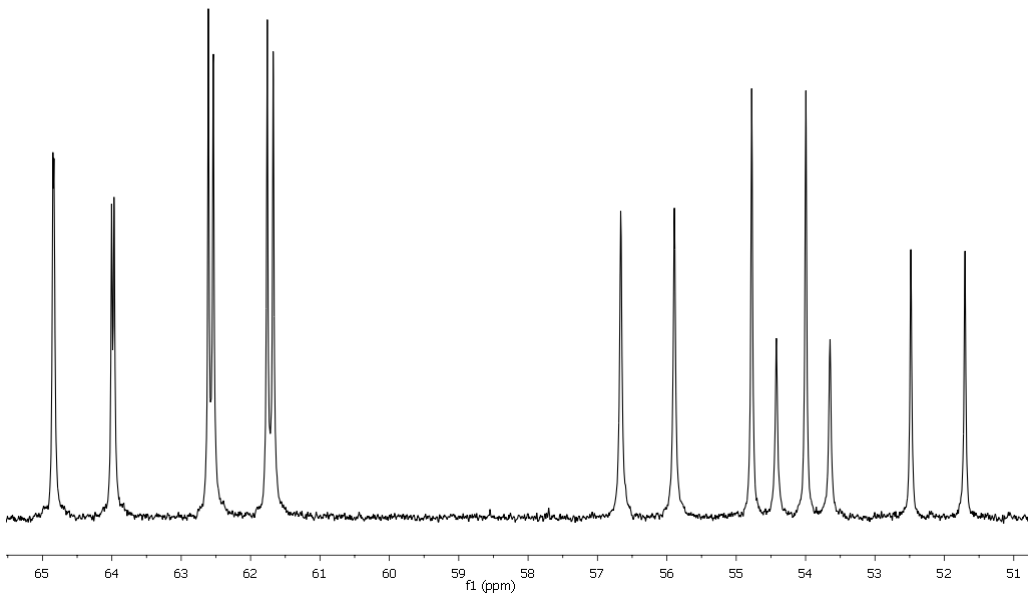

Figure 118. $^{31}P\{^1H\}$ NMR spectrum for compound **25** in $CDCl_3$.

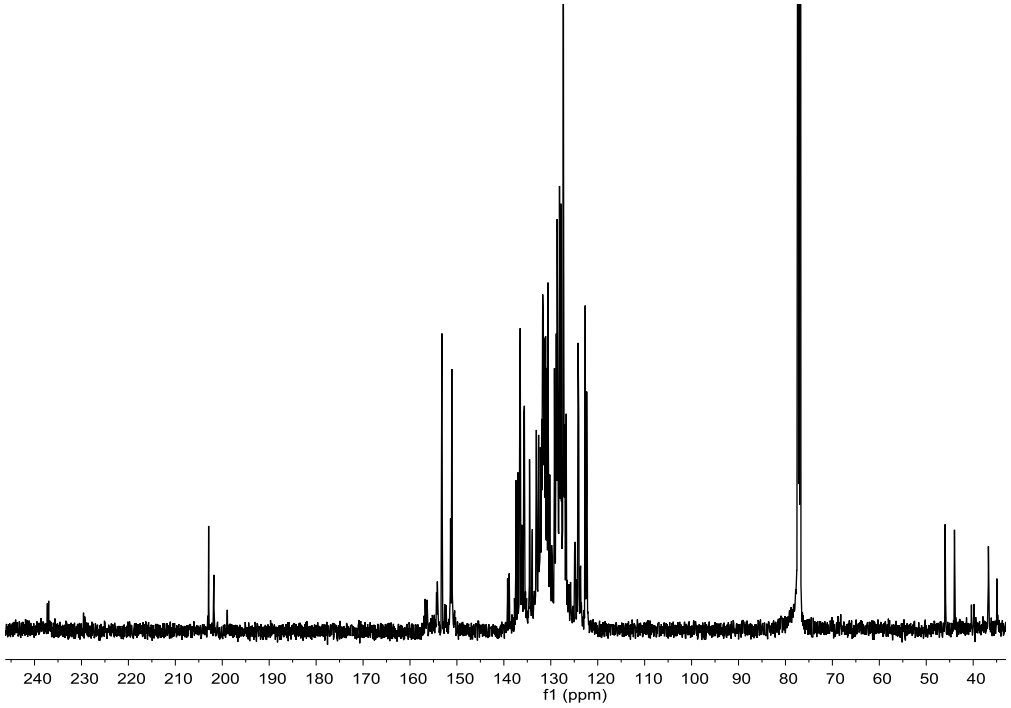

Figure 119. $^{13}C\{^{1}H\}$ NMR spectrum of compound **25** in $CDCl_3$.

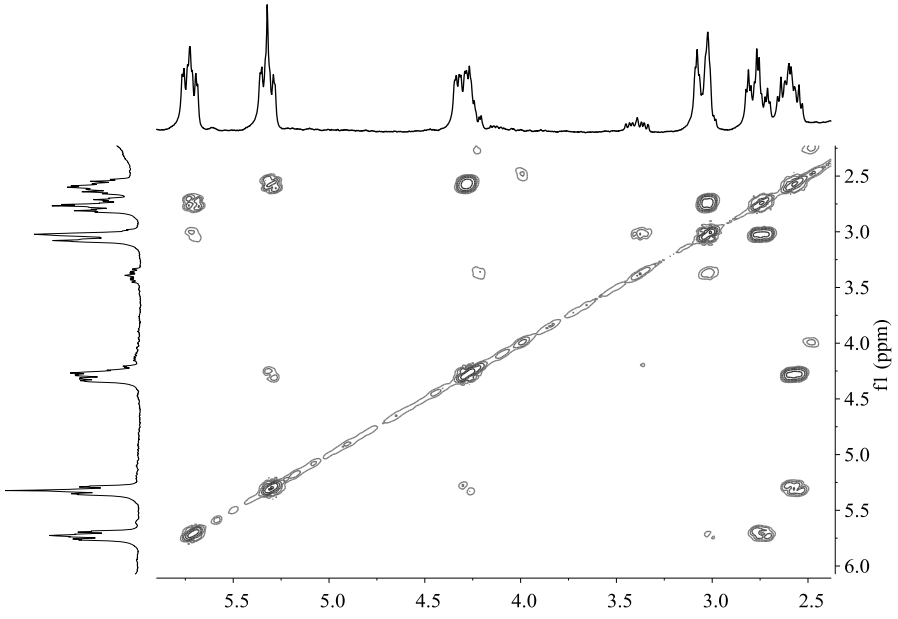

Figure 120. $^{1}H - {}^{1}H$ NMR correlation for compound **25**.

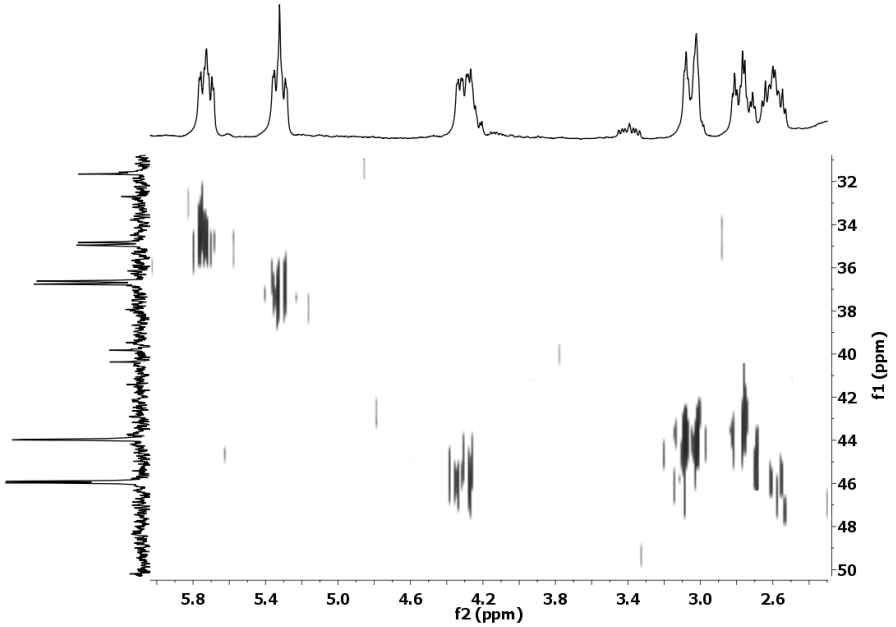

Figure 121. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **25**.

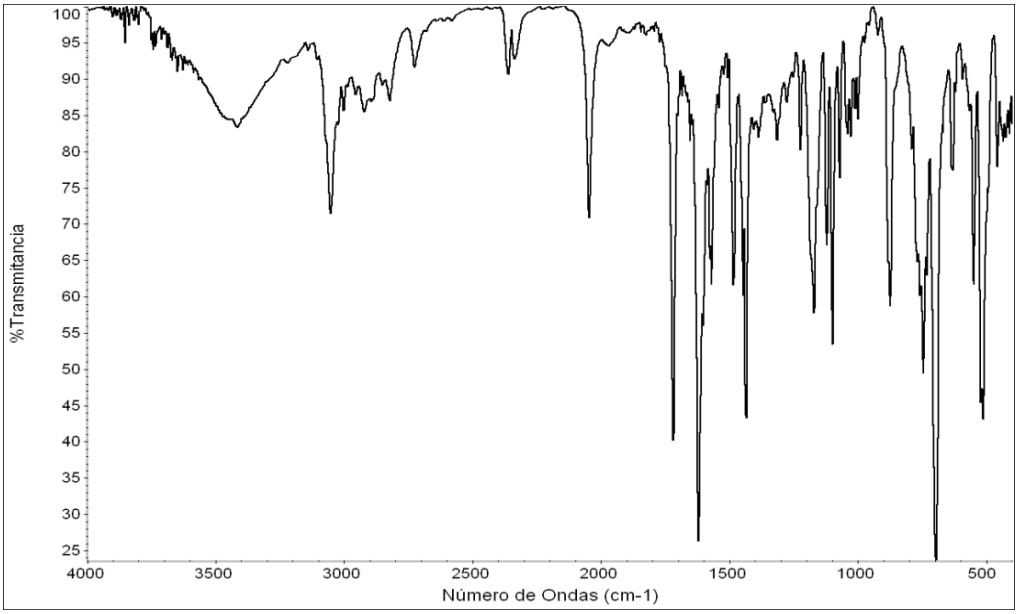

Figure 122. IR spectrum of compound **25**.

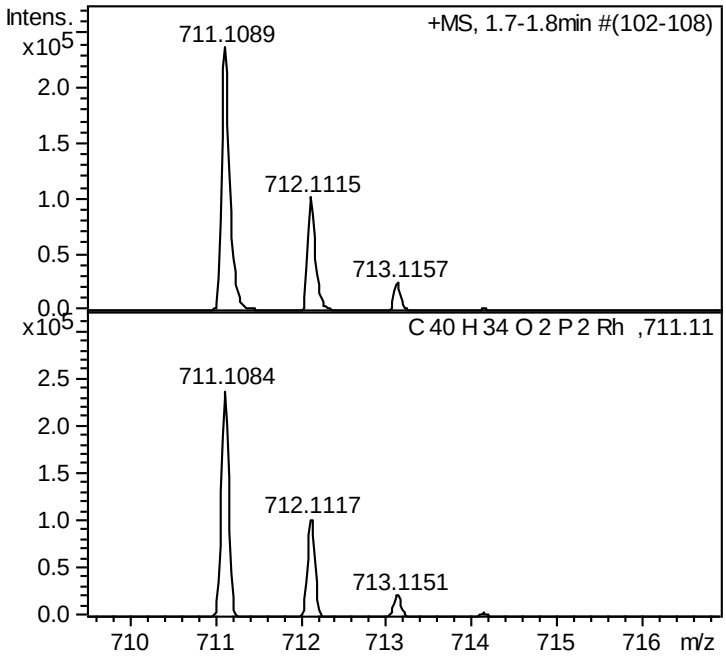

Figure 123. Found (top) and calculated (bottom) ESI-MS of compound **25**.

- **Compound [RhH(phen)(PPh$_2$(*o*-C$_6$H$_4$CO))(κ^1-PPh$_2$(CH(Ph)CH$_2$CHO))]BPh$_4$ (26)**

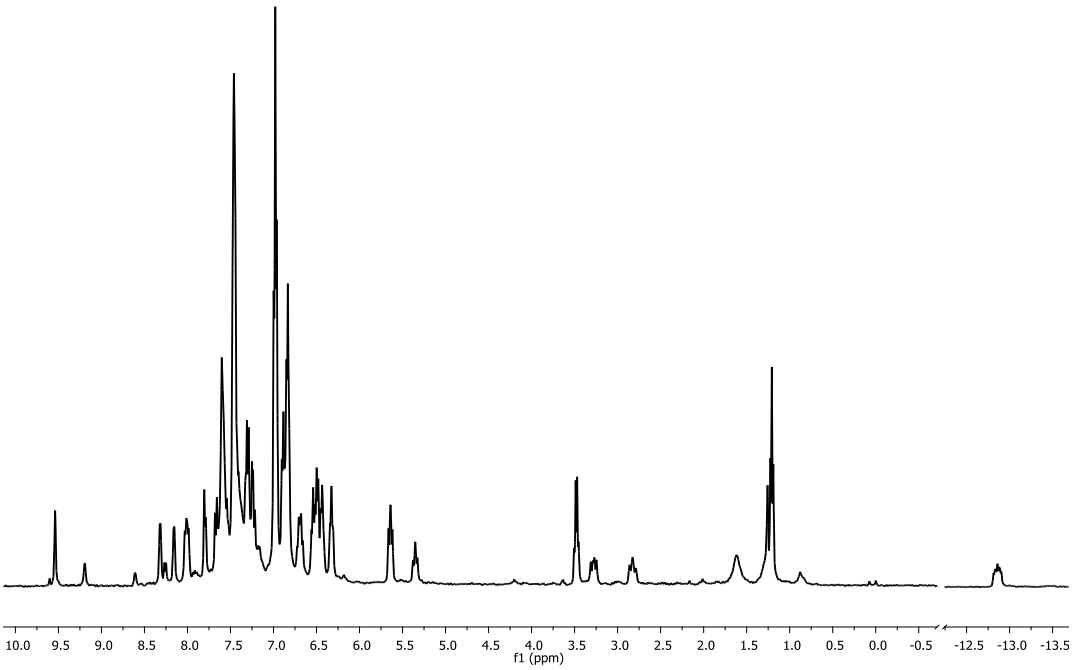

Figure 124. ^{1}H NMR spectrum of compound **26a** in $CDCl_3$.

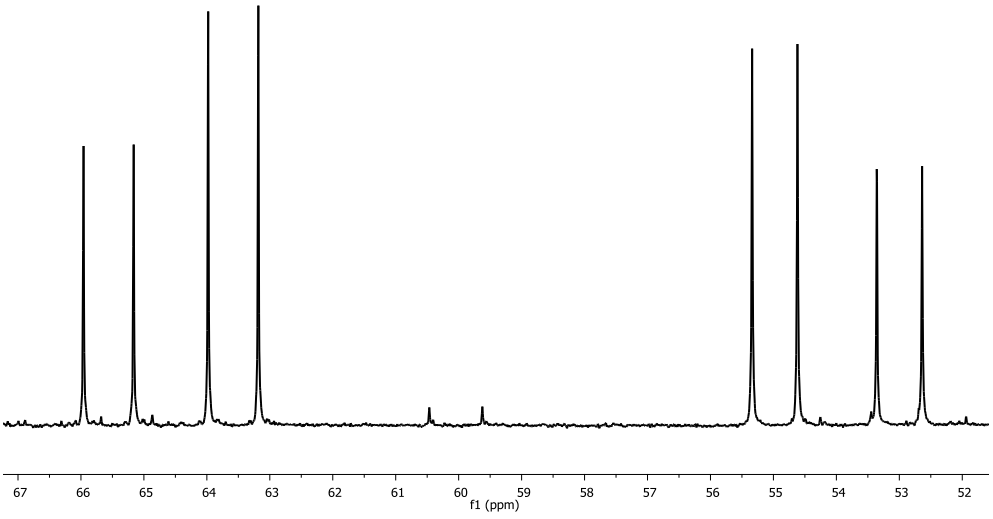

Figure 125. $^{31}P\{^1H\}$ NMR spectrum for compound **26a** in $CDCl_3$.

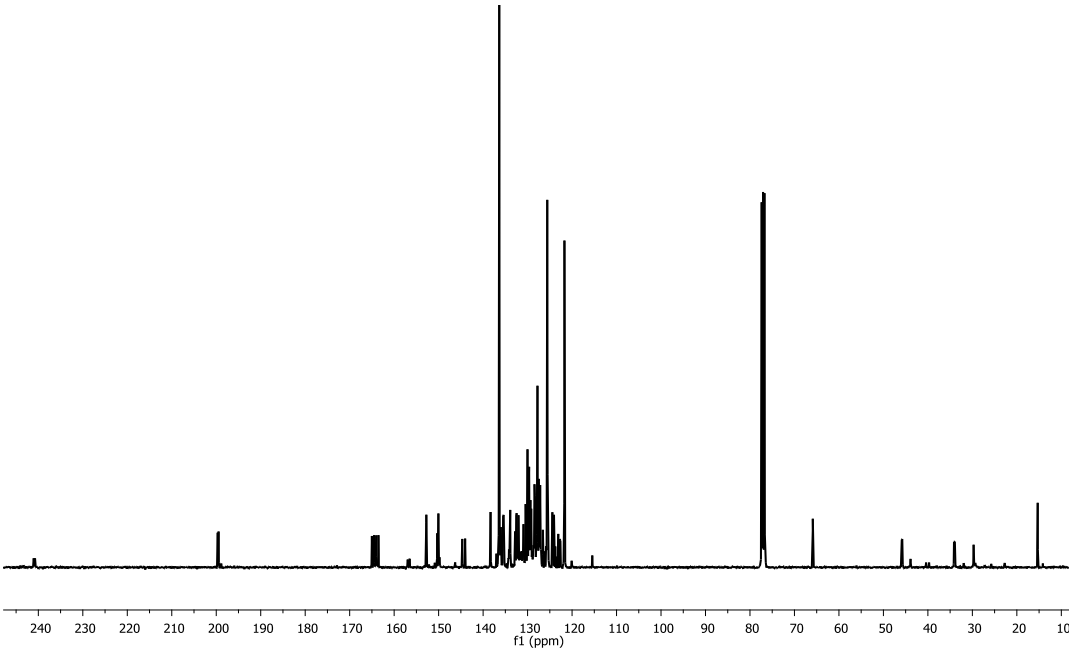

Figure 126. $^{13}C\{^{1}H\}$ NMR spectrum of compound **26a** in $CDCl_3$.

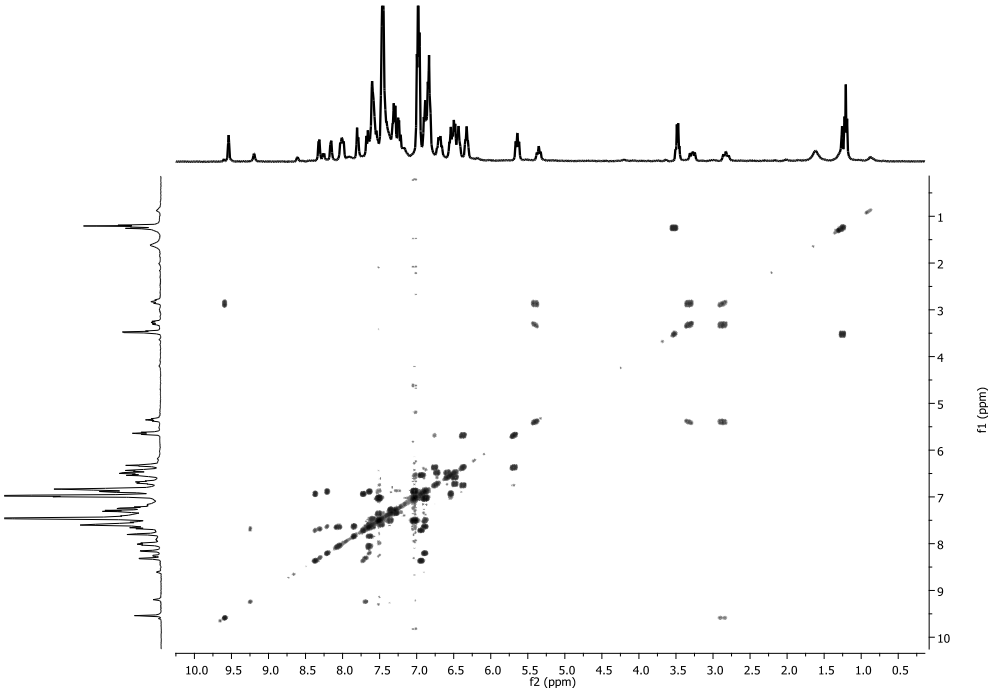

Figure 127. $^{1}H - {}^{1}H$ NMR correlation for compound **26a**.

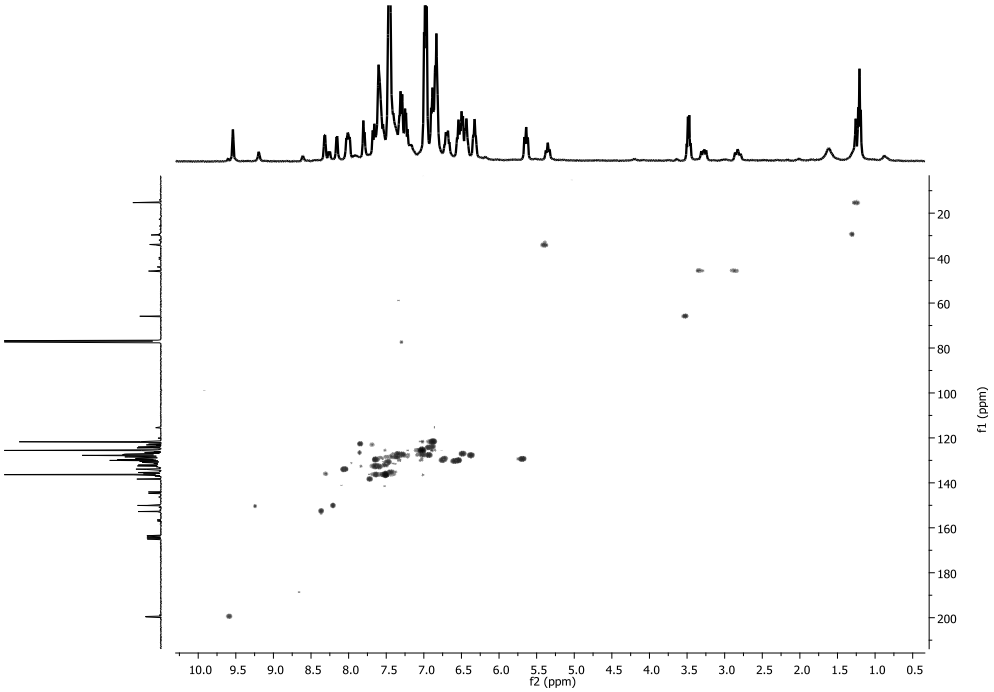

Figure 128. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **26a**.

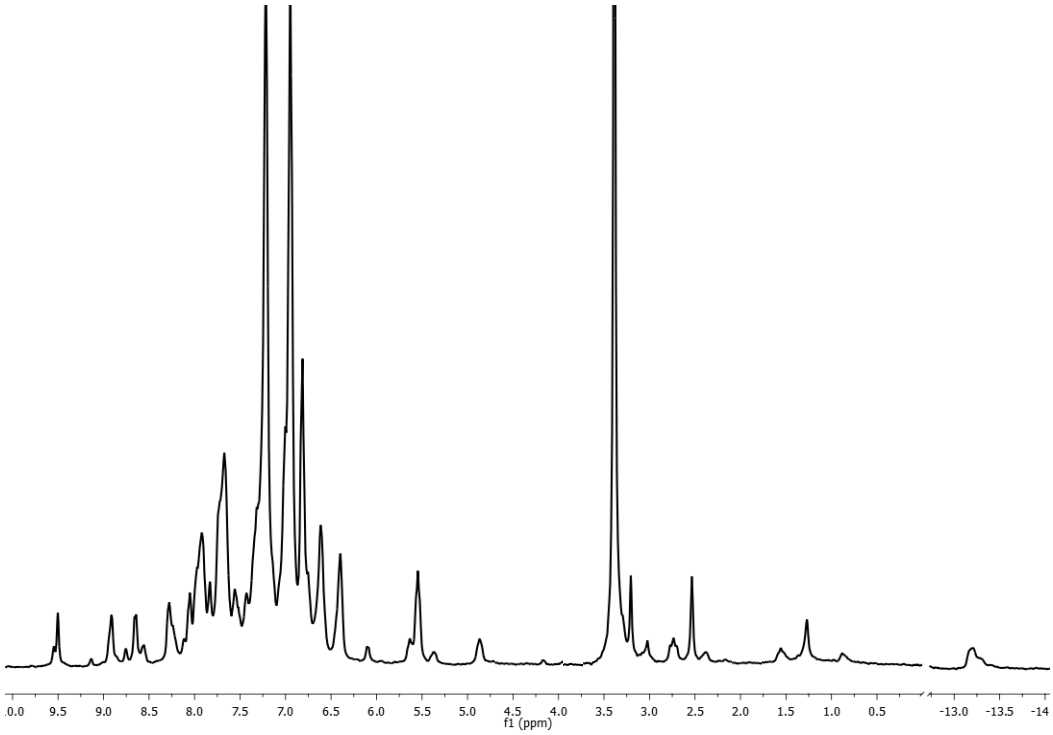

Figure 129. ^{1}H NMR spectrum of compound **26a'** in DMSO-d_6.

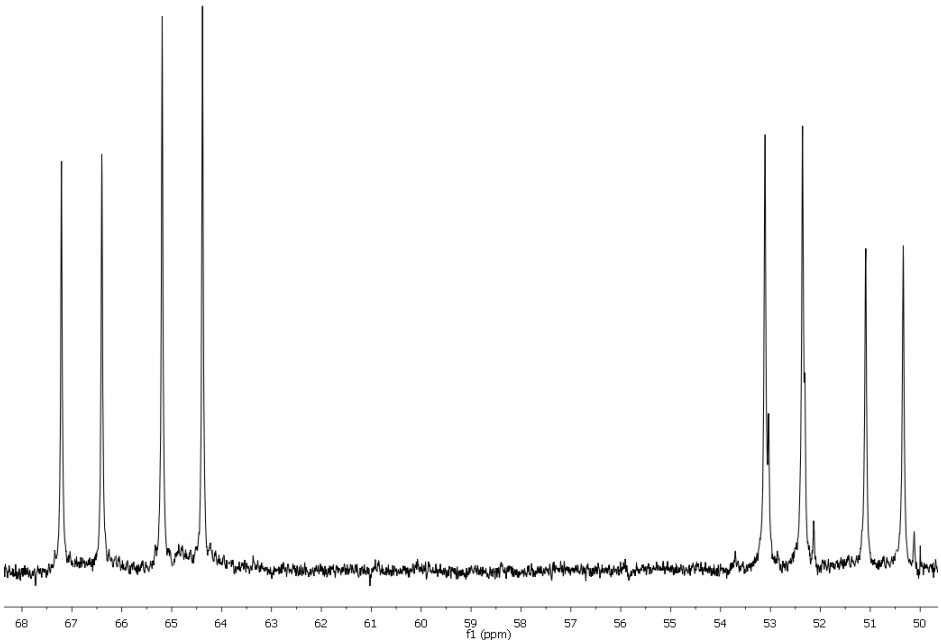

Figure 130. $^{31}P\{^{1}H\}$ NMR spectrum for compound **26a'** in DMSO-d_6.

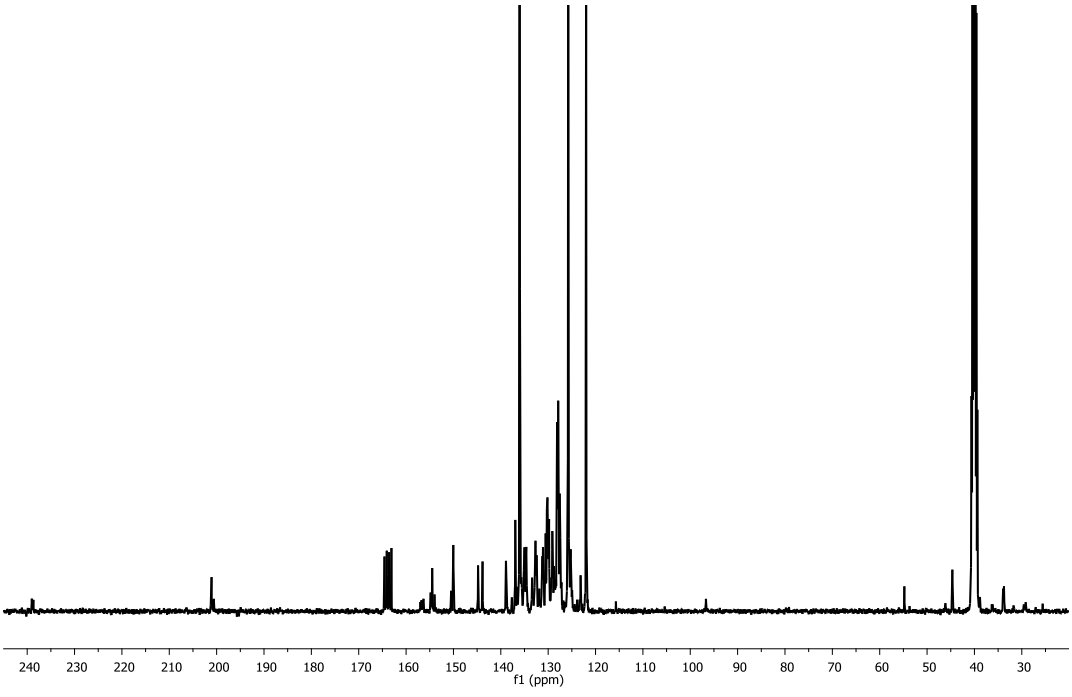

Figure 131. $^{13}C\{^{1}H\}$ NMR spectrum of compound **26a'** in DMSO-d_6.

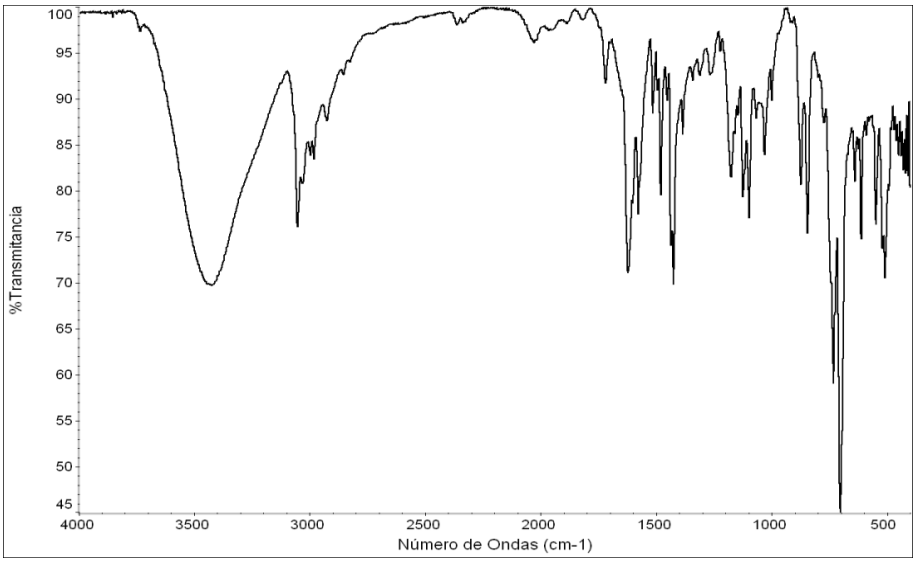

Figure 132. IR spectrum of compound **26**.

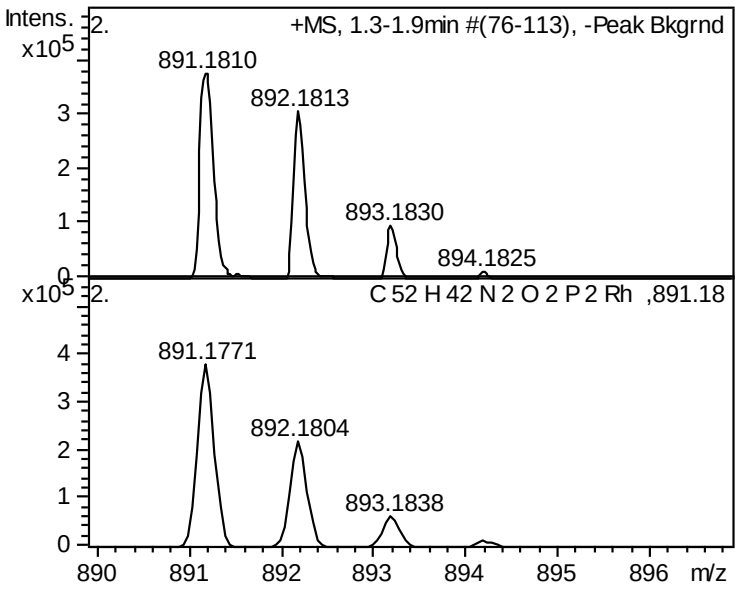

Figure 133. Found (top) and calculated (bottom) ESI-MS of compound **26**.

- **Compound [RhH(bipy)(PPh$_2$(*o*-C$_6$H$_4$CO))(κ^1-PPh$_2$(CH(Ph)CH$_2$CHO))]BPh$_4$ (27)**

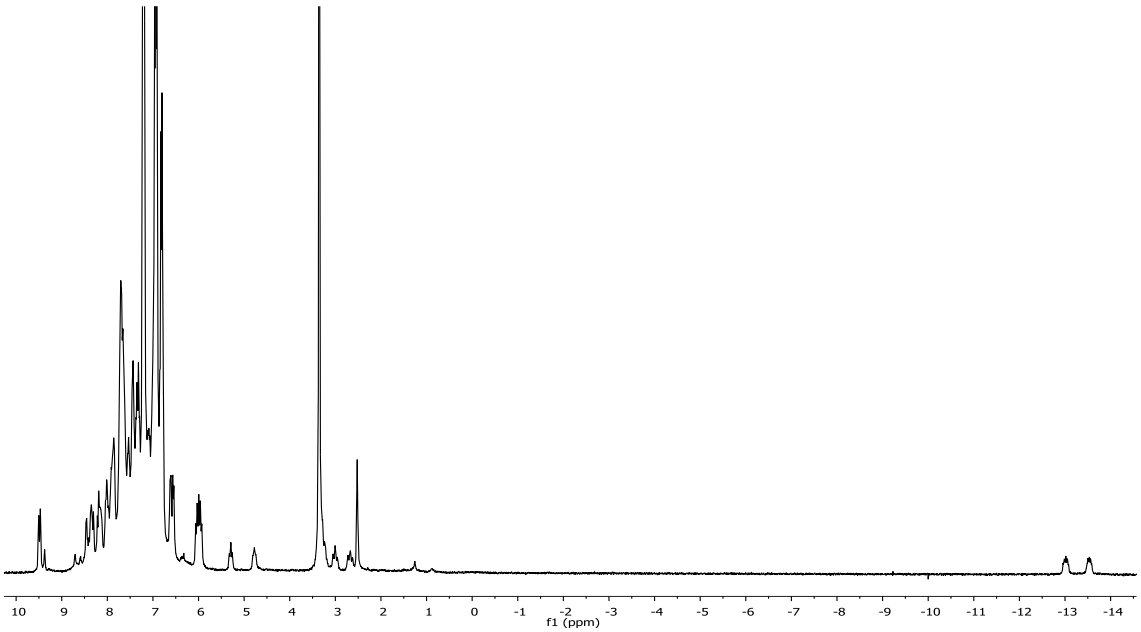

Figure 134. ^{1}H NMR spectrum of compound **27** in DMSO-d$_6$.

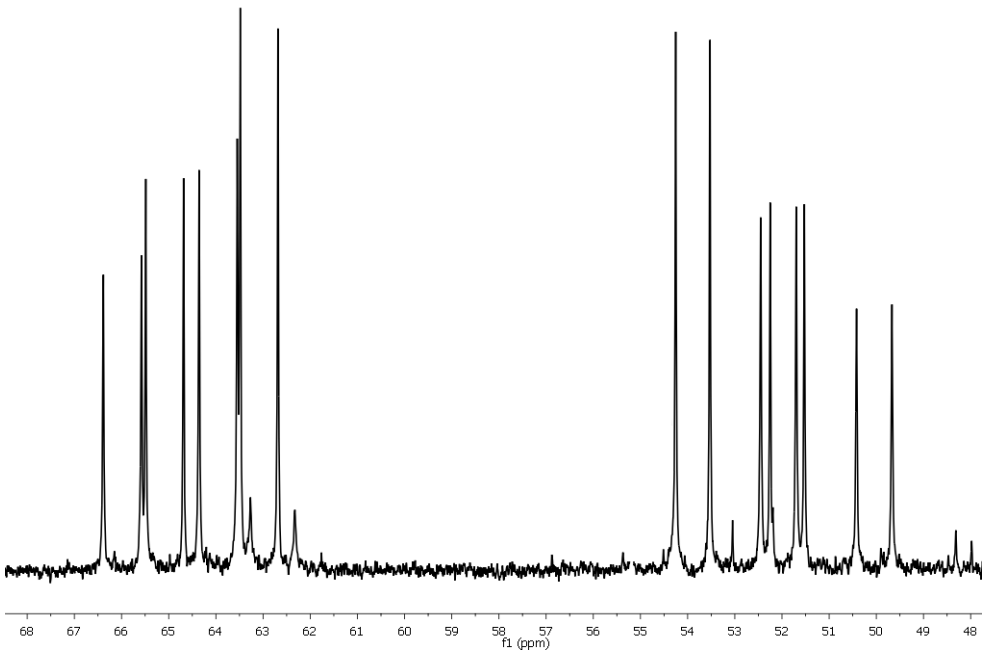

Figure 135. ^{31}P{^{1}H} NMR spectrum for compound **27** in DMSO-d$_6$.

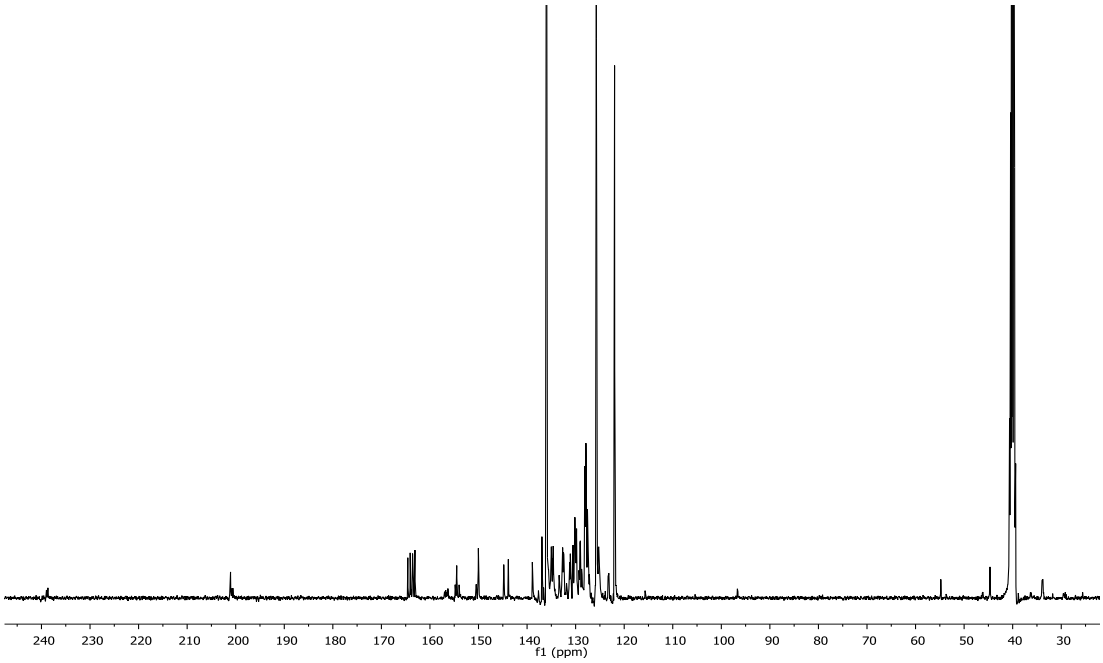

Figure 136. $^{13}C\{^{1}H\}$ NMR spectrum of compound **27** in DMSO-d_6.

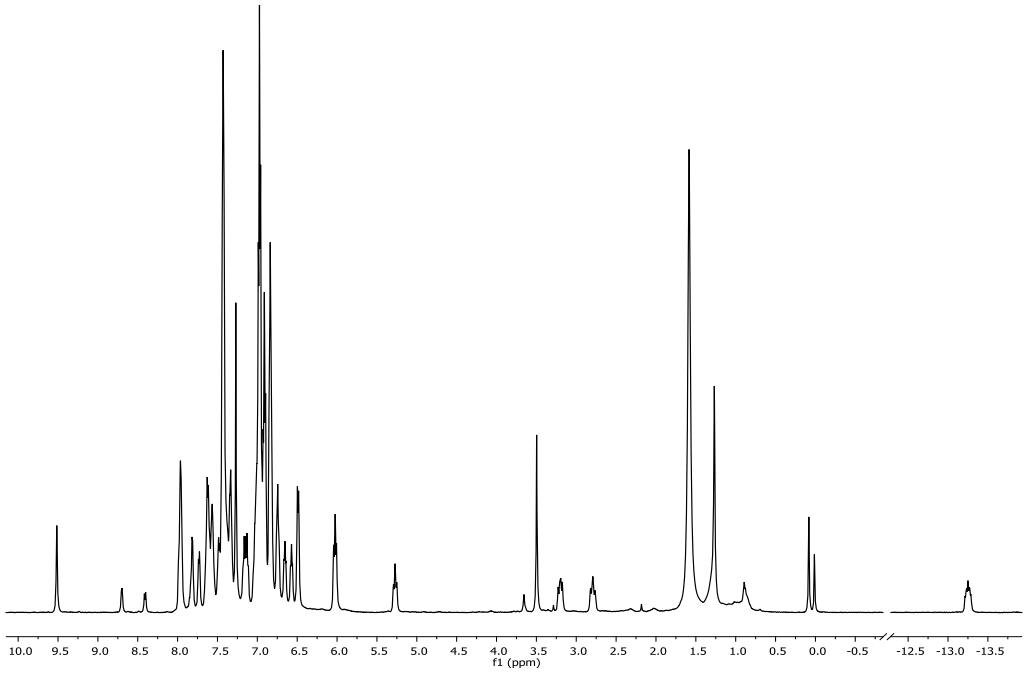

Figure 137. ^{1}H NMR spectrum of compound **27a** in $CDCl_3$.

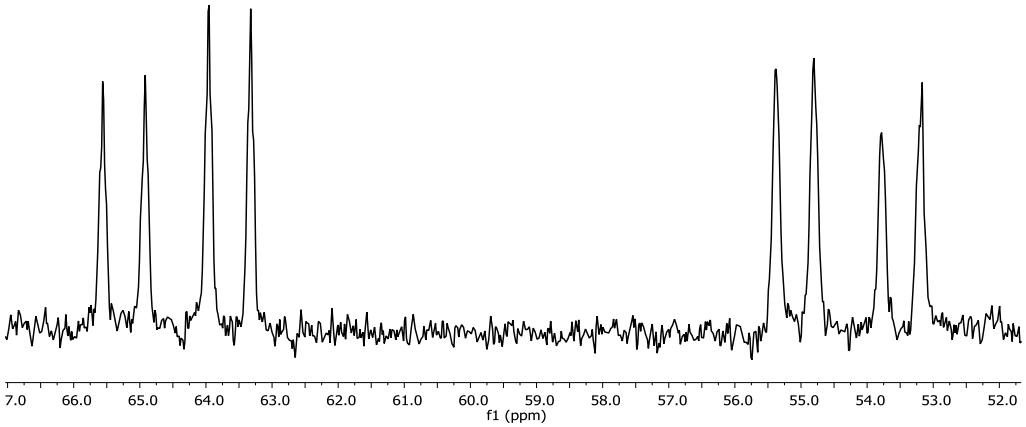

Figure 138. $^{31}P\{^{1}H\}$ NMR spectrum for compound **27a** in $CDCl_3$.

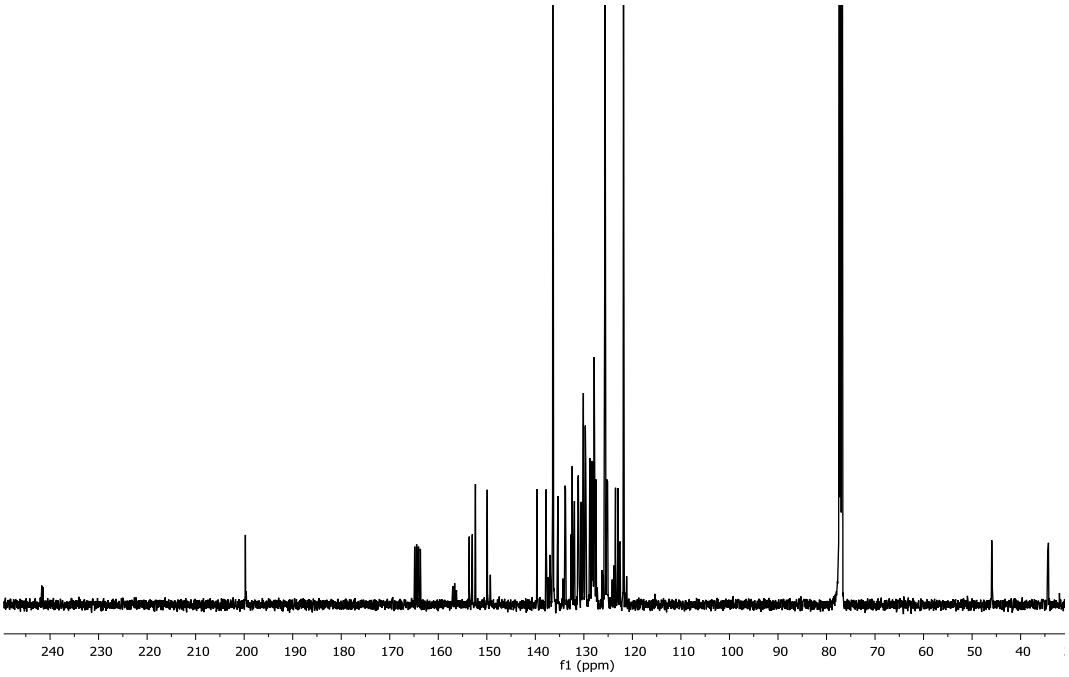

Figure 139. $^{13}C\{^{1}H\}$ NMR spectrum of compound **27a** in $CDCl_3$.

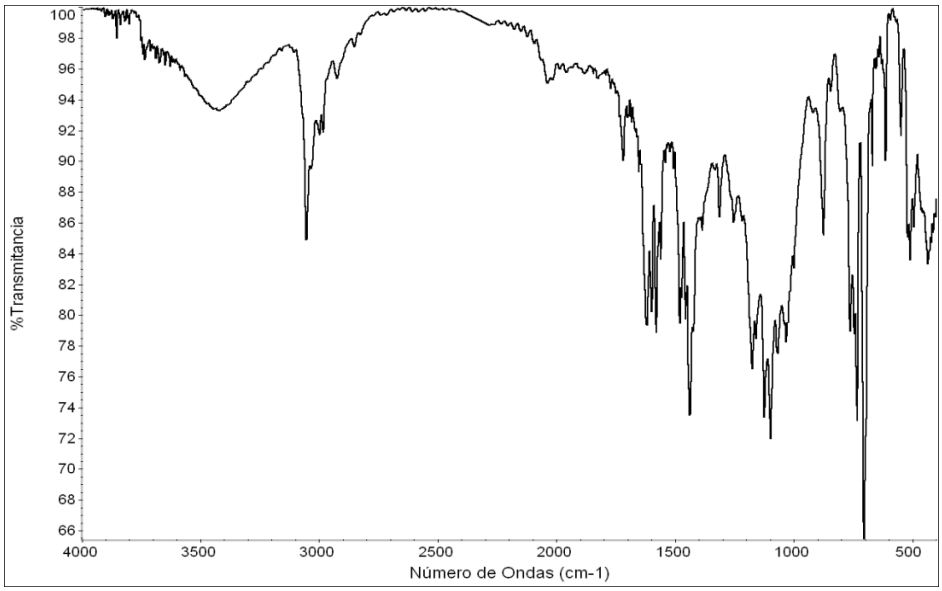

Figure 140. IR spectrum of compound **27**.

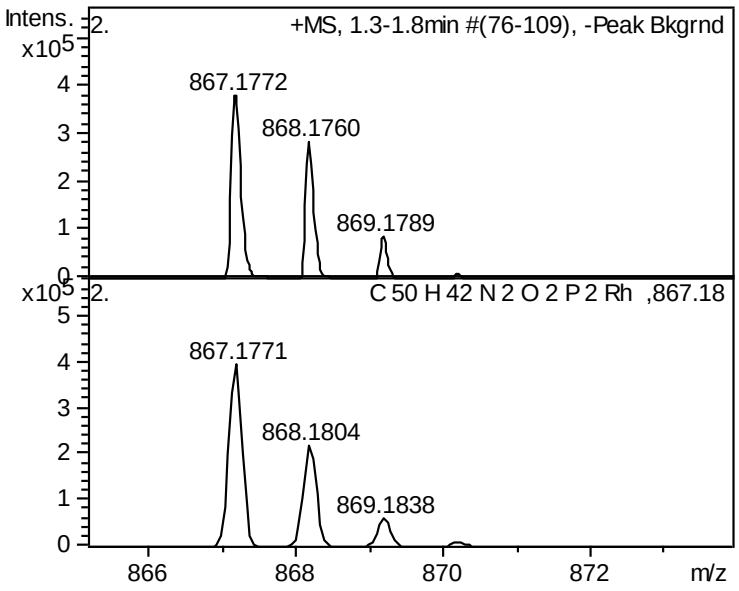

Figure 141. Found (top) and calculated (bottom) ESI-MS of compound **27**.

- **Compound [RhH(PPh_2(*o*-C_6H_4CO))(κ^3-PPh_2($CH(Ph)CH_2CNC_9H_6N$)]BF_4 (28)**

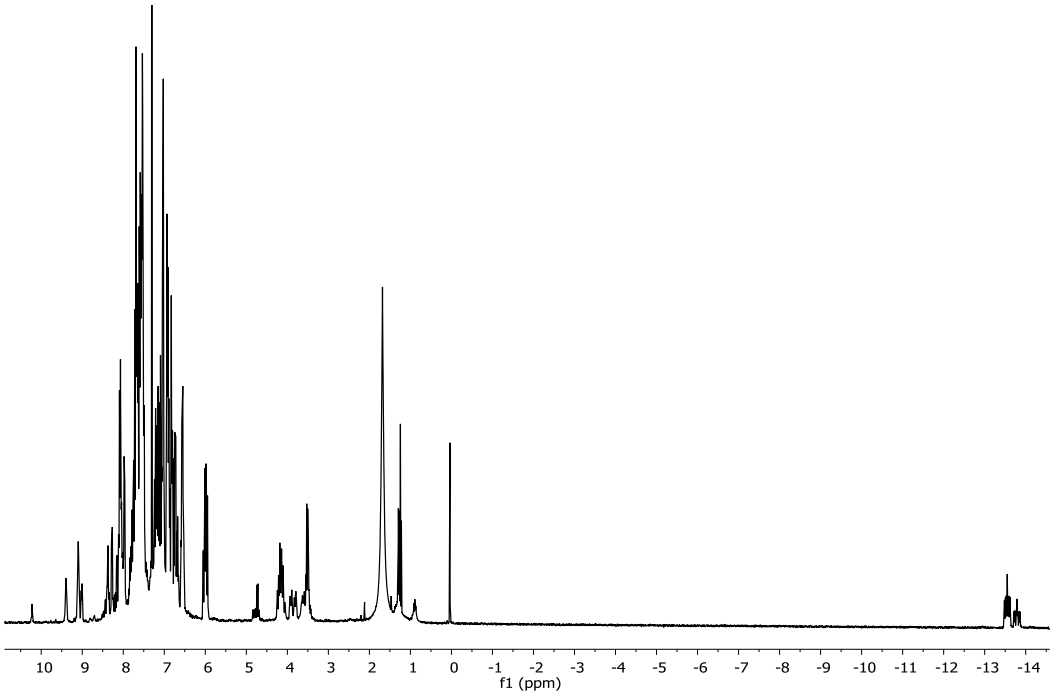

Figure 142. ^1H NMR spectrum of compound **28** in $CDCl_3$.

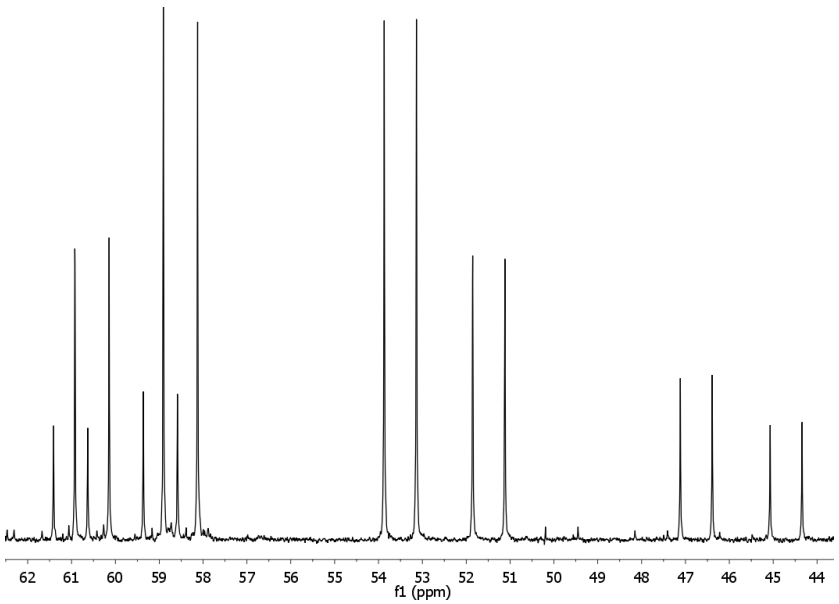

Figure 143. $^{31}P\{^1H\}$ NMR spectrum for compound **28** in $CDCl_3$.

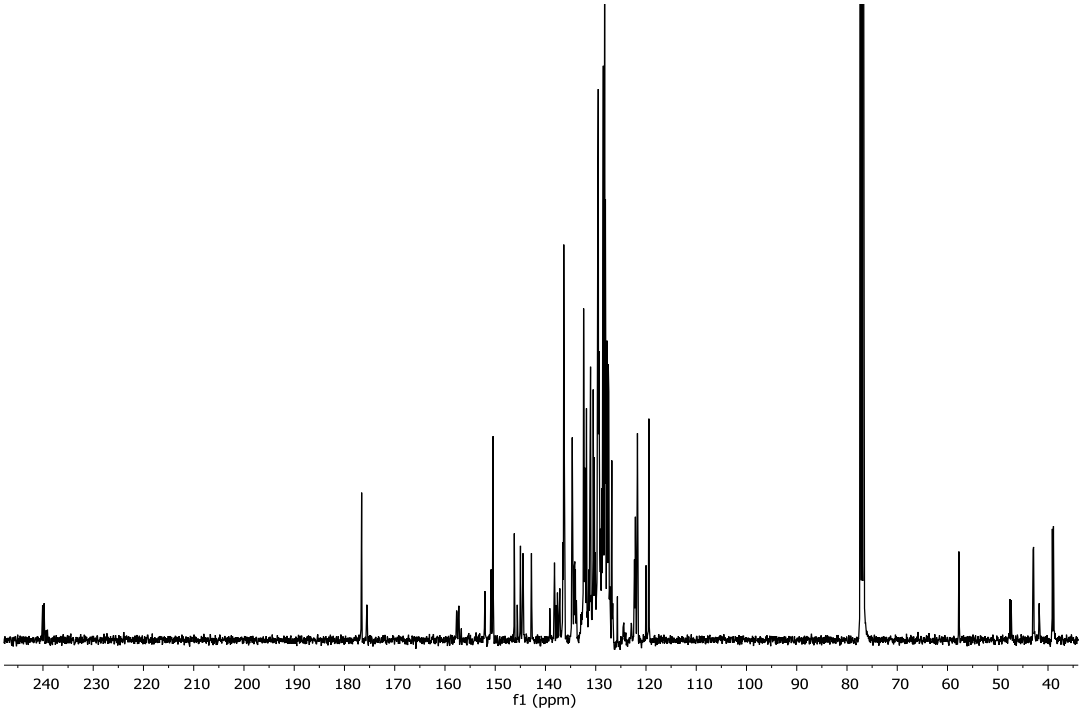

Figure 144. $^{13}C\{^{1}H\}$ NMR spectrum of compound **28** in $CDCl_3$.

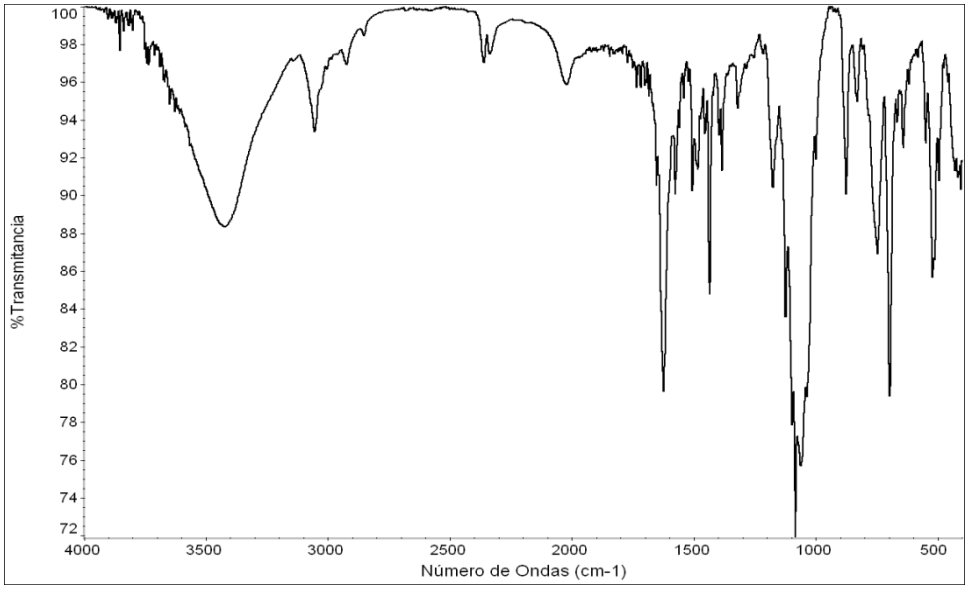

Figure 145. IR spectrum of compound **28**.

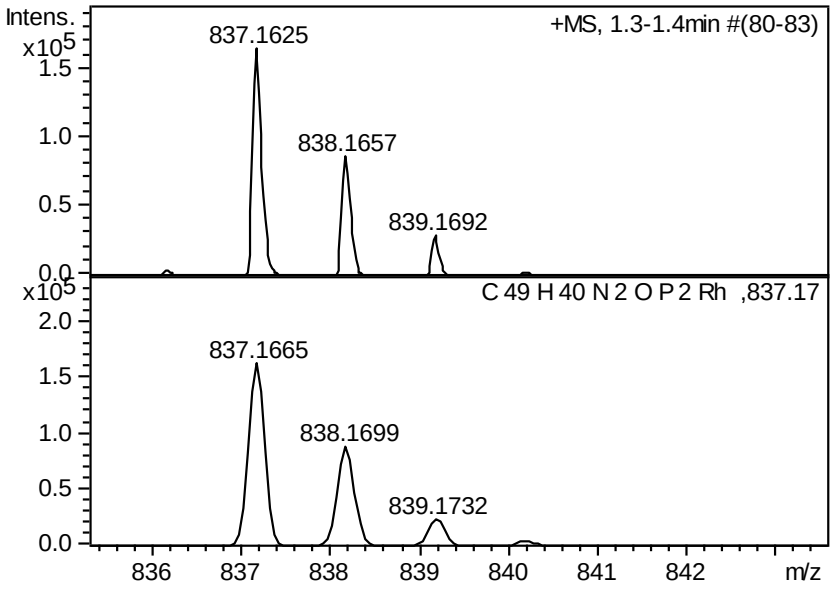

Figure 146. Found (top) and calculated (bottom) ESI-MS of compound **28**.

- **Compound [RhH(PPh$_2$(*o*-C$_6$H$_4$CO))(κ^3-PPh$_2$(CH(Ph)CH$_2$CNCH$_2$C$_5$H$_4$N)]BF$_4$ (29)**

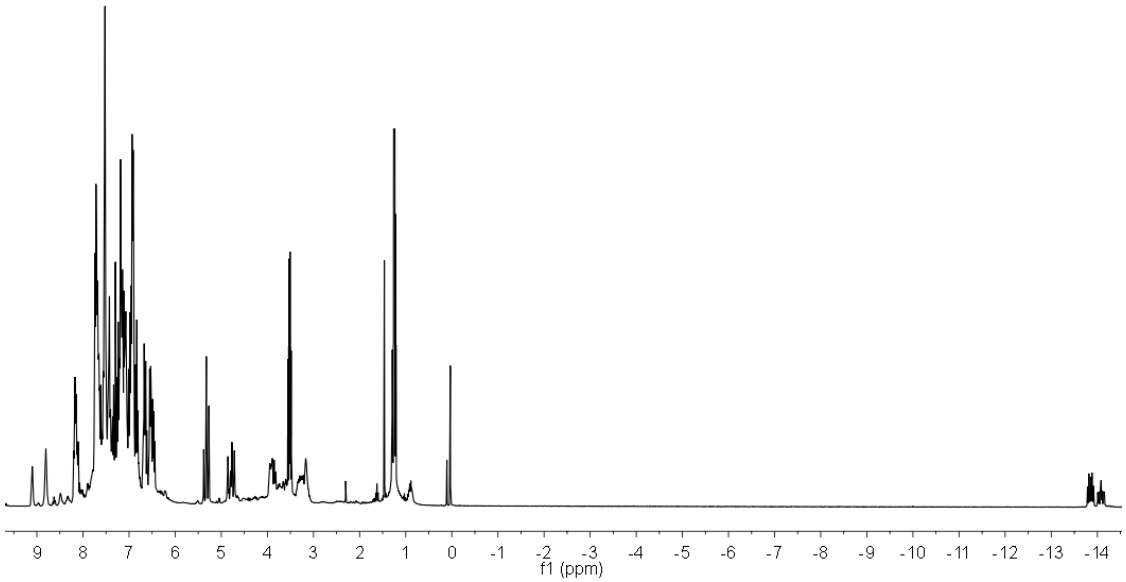

Figure 147. ^{1}H NMR spectrum of compound **29** in $CDCl_3$.

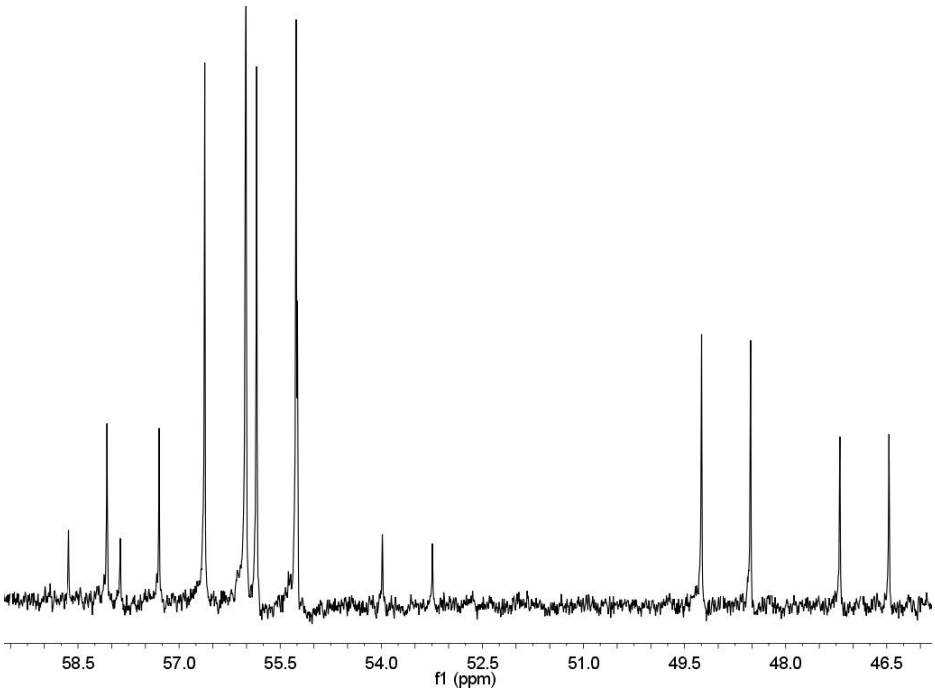

Figure 148. $^{31}P\{^1H\}$ NMR spectrum for compound **29** in $CDCl_3$.

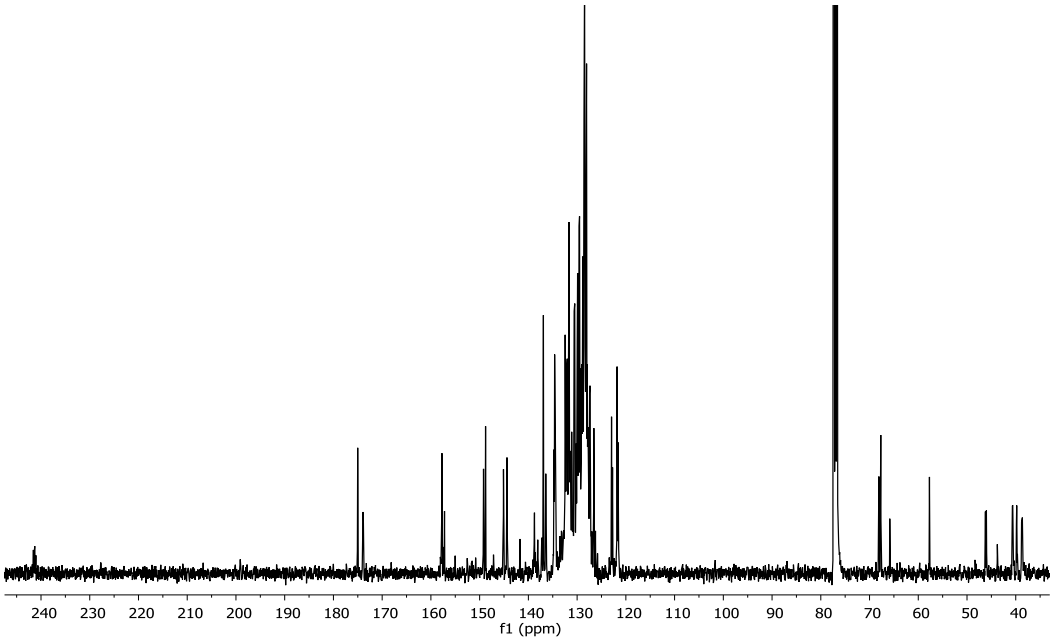

Figure 149. $^{13}C\{^{1}H\}$ NMR spectrum of compound **29** in $CDCl_3$.

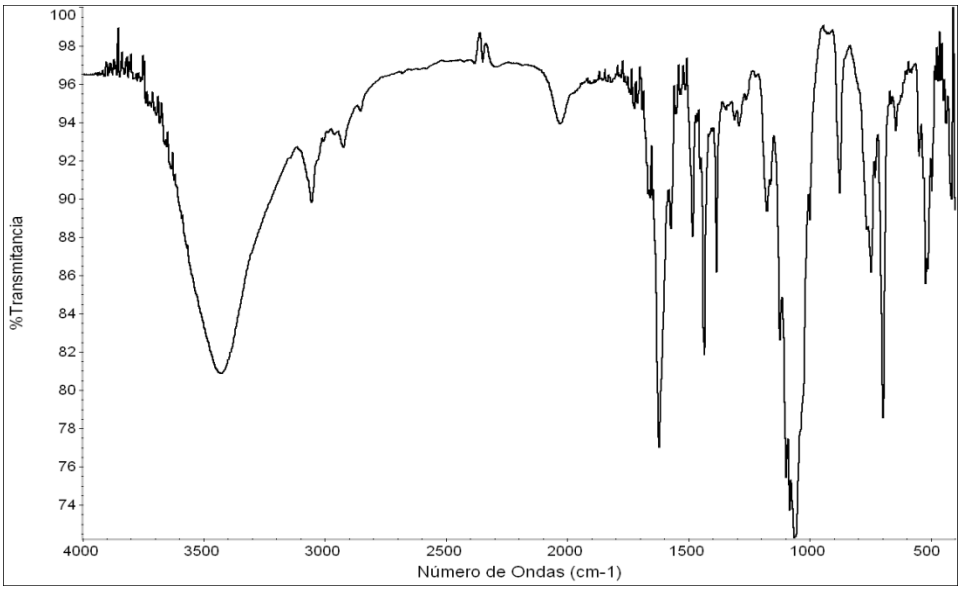

Figure 150. IR spectrum of compound **29**.

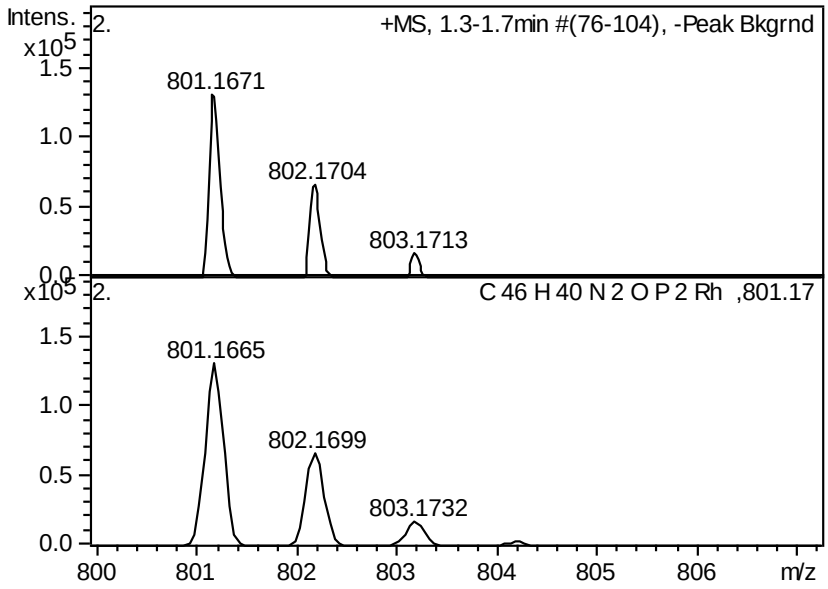

Figure 151. Found (top) and calculated (bottom) ESI-MS of compound **29**.

- **Compound [RhCl(phen)(Ntyl)($PPh_2CH(Ph)CH_2CO$)] (30)**

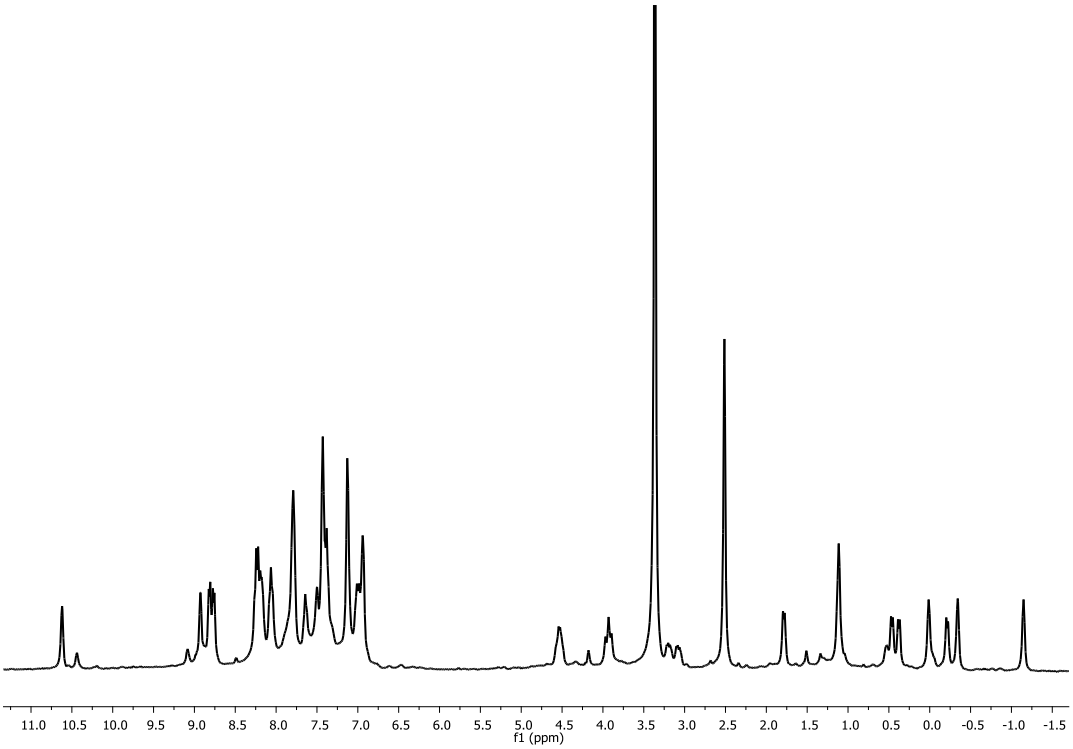

Figure 152. ^{1}H NMR spectrum for compound **30** in DMSO-d_6.

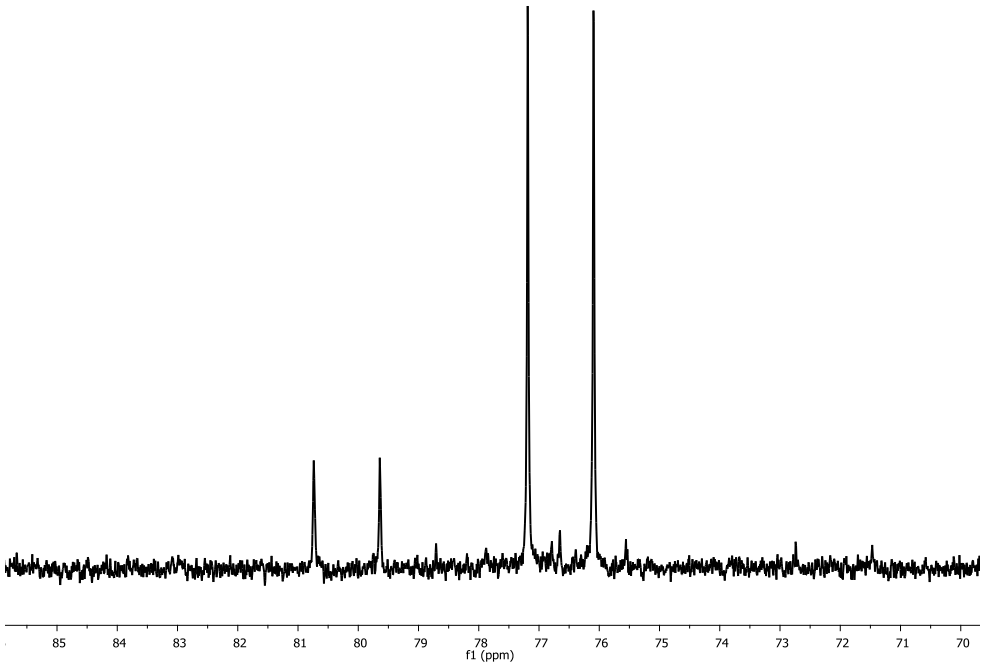

Figure 153. $^{31}P\{^{1}H\}$ NMR spectrum for compound **30** in DMSO-d_6.

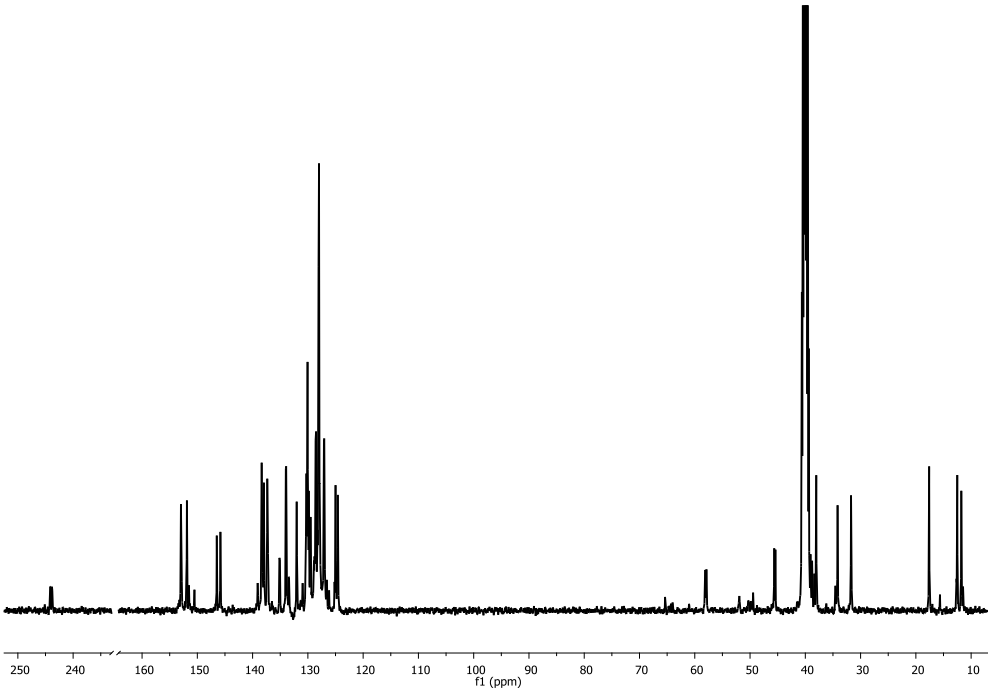

Figure 154. $^{13}C\{^{1}H\}$ NMR spectrum for compound **30** in DMSO-d_6.

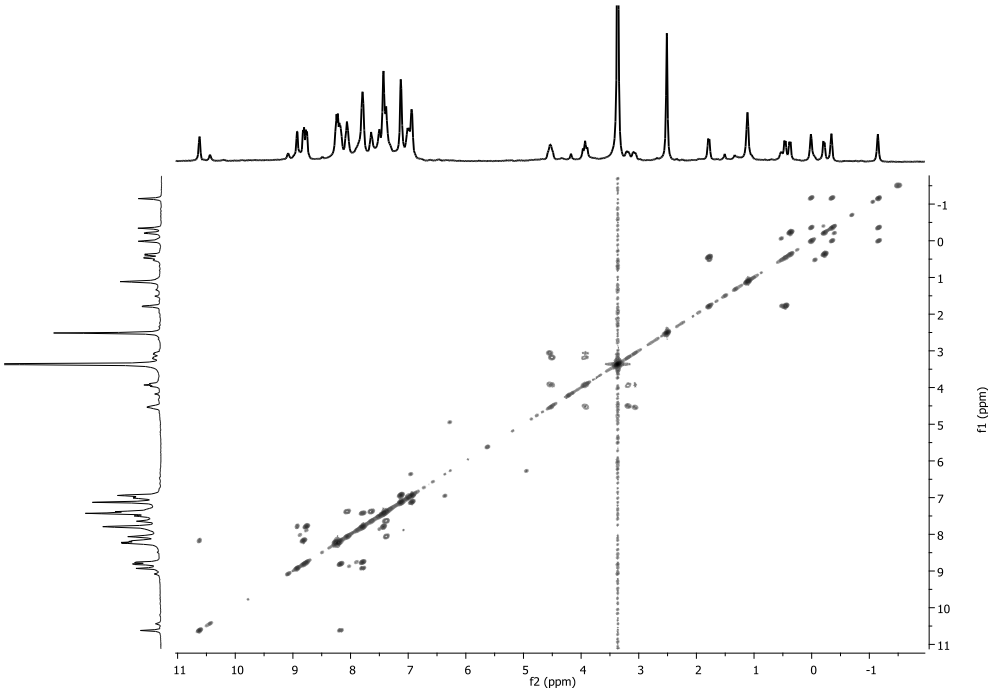

Figure 155. $^{1}H - {}^{1}H$ NMR correlation for compound **30**.

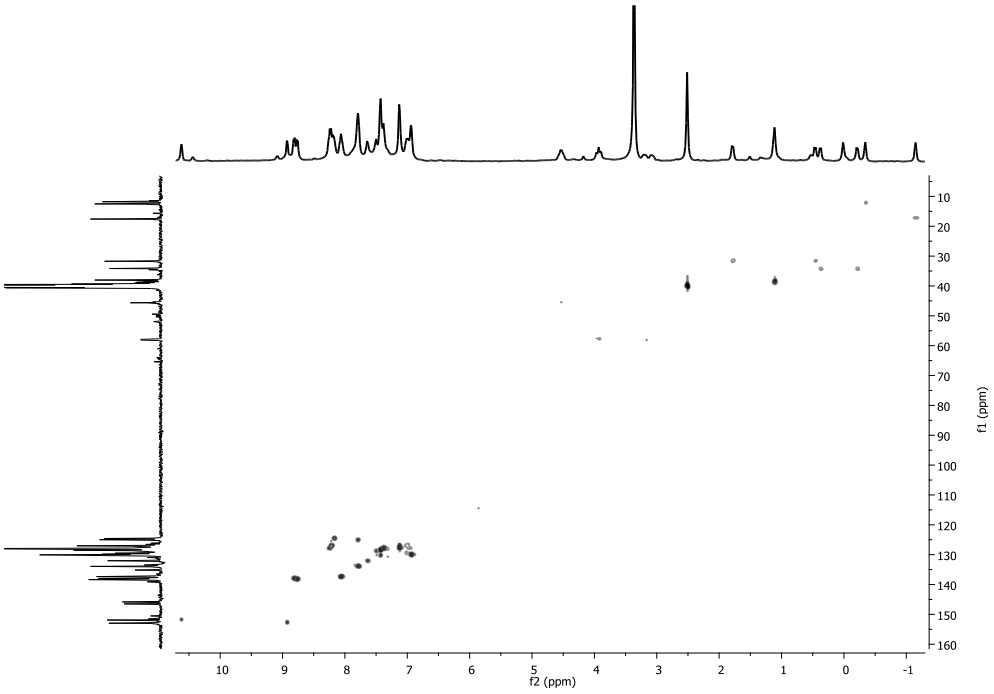

Figure 156. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **30**.

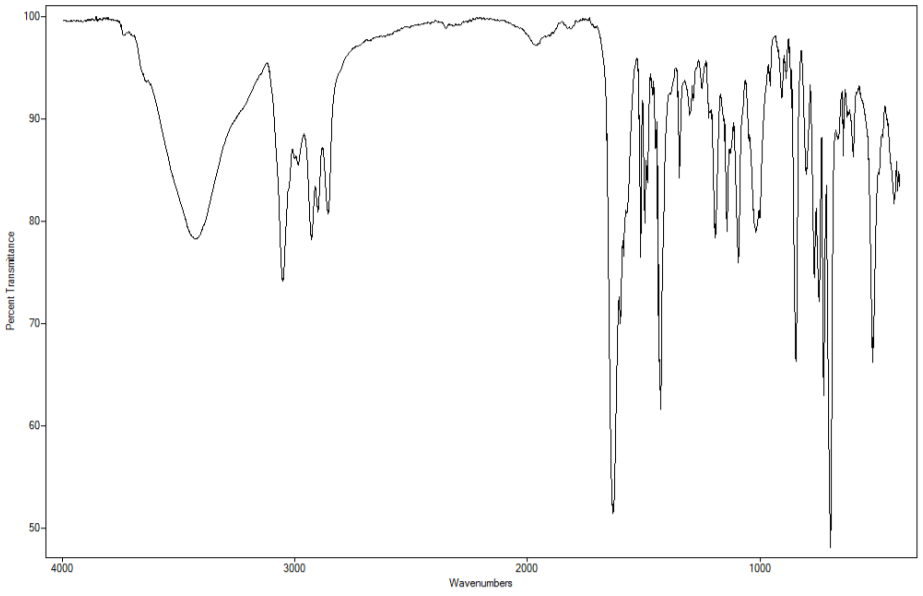

Figure 157. IR spectrum of compound **30**.

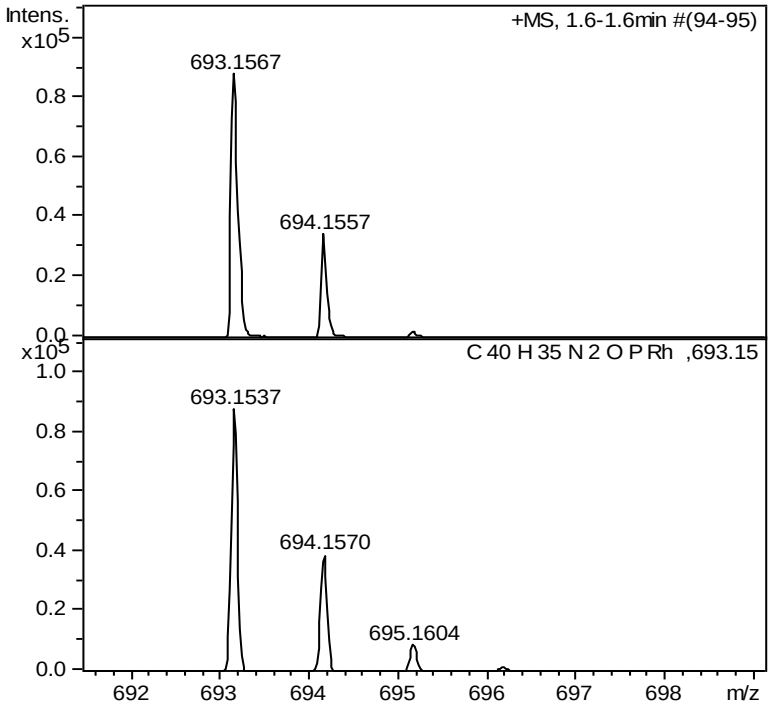

Figure 158. Found (top) and calculated (bottom) ESI-MS of compound **30**.

- **Compound [RhCl(bipy)(Ntyl)($PPh_2CH(Ph)CH_2CO$)] (31)**

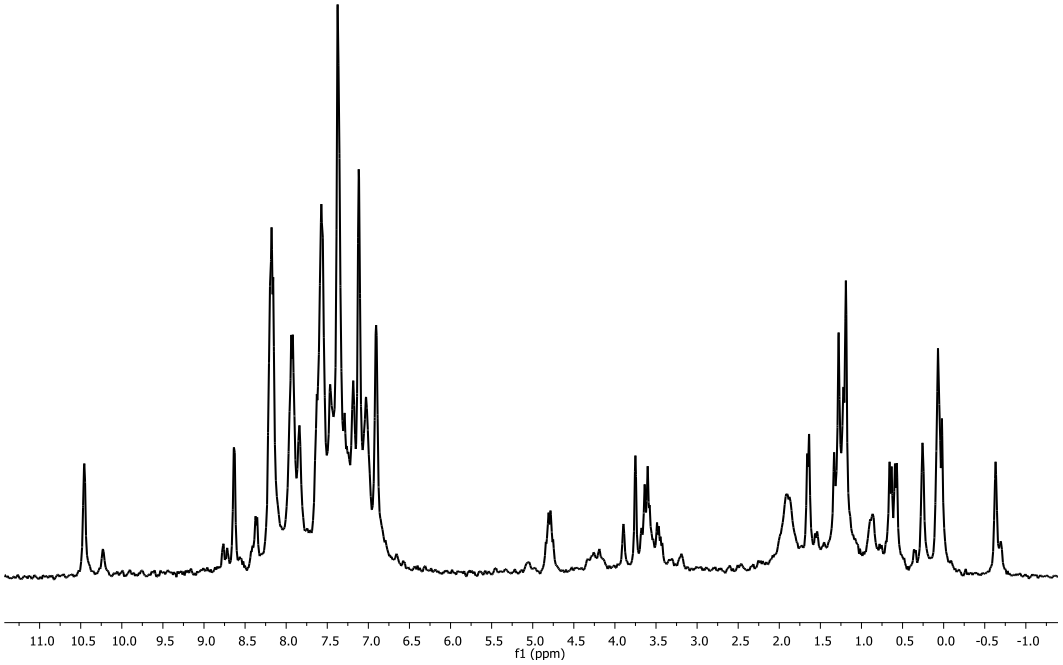

Figure 159. ^{1}H NMR spectrum of compound **31** in $CDCl_3$.

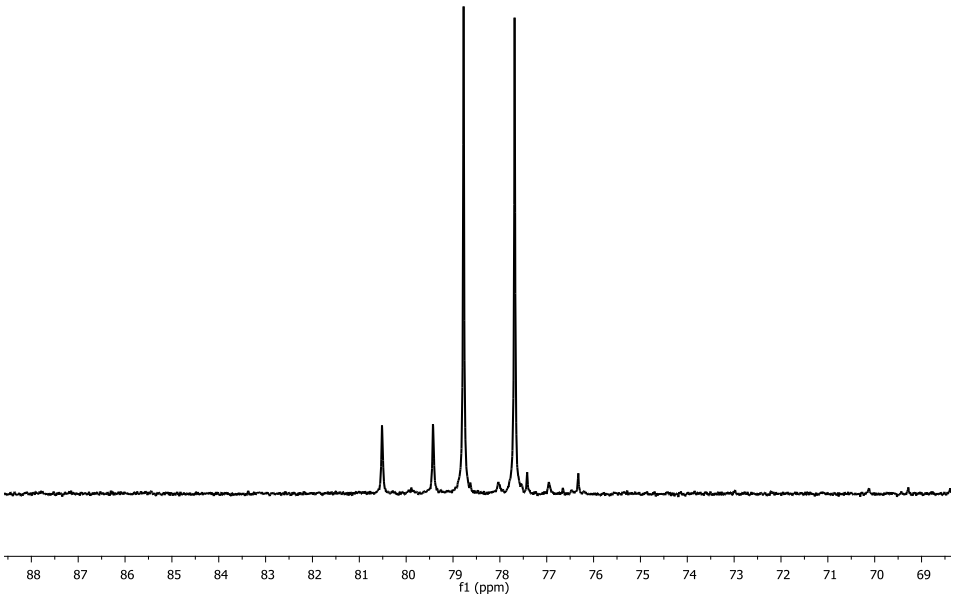

Figure 160. $^{31}P\{^{1}H\}$ NMR spectrum for compound **31** in $CDCl_3$.

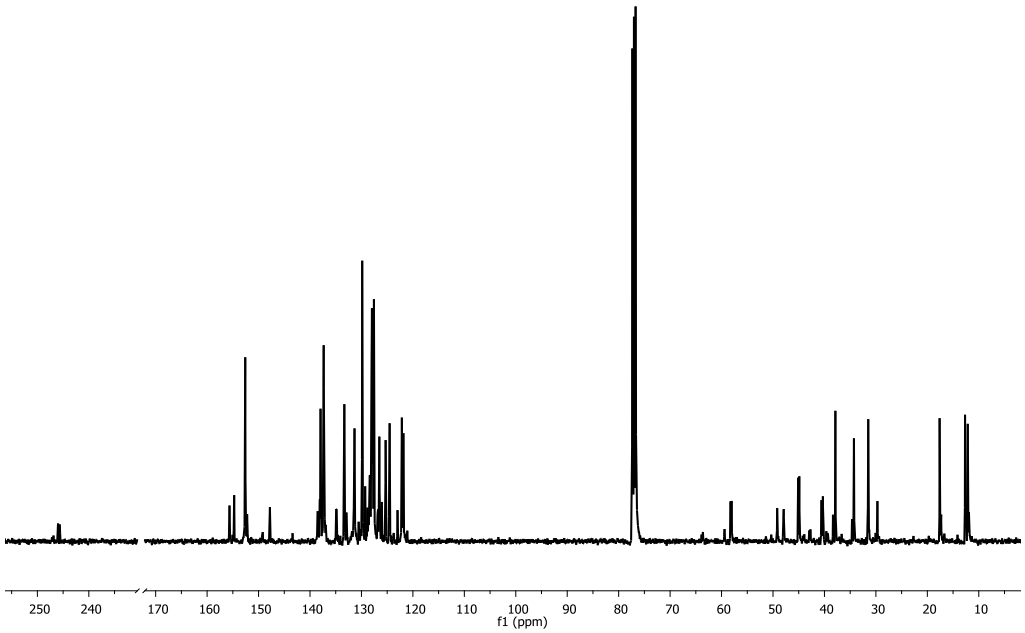

Figure 161. $^{13}C\{^{1}H\}$ NMR spectrum of compound **31** in $CDCl_3$.

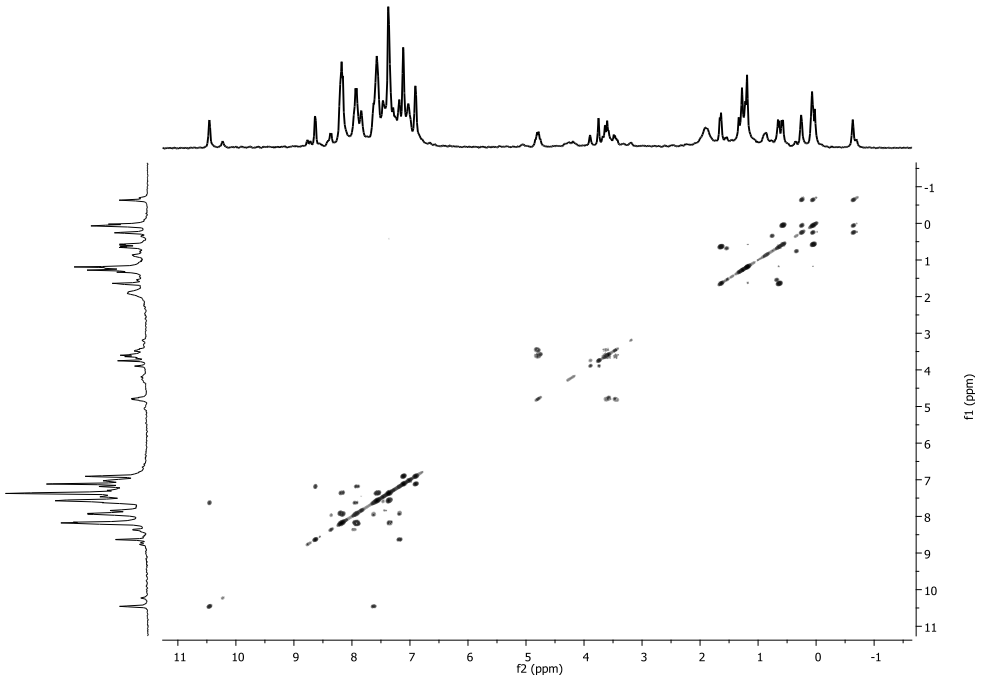

Figure 162. $^{1}H - {}^{1}H$ NMR correlation for compound **31**.

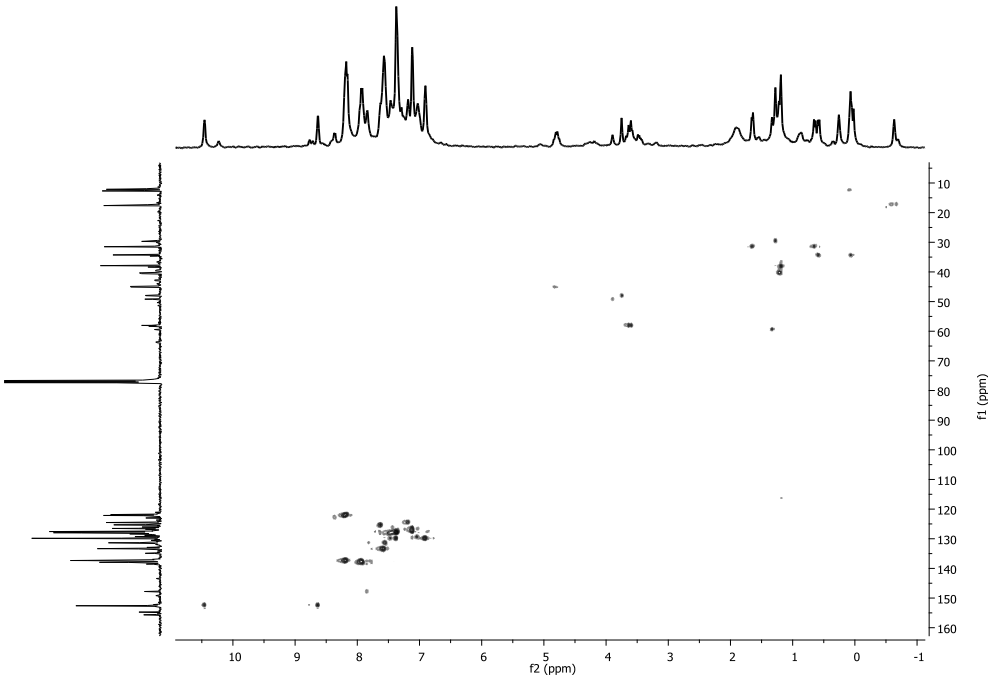

Figure 163. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **31**.

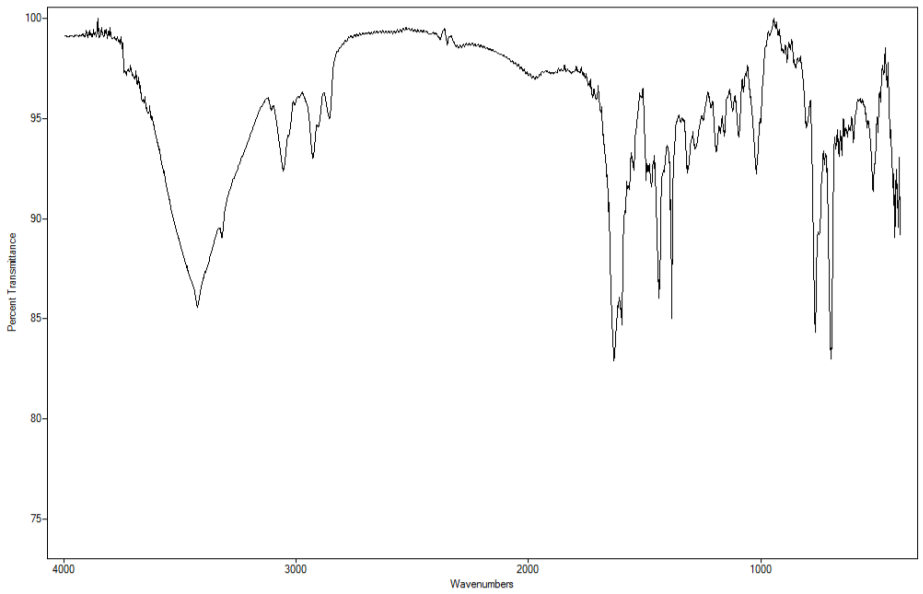

Figure 164. IR spectrum of compound **31**.

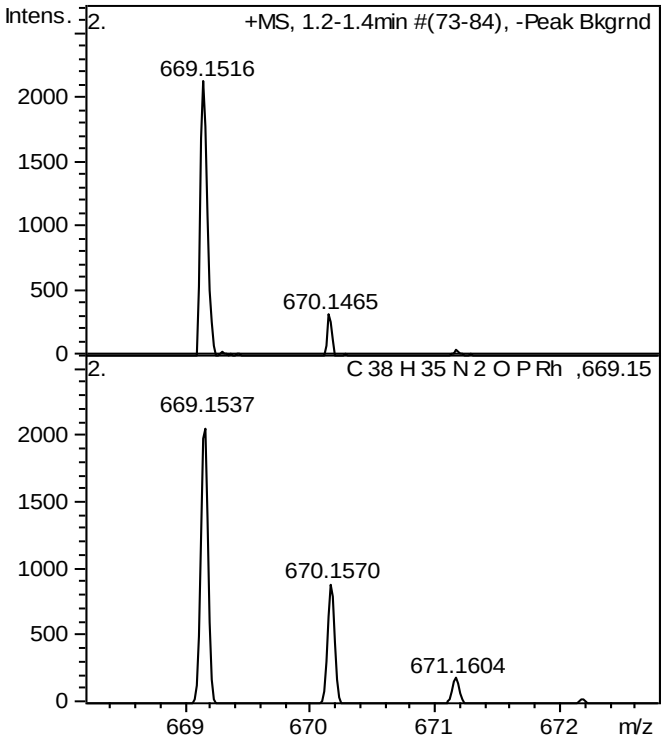

Figure 165. Found (top) and calculated (bottom) ESI-MS of compound **31**.

- **Compound [RhCl(Ntyl)(C_9H_6NCO)(k^2-$PPh_2CH(Ph)CH_2CO(OCH_3)$)] (32)**

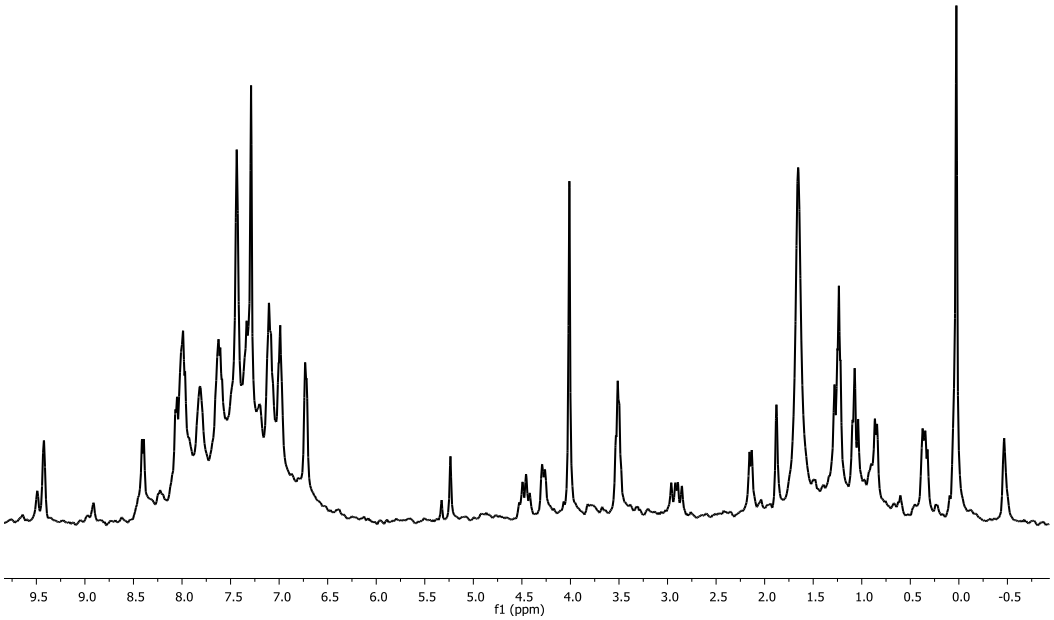

Figure 166. ^{1}H NMR spectrum of compound **32** in $CDCl_3$.

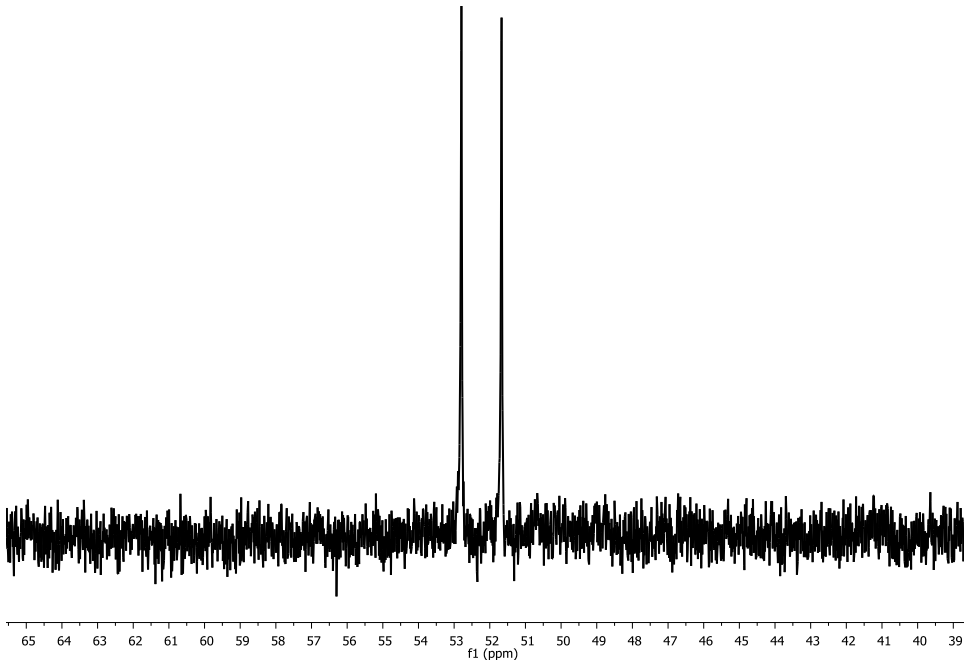

Figure 167. $^{31}P\{^{1}H\}$ NMR spectrum for compound **32** in MeOD.

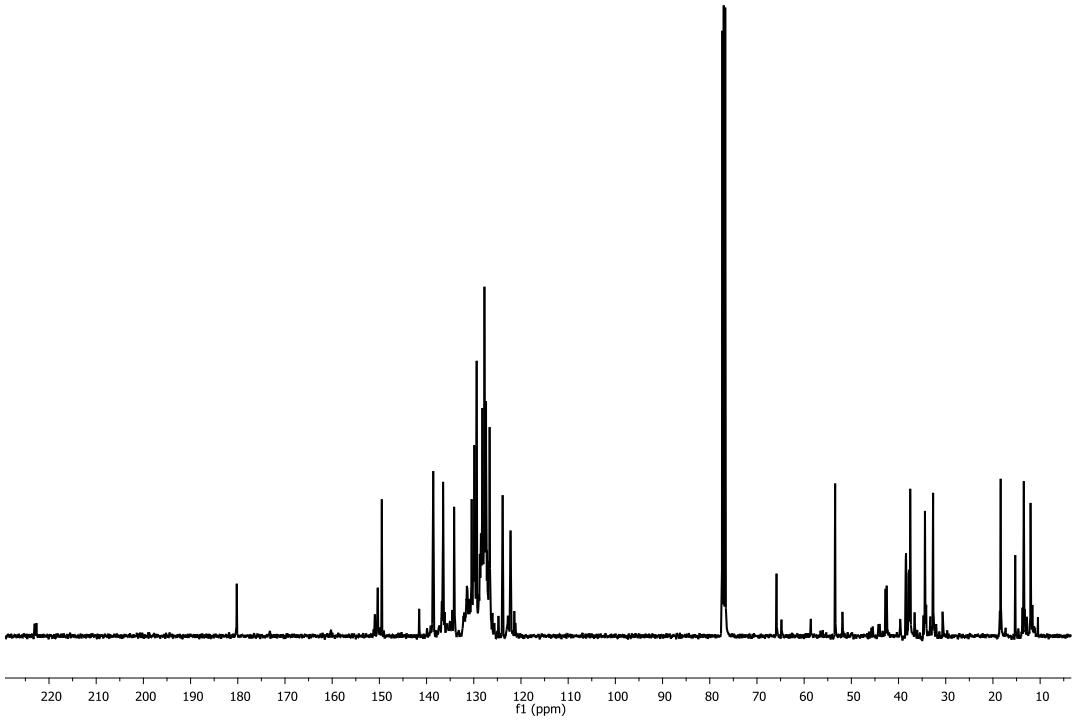

Figure 168. $^{13}C\{^{1}H\}$ NMR spectrum of compound **32** in $CDCl_3$.

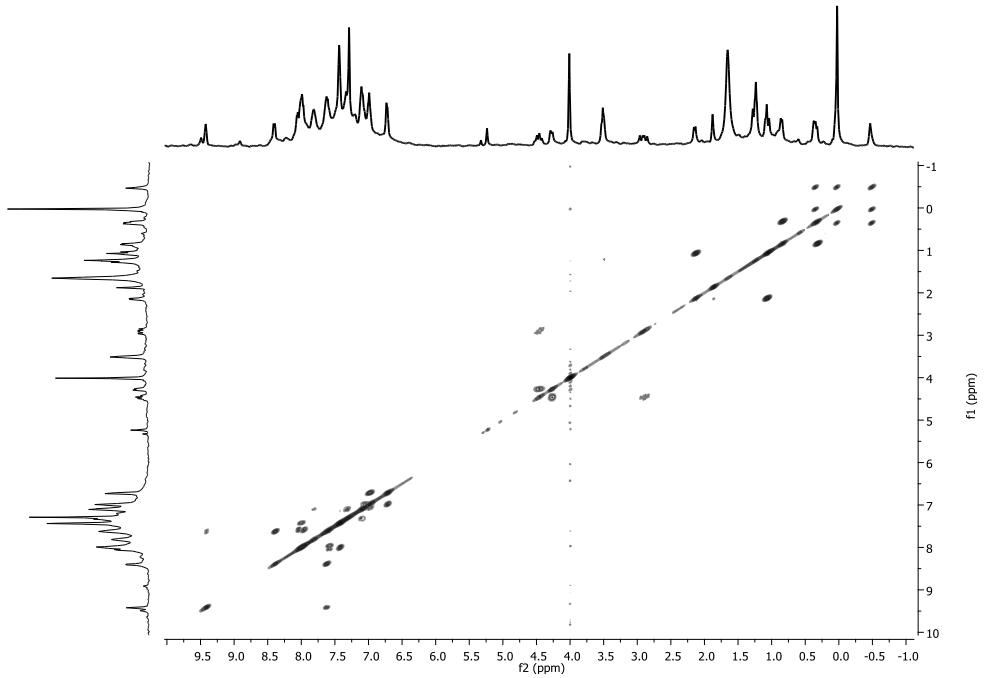

Figure 169. $^{1}H - {}^{1}H$ NMR correlation for compound **32**.

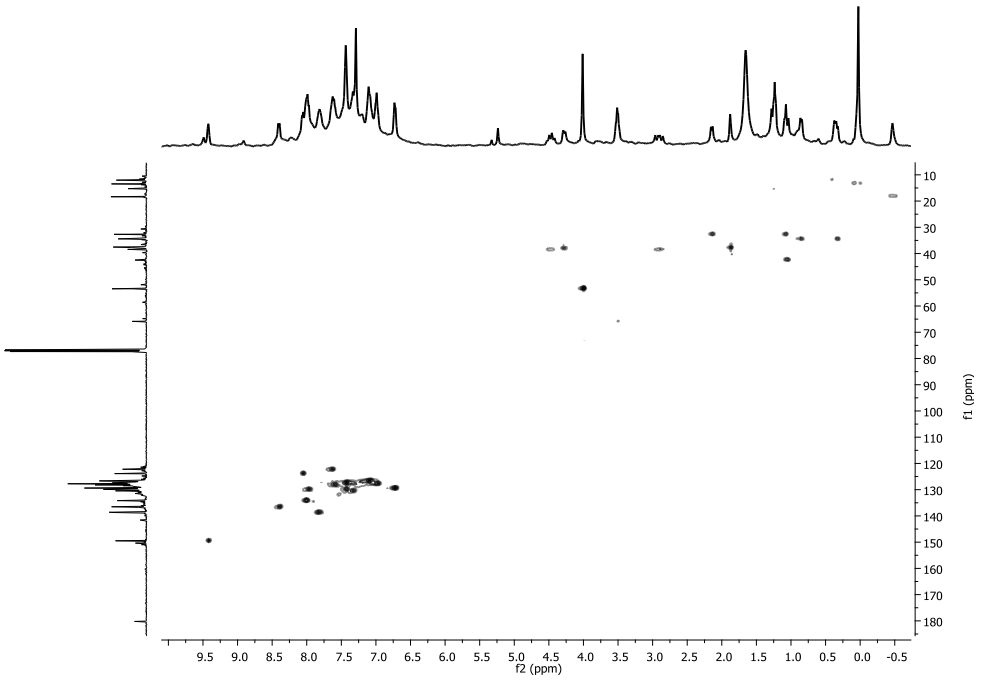

Figure 170. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **32**.

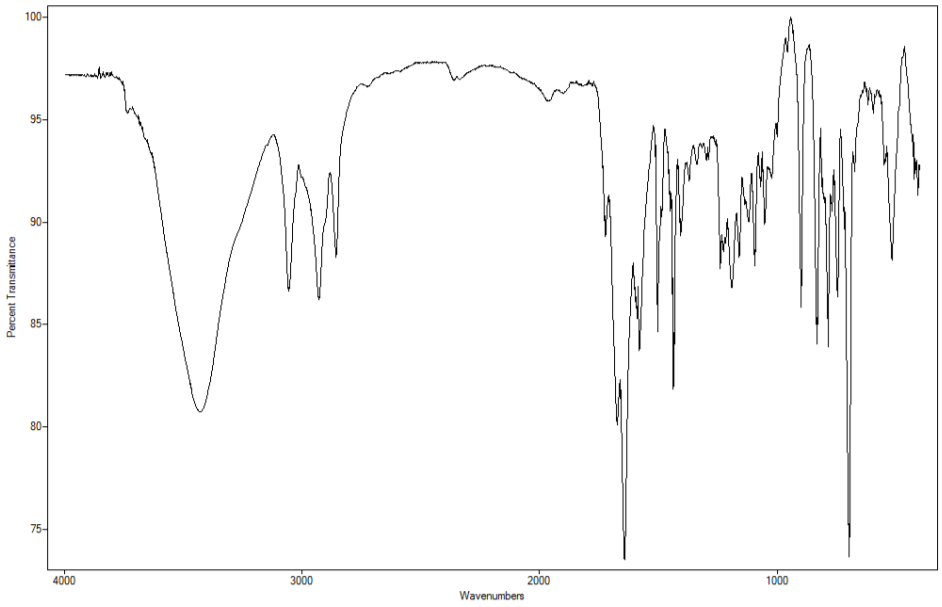

Figure 171. IR spectrum of compound **32**.

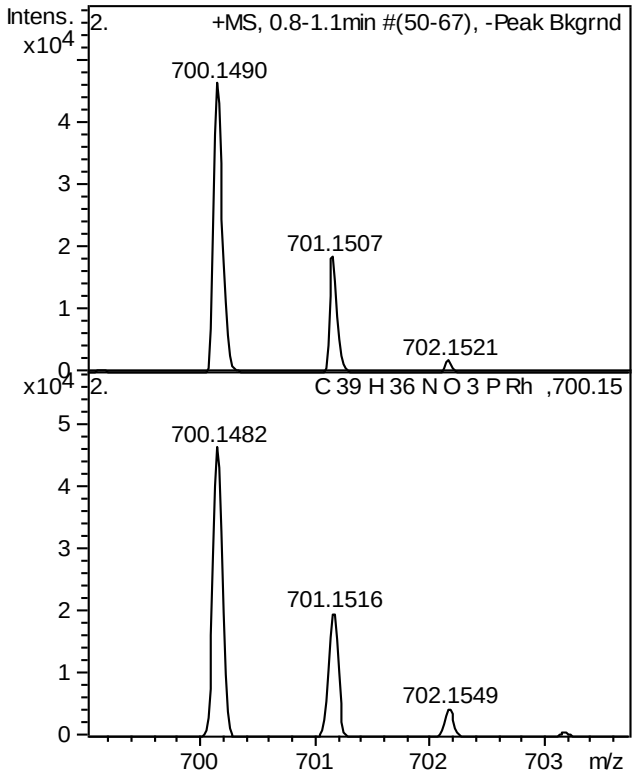

Figure 172. Found (top) and calculated (bottom) ESI-MS of compound **32**.

- **Compound [RhCl(C_9H_6NCO))(Hpz)(ntyl)]$_2$ (33)**

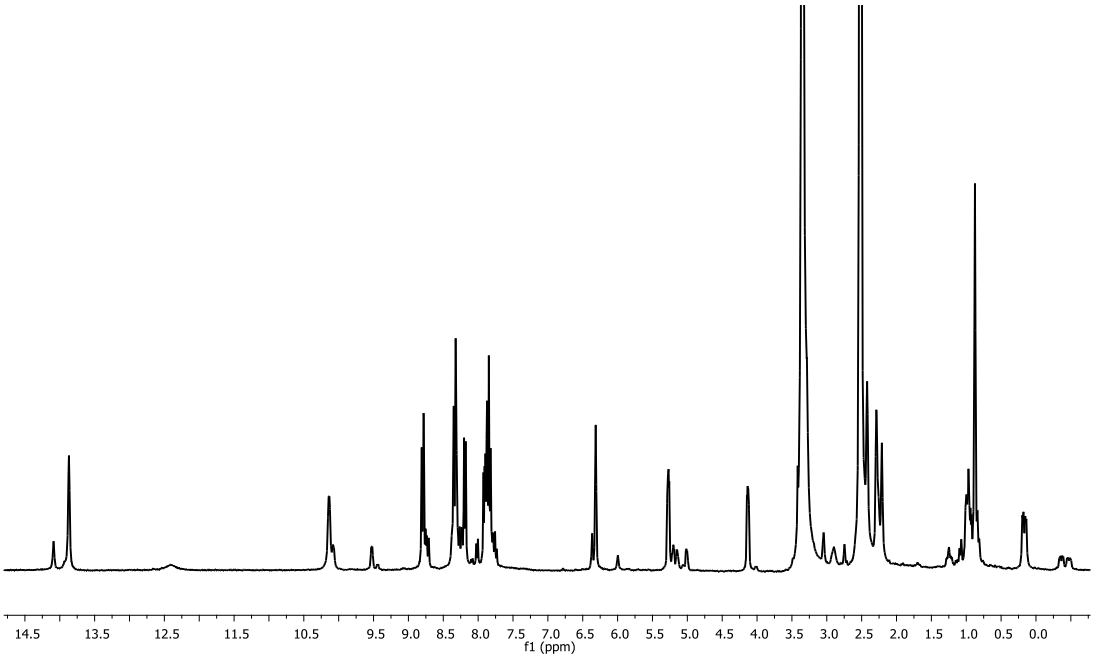

Figure 173. ^{1}H NMR spectrum of compound **33** in DMSO-d_6.

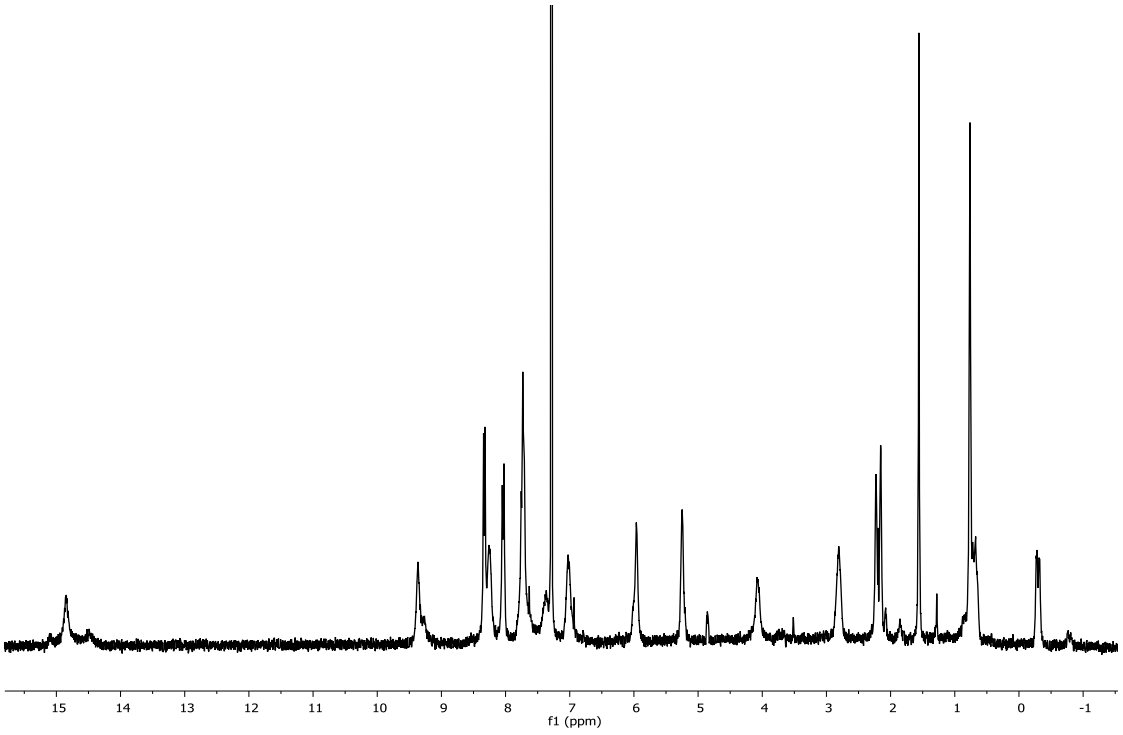

Figure 174. ^{1}H NMR spectrum of compound **33** in $CDCl_3$.

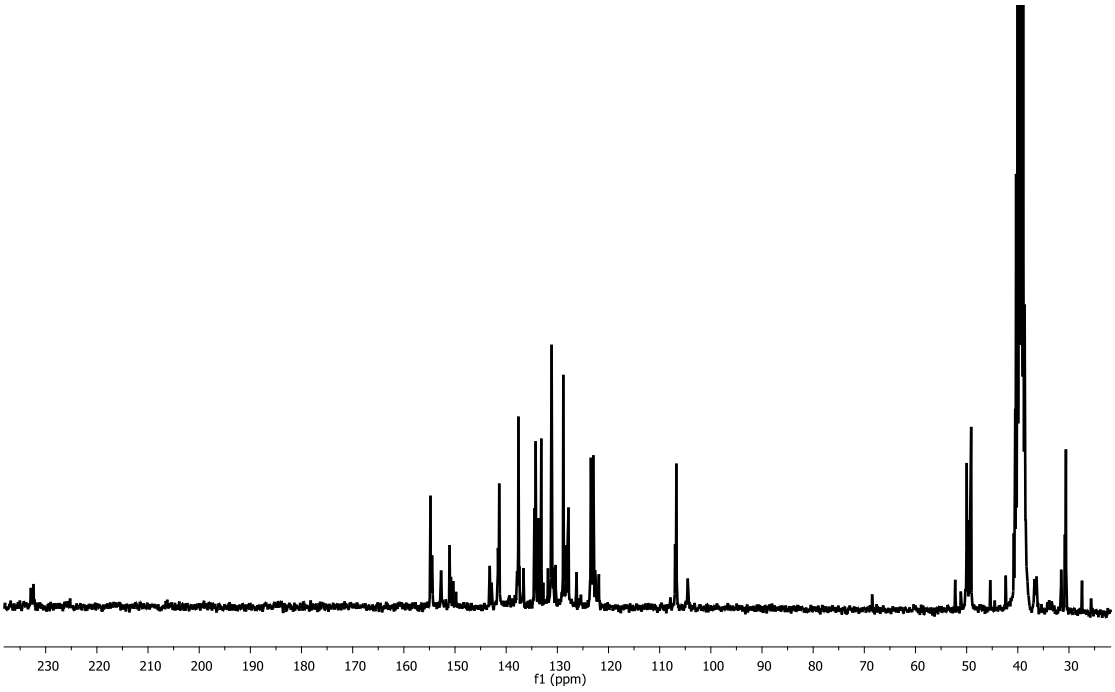

Figure 175. $^{13}C\{^{1}H\}$ NMR spectrum of compound **33** in DMSO-d_6.

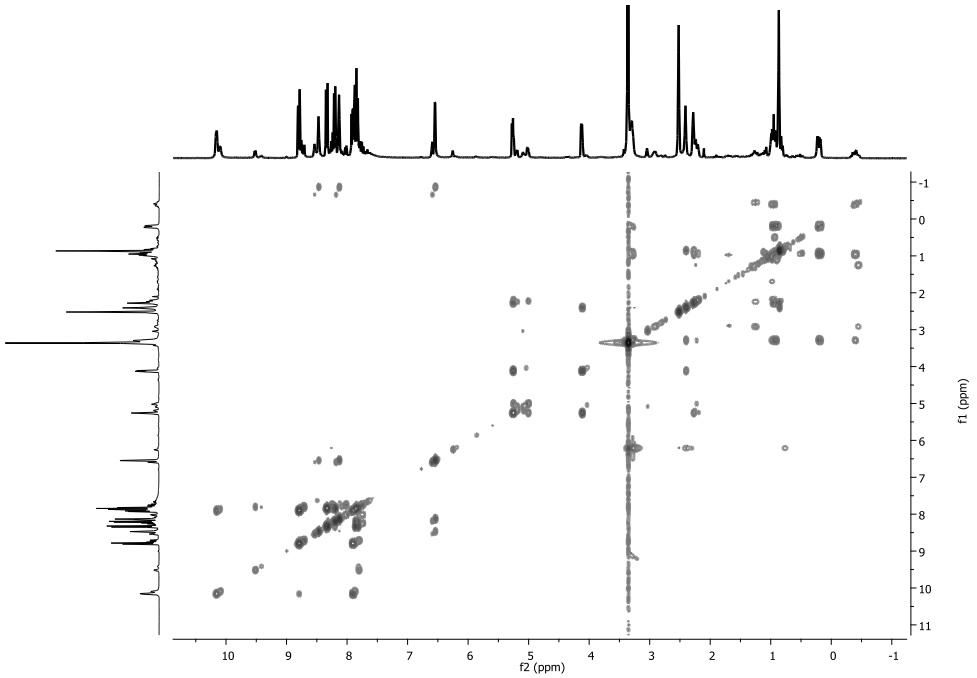

Figure 176. $^{1}H - {}^{1}H$ NMR correlation for compound **33**.

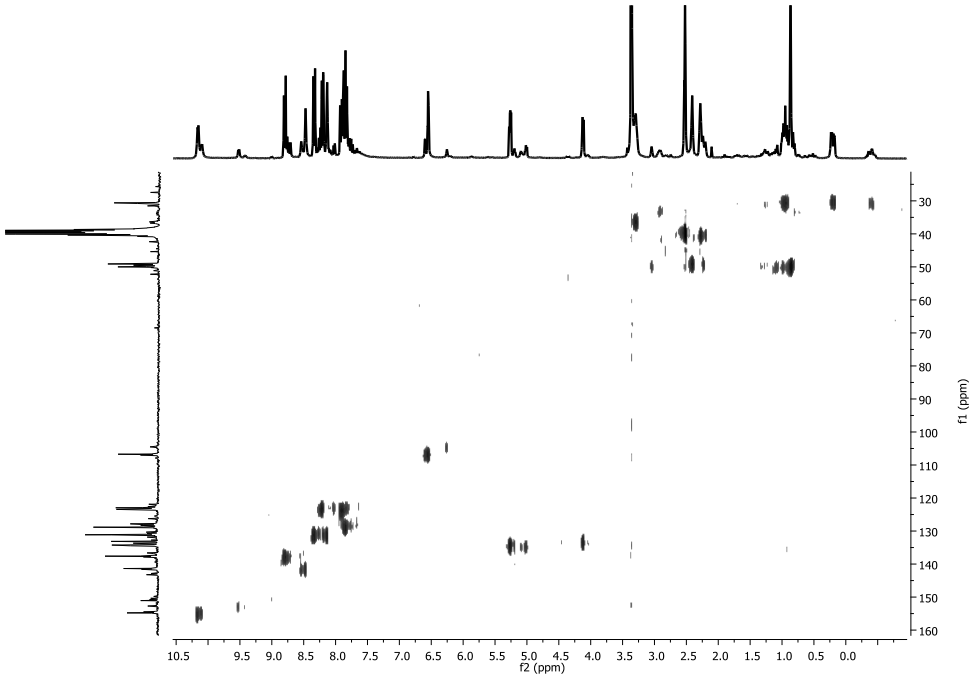

Figure 177. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **33**.

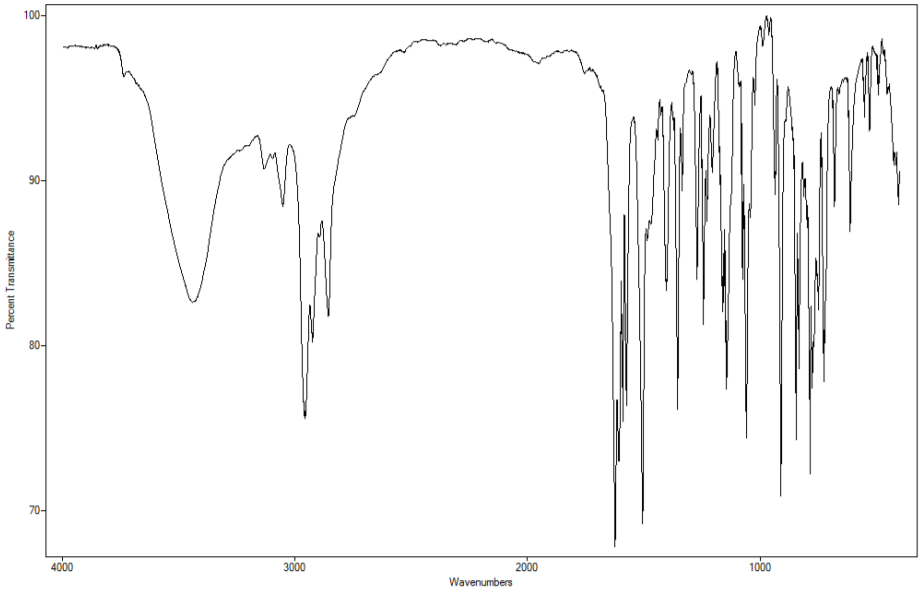

Figure 178. IR spectrum of compound **33**.

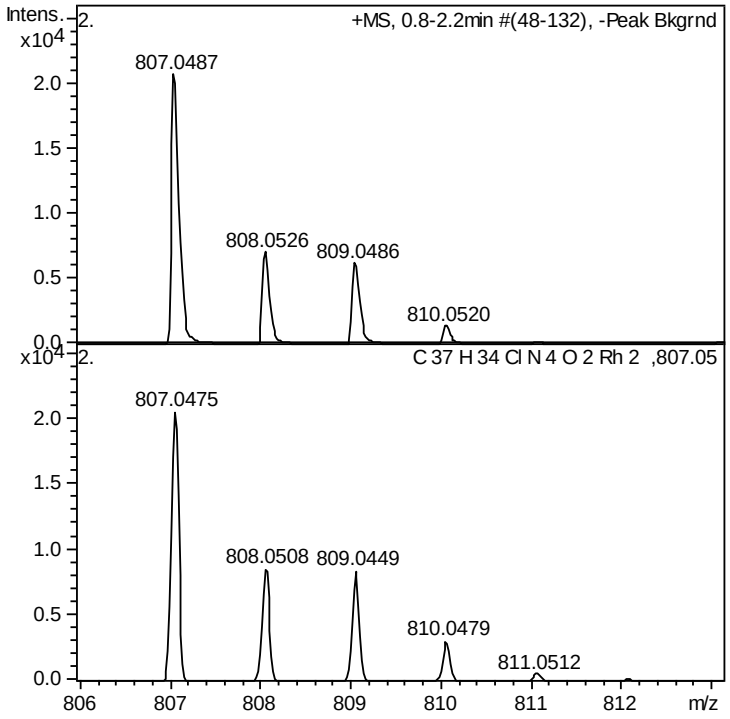

Figure 179. Found (top) and calculated (bottom) ESI-MS of compound **33**.

- **Compound [RhCl(C_9H_6NCO))($Hpz)_2$(nbyl)] (34)**

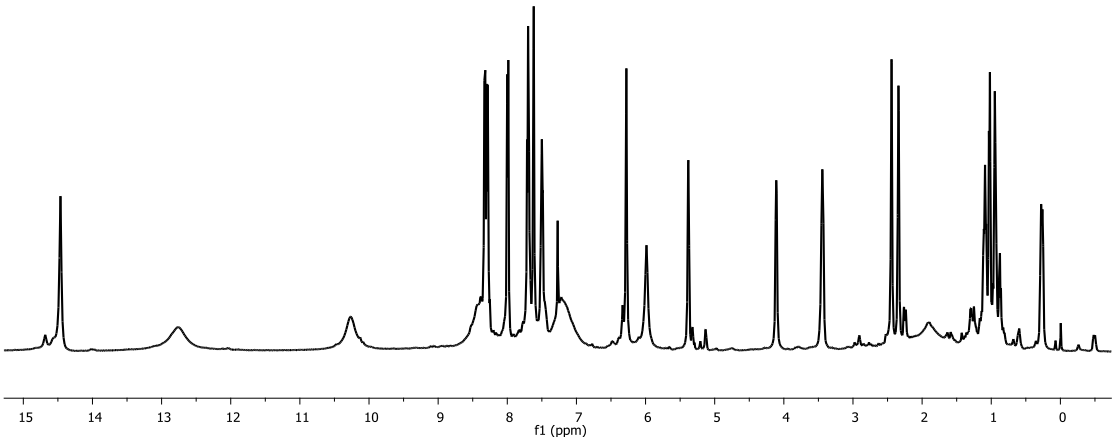

Figure 180. ^{1}H NMR spectrum of compound **34** at 293K in $CDCl_3$.

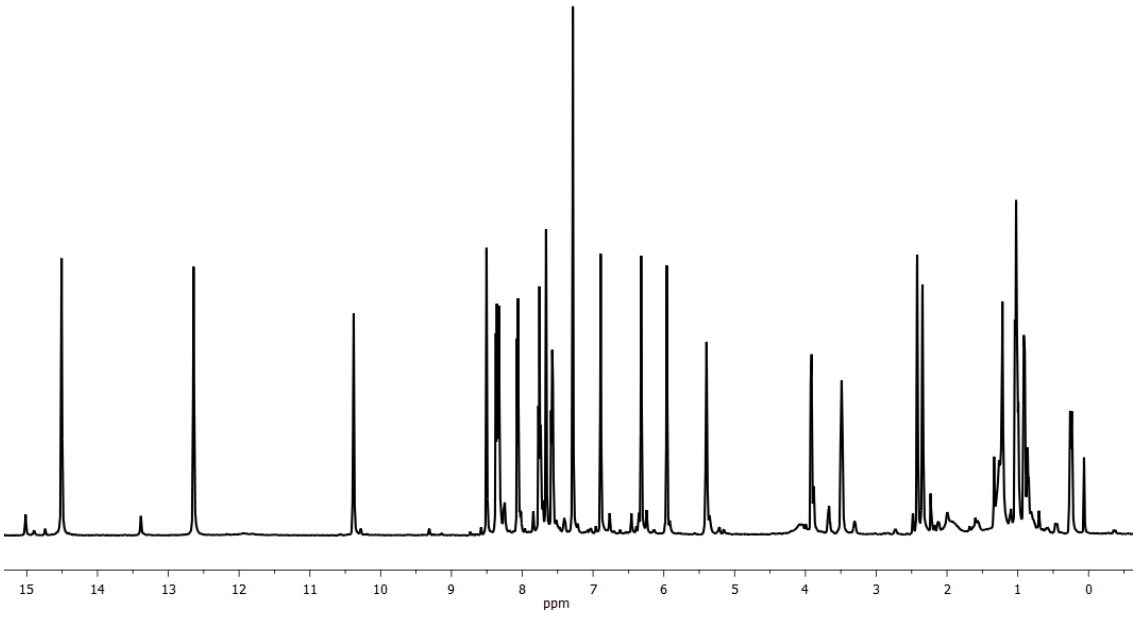

Figure 181. ^{1}H NMR spectrum of compound **34** at 233K in $CDCl_3$.

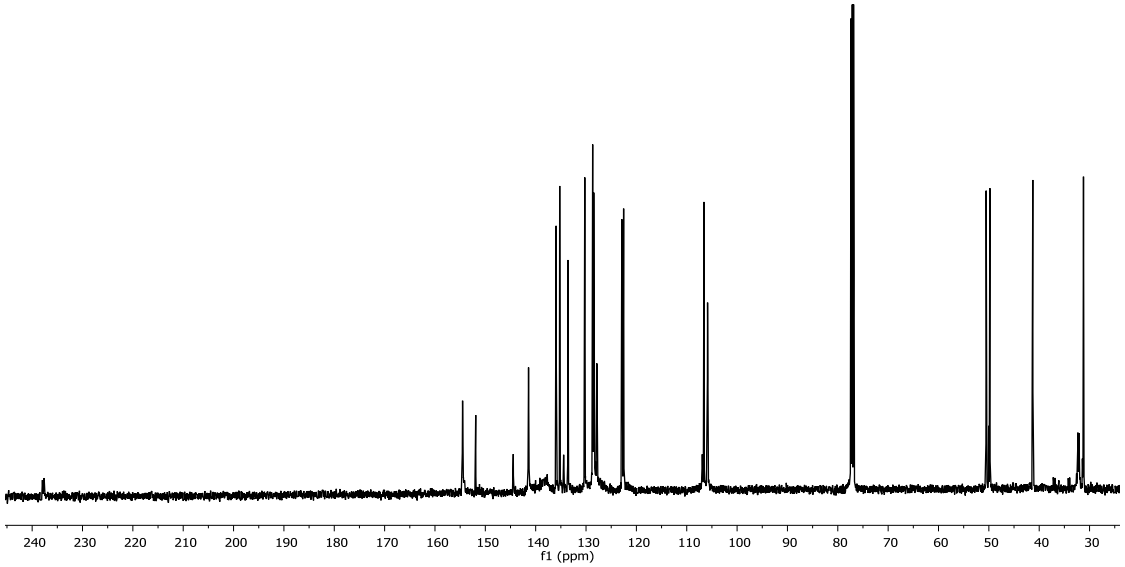

Figure 182. $^{13}C\{^{1}H\}$ NMR spectrum of compound **34** in $CDCl_3$.

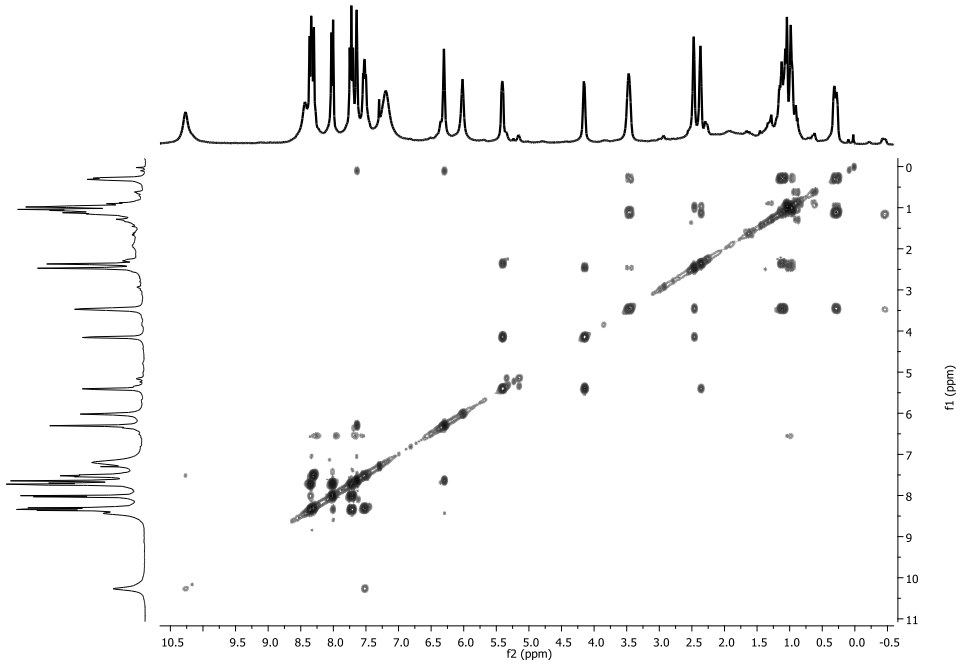

Figure 183. $^{1}H - {}^{1}H$ NMR correlation for compound **34**.

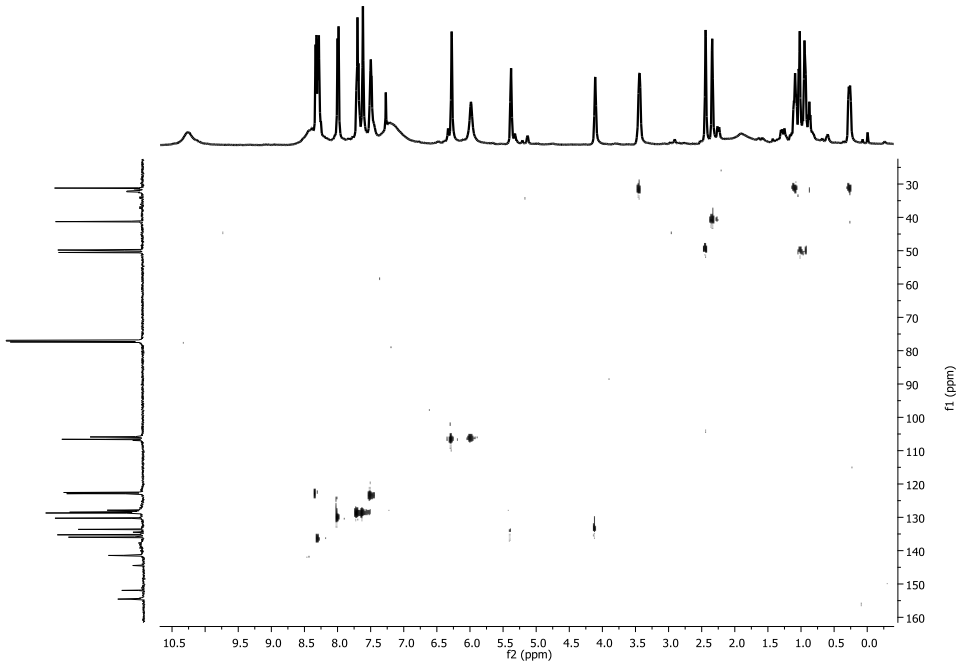

Figure 184. ^{1}H – ^{13}C NMR correlation for compound **34**.

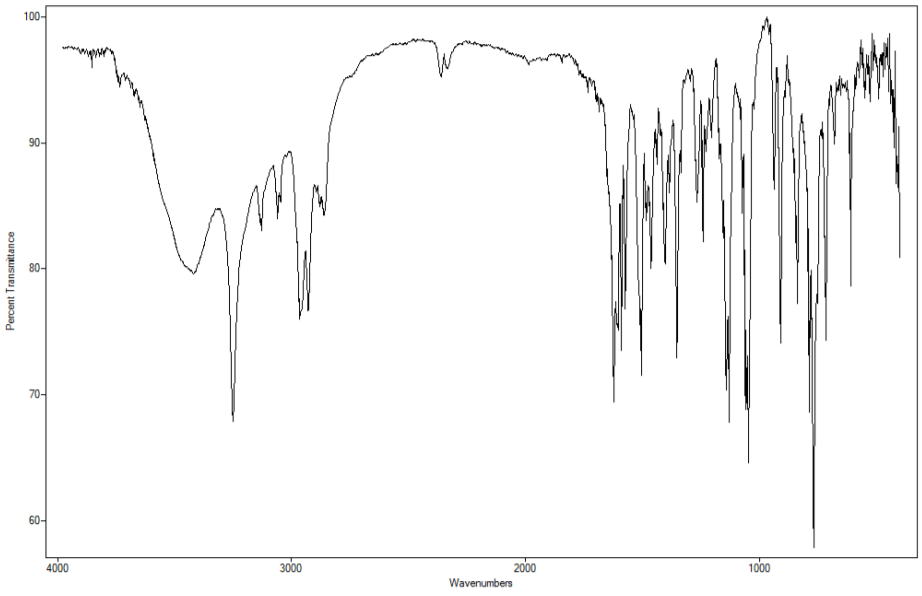

Figure 185. IR spectrum of compound **34**.

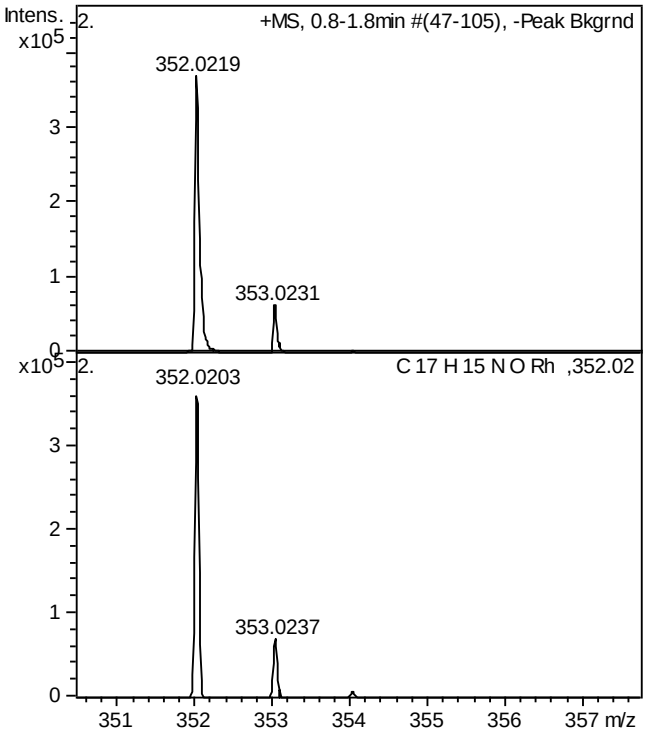

Figure 186. Found (top) and calculated (bottom) ESI-MS of compound **34**.

- **Compound [Rh(C_9H_6NCO))($Hpz)_3$(nbyl)]BPh_4 (35)**

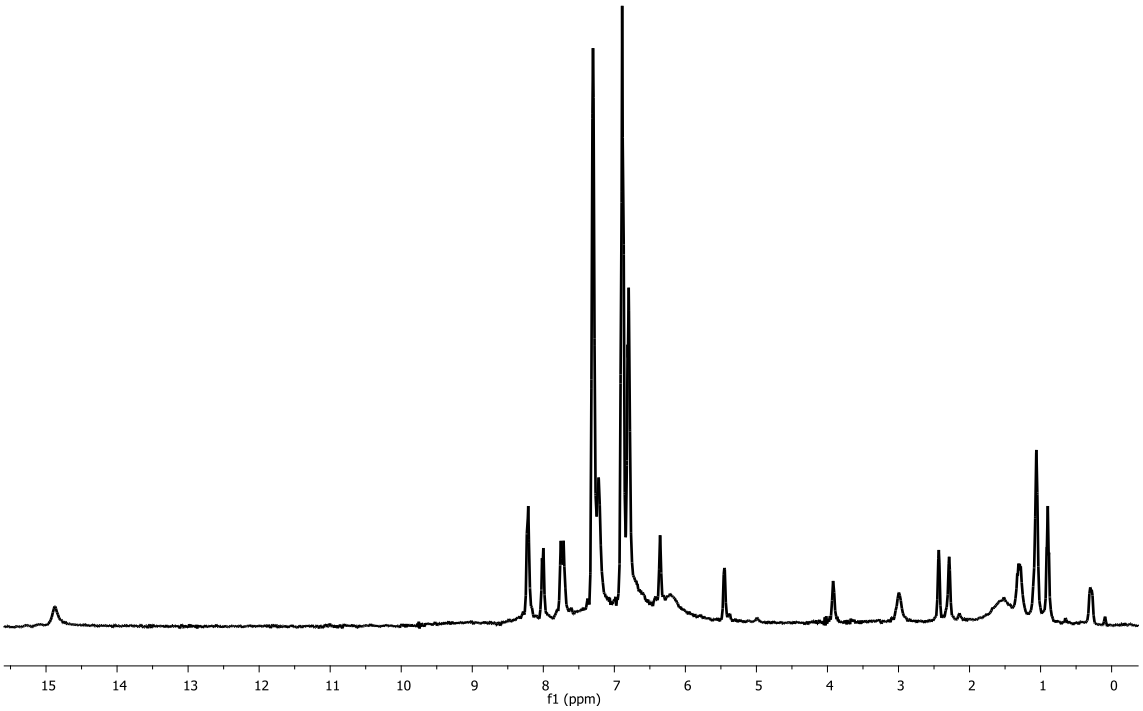

Figure 187. ^{1}H NMR spectrum of compound **35** in $CDCl_3$.

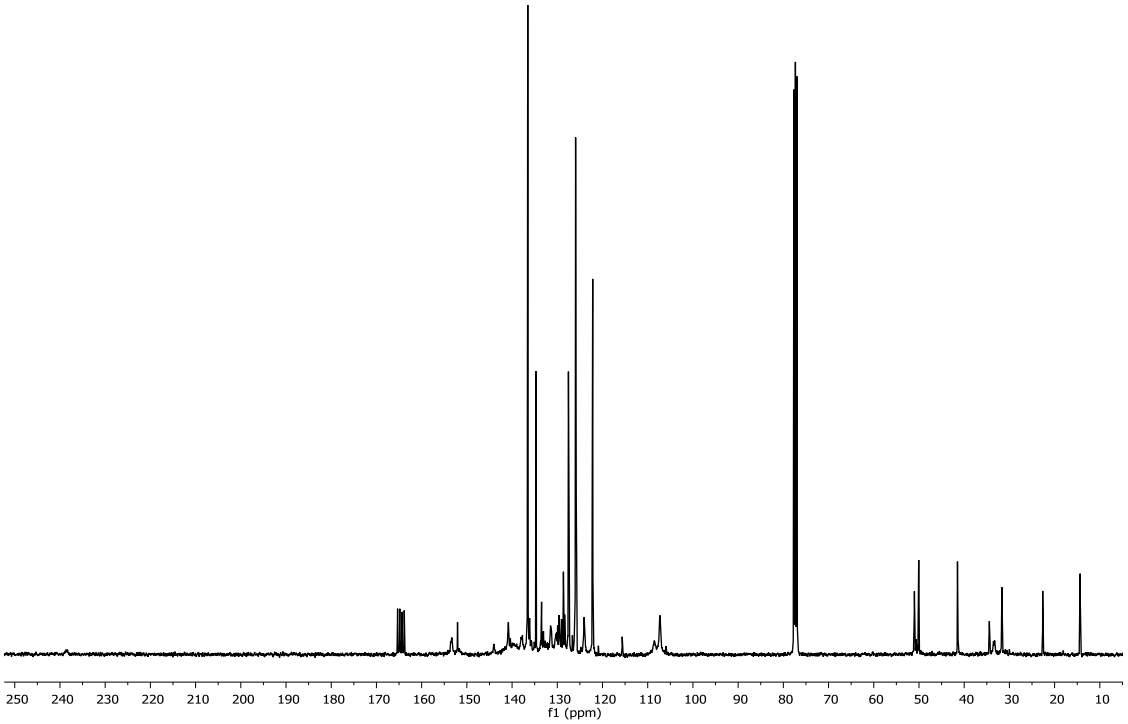

Figure 188. $^{13}C\{^{1}H\}$ NMR spectrum of compound **35** in $CDCl_3$.

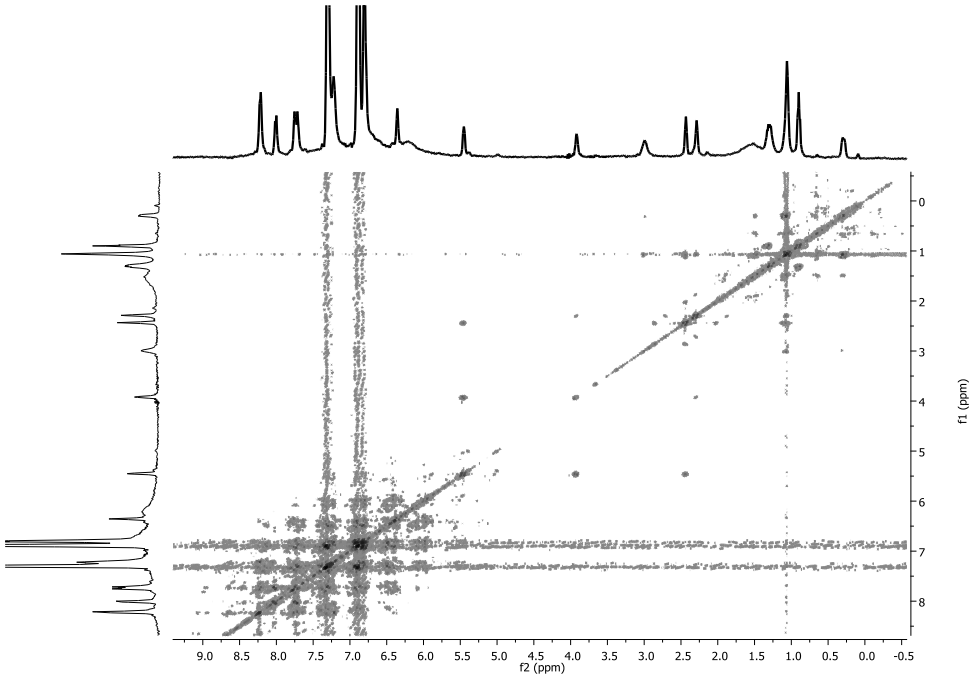

Figure 189. $^{1}H - {}^{1}H$ NMR correlation for compound **35**.

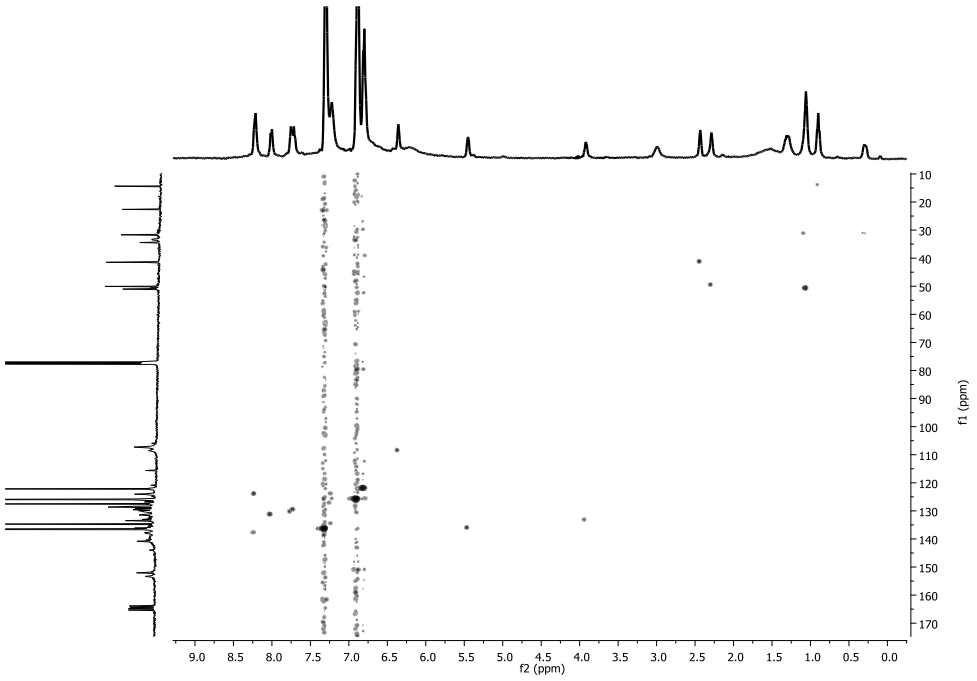

Figure 190. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **35**.

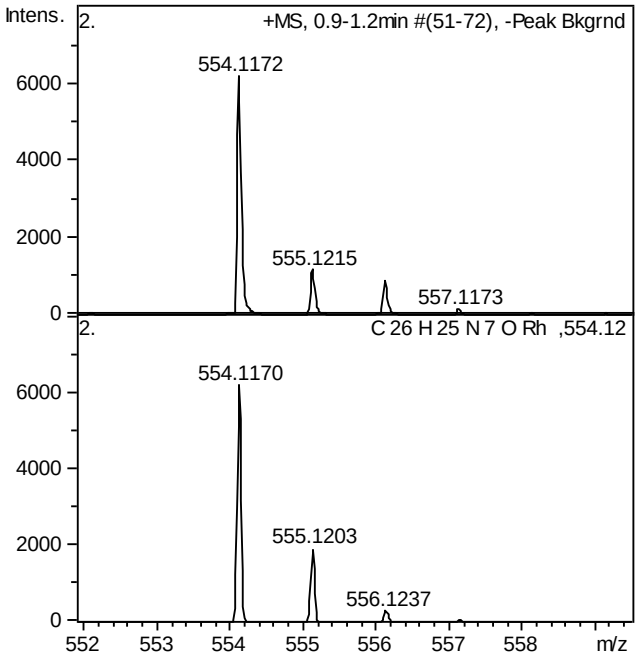

Figure 191. Found (top) and calculated (bottom) ESI-MS of compound **35**.

- **Reaction product of [RhCl(C_9H_6NCO))($Hpz)_2$(nbyl)] (34) with PPh_3**

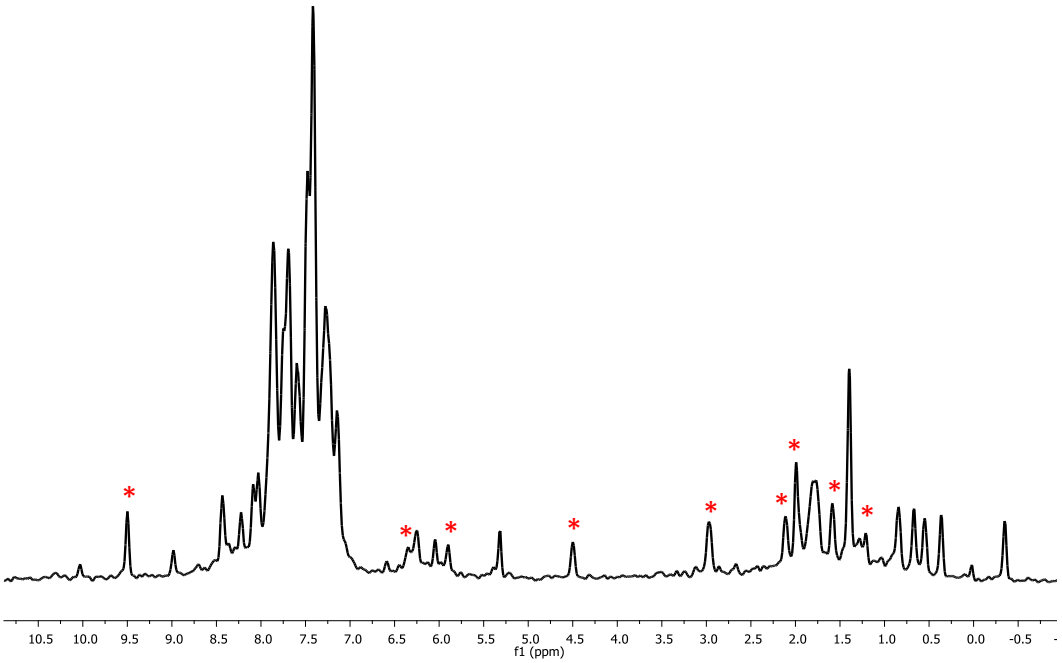

Figure 192. ^{1}H NMR spectrum of the reaction product of **34** with PPh_3 in $CDCl_3$.

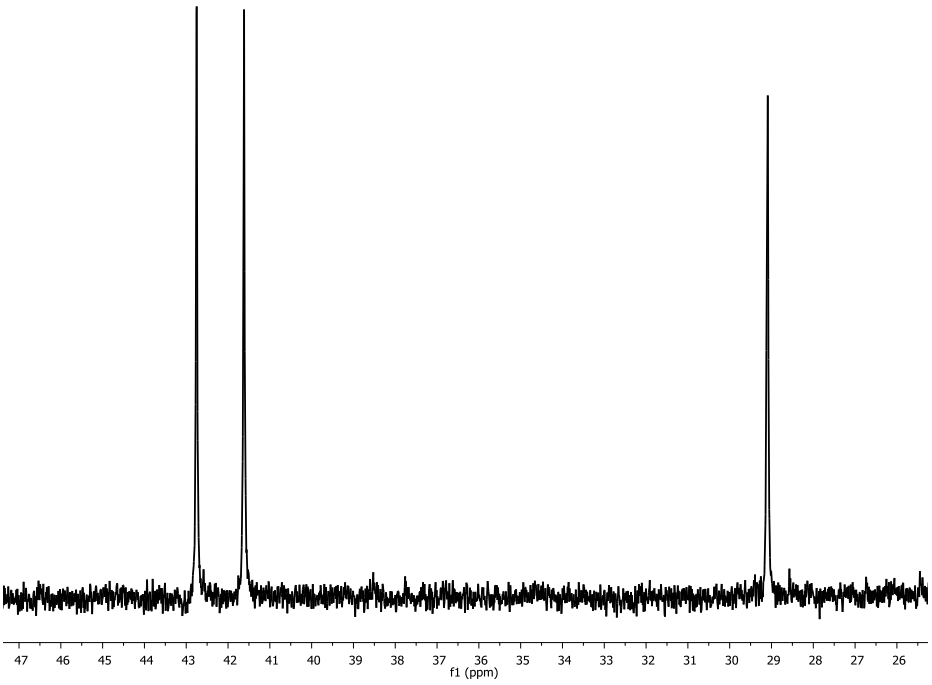

Figure 193. $^{31}P\{^{1}H\}$ NMR spectrum of $[RhCl(PPh_3)_2]_2$ as the reaction product of **34** with PPh_3 in $CDCl_3$.

- **Compound [RhCl(C_9H_6NC(nbyl)OH))(Hpz)(Ph_2PO)] (36)**

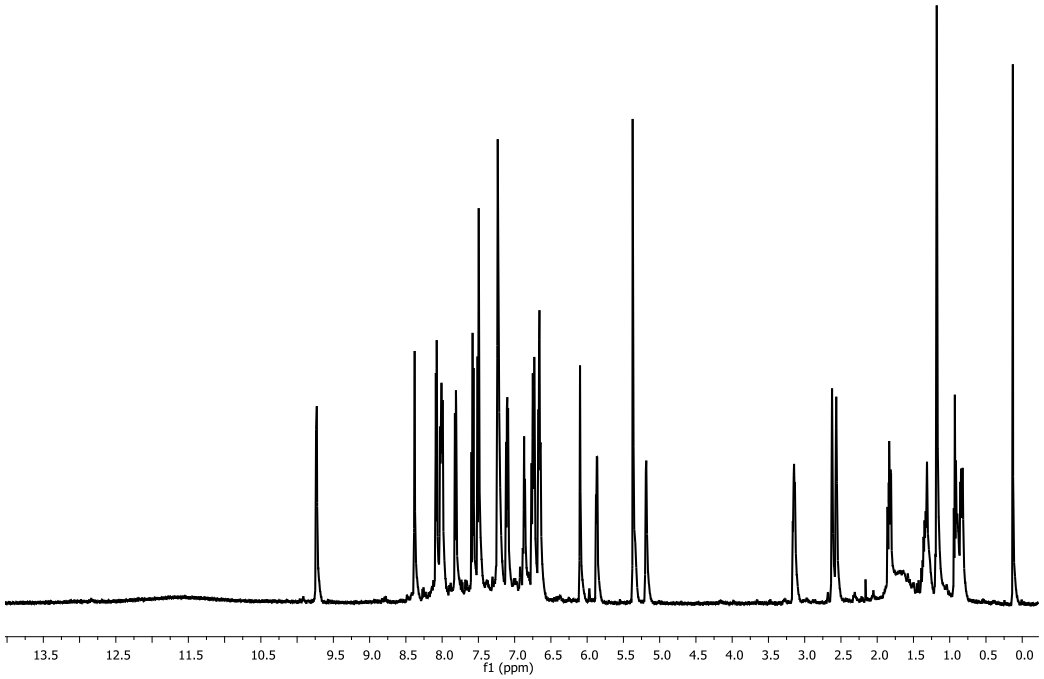

Figure 194. ^{1}H NMR spectrum of compound **36** at 293K in $CDCl_3$.

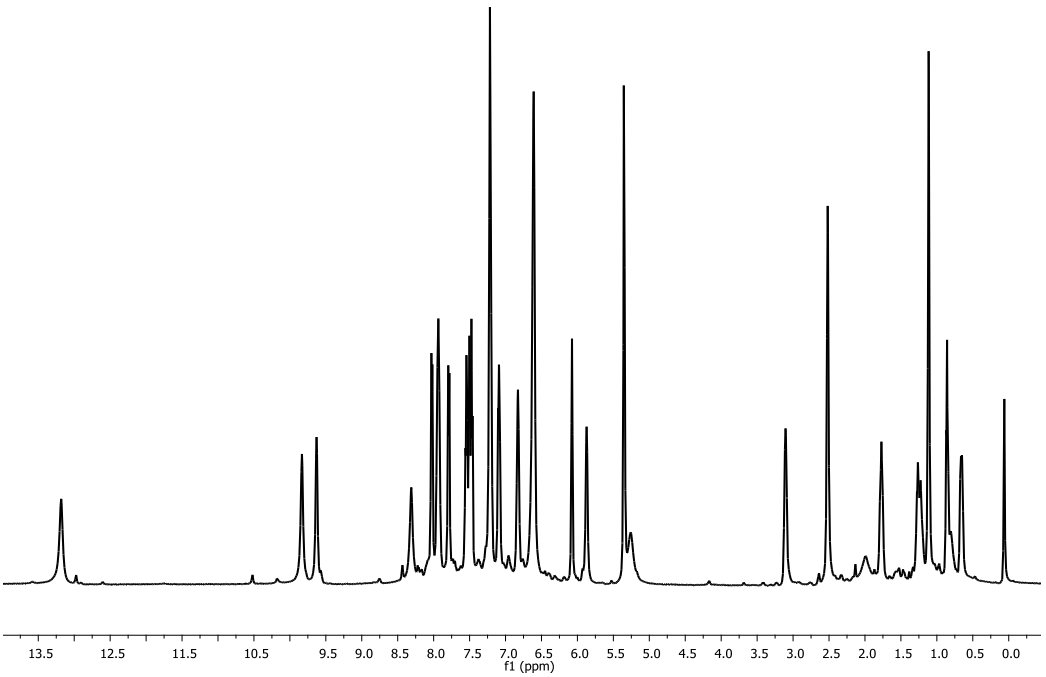

Figure 195. ^{1}H NMR spectrum of compound **36** at 193K in $CDCl_3$.

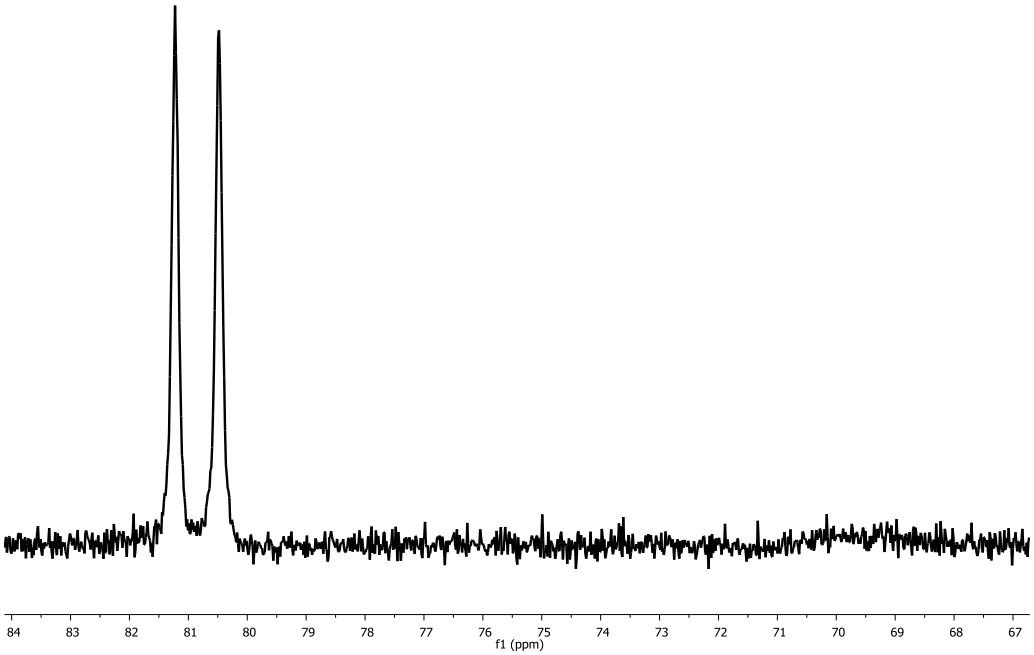

Figure 196. $^{31}P\{^{1}H\}$ NMR spectrum for compound **36** at 293K in CD_2Cl_2.

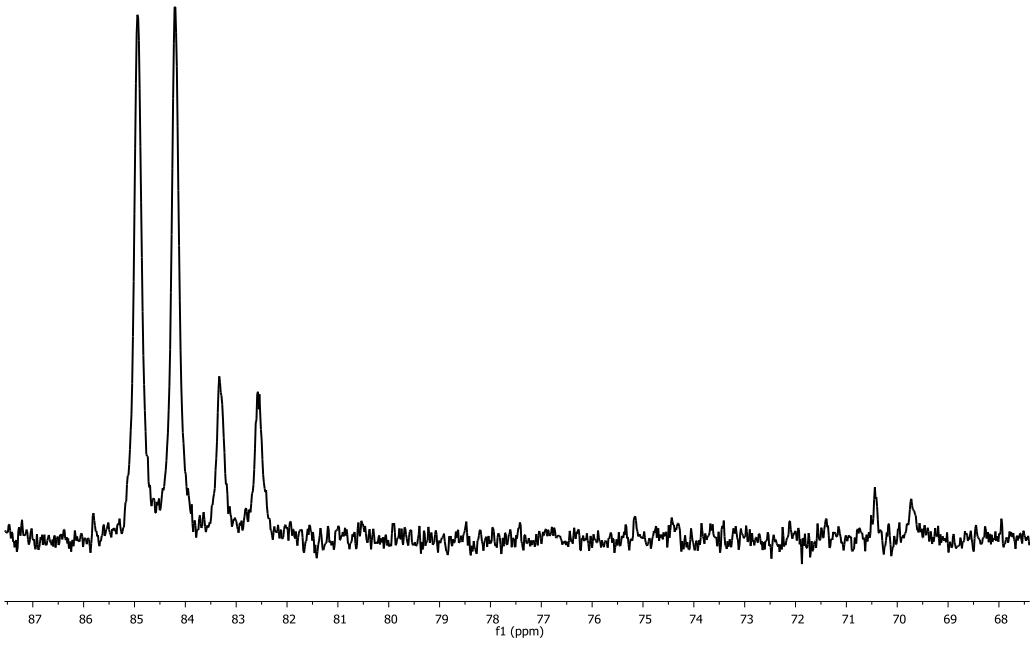

Figure 197. $^{31}P\{^{1}H\}$ NMR spectrum for compound **36** at 193K in CD_2Cl_2.

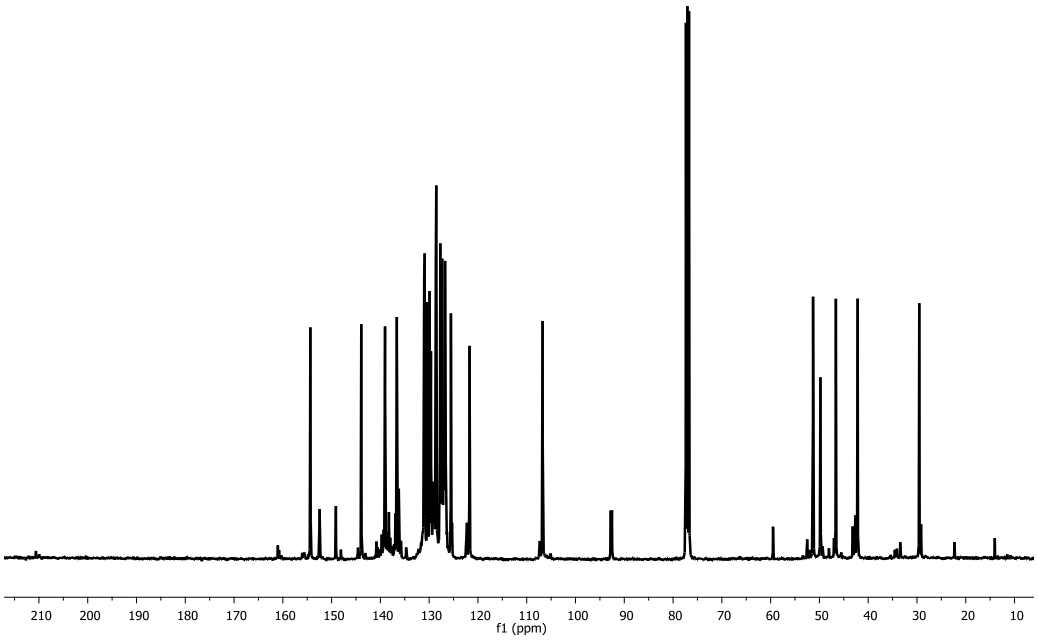

Figure 198. $^{13}C\{^{1}H\}$ NMR spectrum of compound **36** at 293K in $CDCl_3$.

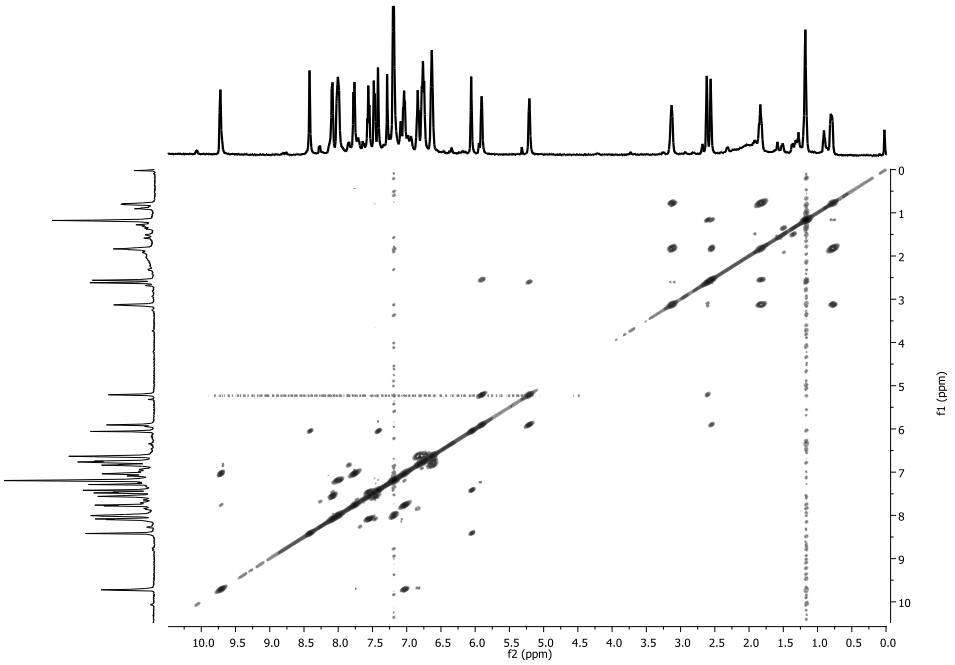

Figure 199. $^{1}H - {}^{1}H$ NMR correlation for compound **36**.

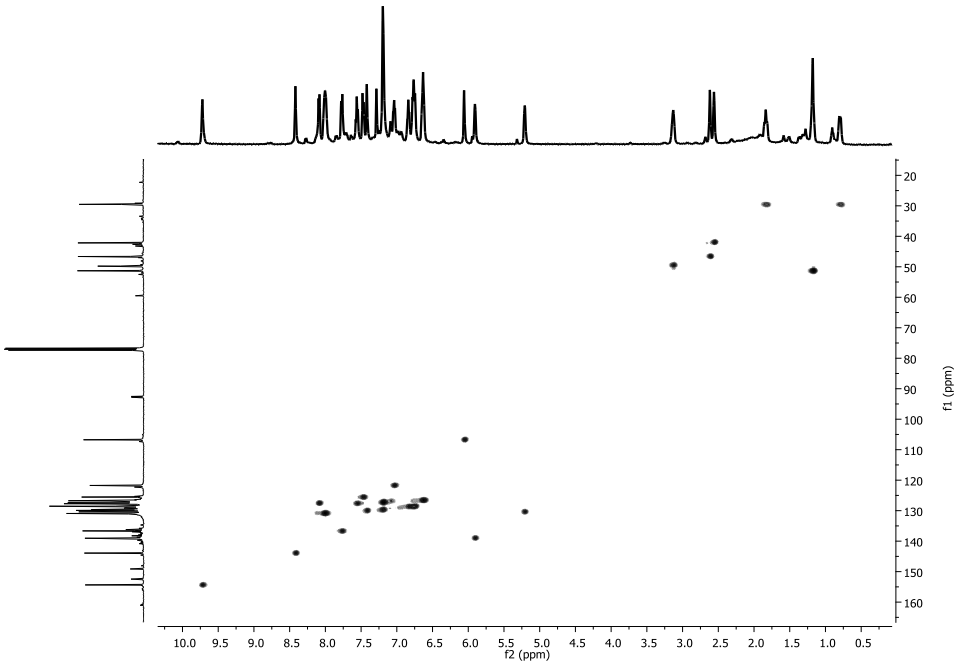

Figure 200. $^{1}H - {}^{13}C\{^{1}H\}$ NMR correlation for compound **36**.

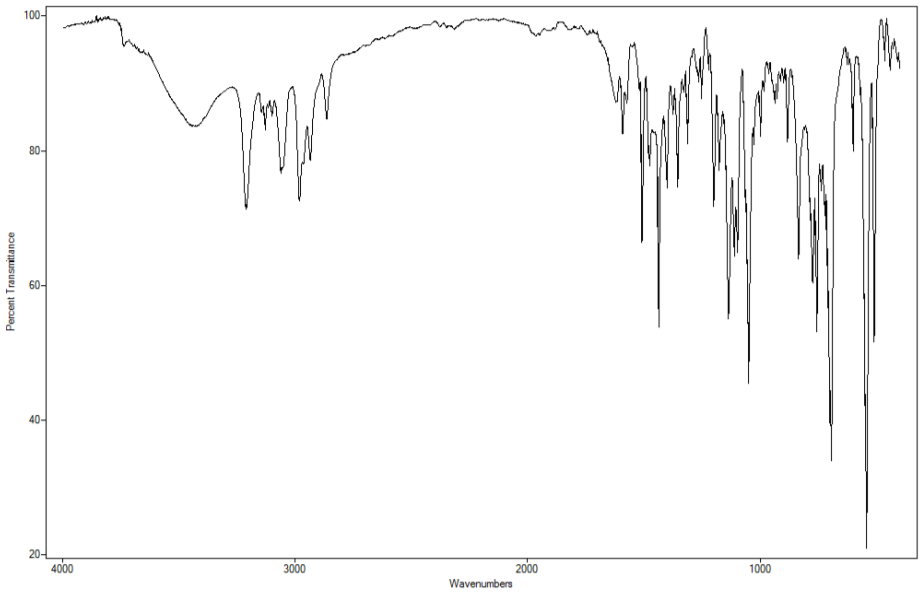

Figure 201. IR spectrum of compound **36**.

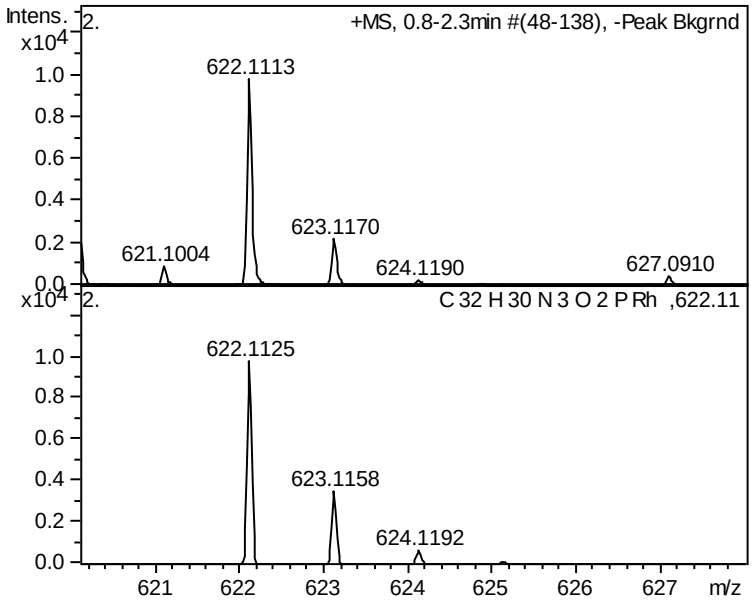

Figure 202. Found (top) and calculated (bottom) ESI-MS of compound **36**.

X-RAY DIFFRACTION

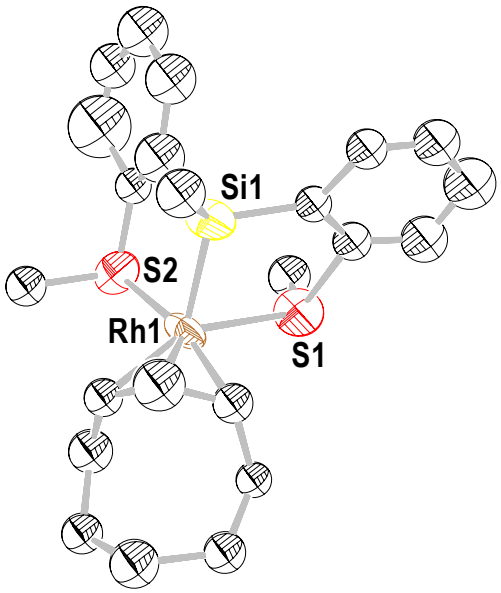

Figure 203. Molecular structure of **4**. The anion and hydrogen atoms are omitted for clarity.

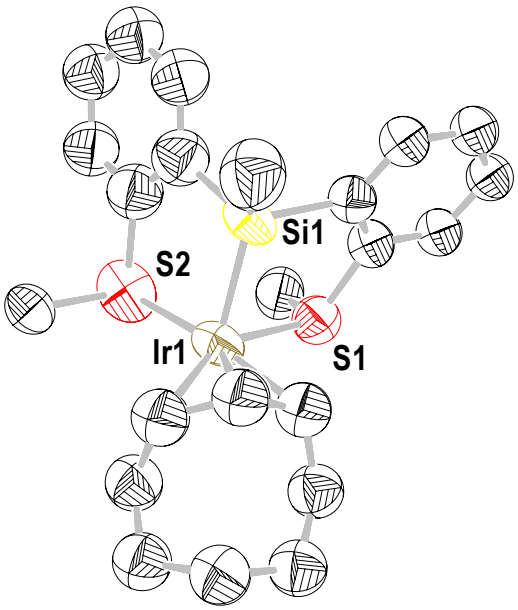

Figure 204. Molecular structure of **6**. The anion and hydrogen atoms are omitted for clarity.

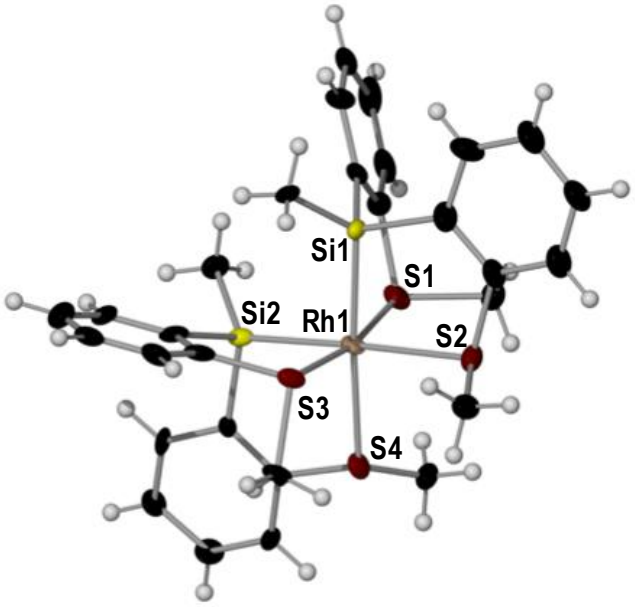

Figure 205. Molecular structure of **21**. The anion and hydrogen atoms are omitted for clarity.

II.1. 2. ACTIVATION OF Si-H BONDS - SYNTHESIS OF SILYL-THIOETHER MULTIDENTATE PRELIGANDS AND THEIR REACTIVITY WITH DIOLEFINIC RHODIUM(I) AND IRIDIUM(I) COMPLEXES

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{37}H_{54}Cl_4S_4Si_4Rh_2$	$C_{26}H_{38}Cl_2S_2Si_2Rh_2$	$C_{24}H_{31}Cl_4S_2SiRh$	$C_{55}H_{42}BF_{24}S_2SiRh$	$C_{33}H_{33}ClPS_2SiRh$	$C_{65}H_{45}BF_{24}PS_2SiRh$
M	1087.02	747.58	656.41	1364.81	691.13	1518.91
T (K)	100	100	100	100	100	100
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*C 2/c*	*P 21/n*	*P-1*	*P-1*	*P 21/n*	*P-1*
a (Å)	27.886(2)	12.8583(6)	10.344(5)	12.212(3)	16.2131(12)	13.0823(11)
b (Å)	14.623(3)	15.5469(8)	11.397(5)	12.428(3)	11.0235(14)	13.1097(12)
c (Å)	11.309(2)	29.6649(9)	13.499(5)	18.878(5)	18.163(2)	19.2485(18)
α (°)	90	90	66.469(5)	84.071(6)	90	84.625(2)
β (°)	99.243(3)	94.676(2)	70.490(5)	83.693(6)	103.454(3)	87.239(2)
γ (°)	90	90	84.258(5)	80.925(6)	90	88.179(3)
V (Å^3)	4551.7(11)	5910.5(5)	1374.28(14)	2801.2(12)	3157.2(6)	3281.6(5)
Z	4	8	2	2	4	2
GOF[a]				1.093	1.083	1.016
ρ_{calcd} (g cm^{-1})	1.586	1.680	1.586		1.454	1.537
μ (mm^{-1})	1.276	1.535	1.218		0.868	0.475
θ range (°)	2.22 to 28.76	2.40 to 28.73	2.25 to 28.73			
Reflections collec.	34914	312501	31844		48556	76837
R_{int}	0.0324	0.1017	0.0400	0.1549	0.139	0.049
Completeness	99.6 %	99.7 %	99.7 %			
Data/restr/param	5899 / 0 / 223	15394 / 0 / 625	7106 / 0 / 317			
R_1[b][(I)>2σ(I)]	0.0503	0.0381	0.0273	0.2598	0.049	0.059
wR_2[c] (all refls)	0.1100	0.0587	0.0612	0.5891	0.099	0.134
Largest diff. Peak and hole (eÅ^{-3})	2.309 and -3.407	0.899 and -1.110	0.667 and -0.734			

[a] $S = [\Sigma w(F0^2 - Fc^2)^2 / (Nobs - Nparam)]^{1/2}$ [b] $R1 = \Sigma||F0|-|Fc|| / \Sigma|F0|$ [c] $wR2 = [\Sigma w(F0^2 - Fc^2)^2 / \Sigma wF0^2]^{1/2}$; $w = 1/[\sigma^2(F0^2) + (aP)^2 + bP]$ where $P = (\max(F0^2,0) + 2Fc^2)/3$

Compound	**7**	**8**	**9**	**11**	**12**	**13**	**16**
Empirical formula	$C_{23}H_{30}ClS_2SiIr$	$C_{55}H_{42}BF_{24}S_2SiIr$	$C_{55}H_{41}BF_{24}S_2SiIr$	$C_{54}H_{38}BF_{24}S_2SiRh$	$C_{57}H_{46}BF_{24}S_2SiRh$	$C_{57}H_{44}BF_{24}S_2SiRh$	$C_{52}H_{38}BF_{24}N_2S_2SiRh$
M	626.37	1454.10	1453.10	1348.77	1463.77	1532.65	1352.76
T (K)	100	100	100	100	150	150	150
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*	*P-1*	*P-1*	*I 2/a*	*P-1*
a (Å)	10.3166(6)	12.316(3)	12.2683(5)	12.2532(6)	12.4418(3)	26.2033(2)	13.0277(4)
b (Å)	11.3775(7)	12.382(4)	12.4775(5)	12.7478(7)	12.9564(3)	12.7500(1)	14.6755(5)
c (Å)	13.4886(8)	19.003(4)	19.1517(9)	19.0546(11)	20.2172(6)	38.5848(3)	16.5967(6)
α (°)	66.355(2)	83.660(7)	73.970(2)	73.523(2)	99.872(2)	90	64.948(3)
β (°)	70.426(2)	83.383(7)	89.285(2)	89.902(2)	101.171(2)	105.003(1)	82.485(3)
γ (°)	84.189(2)	80.909(7)	81.529(2)	79.469(2)	97.292(2)	90	74.513(3)
V ($Å^3$)	1365.51(14)	2829.7(12)	2785.7(2)	2802.1(3)	3106.41(14)	12451.46(18)	2769.6(3)
Z	2	2	2	2	2	8	
GOF[a]	1.054	2.426	1.043	1.031			
μ (mm^{-1})					4.818	5.610	
R_{int}	0.0502	0.1748	0.0456	0.1208	0.0400	0.139	
Completeness					98.6 %	99.3 %	
R_1[b][(I)>2σ(I)]	0.0299	0.2557	0.0893	0.0827	0.0464	0.0306	
wR_2[c] (all refls)	0.0710	0.6363	0.2469	0.2415	0.1265	0.0828	

[a] $S = [\Sigma w(F0^2 - Fc^2)^2 / (Nobs - Nparam)]^{1/2}$ [b] $R1 = \Sigma||F0|-|Fc|| / \Sigma|F0|$ [c] $wR2 = [\Sigma w(F0^2 - Fc^2)^2 / \Sigma wF0^2]^{1/2}$; $w = 1/[\sigma^2(F0^2) + (aP)^2 + bP]$ where $P = (\max(F0^2,0) + 2Fc^2)/3$

II.1. 3. ACTIVATION OF Si-H BONDS – SYNTHESIS AND CATALYTIC APPLICATIONS OF SILYL-HYDRIDE RHODIUM(III) AND IRIDIUM(III) COMPLEXES DERIVED FROM L1 AND L2

Compound	**18**	**19**	**21**
Empirical formula	$C_{33}H_{33}ClPS_2SiIr$	$C_{26}H_{38}Cl_2Rh_2S_2Si_2$	$C_{252}H_{190}B_4Cl_7F_{96}Rh_4S_{16}Si_8$
M	780.42	1491.96	6482.74
T (K)	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P 21/c*	*C 2/c*	*C 2/c*
a (Å)	16.2661(8)	37.703(6)	33.9354(15)
b (Å)	10.9845(8)	8.9890(14)	25.7500(11)
c (Å)	21.3844(12)	21.886(3)	31.9893(18)
α (°)	90	90	90
β (°)	124.333(15)	125.321(2)	104.9430(10)
γ (°)	90	90	90
V ($Å^3$)	3155.2(6)	6052.2(16)	27008(2)
Z	4	4	4
GOF[a]	1.127	1.024	1.101
ρ_{calcd} (g cm^{-1})			1.594
μ (mm^{-1})			0.588
R_{int}	0.0424	0.0410	0.092
R_1[b] [(I)>2σ(I)]	0.024	0.0333	0.107
wR_2[c] (all refls)	0.0516	0.0876	0.249

[a] $S = [\Sigma w(F0^2 - Fc^2)^2 / (Nobs - Nparam)]^{1/2}$ [b] $R1 = \Sigma||F0|-|Fc|| / \Sigma|F0|$ [c] $wR2 = [\Sigma w(F0^2 - Fc^2)^2 / \Sigma wF0^2]^{1/2}$; $w = 1/[\sigma^2(F0^2) + (aP)^2 + bP]$ where $P = (\max(F0^2,0) + 2Fc^2)/3$

II.2.2. ACTIVATION OF C-H BONDS - *REACTIVITY OF PHOSPHINE-ALDEHYDE $PPh_2CH(Ph)CH_2CHO$ WITH DIOLEFINIC RHODIUM(I) COMPLEXES*

Compound	***cis*-Cl-23b**	**26a**	**28a**	**31a**	**32**
Empirical formula	$C_{31}H_{28}Cl_2N_2OPRh$	$C_{83}H_{76}Cl_9N_2O_3P_2Rh$	$C_{57}H_{59}BF_4N_2O_3P_2Rh$	$C_{43}H_{47}Cl_3N_2O_2PRh$	$C_{43}H_{44}ClNO_4PRh$
M	649.33	627.46	1071.72	864.05	808.12
T (K)	100	100	100	100	100
crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
space group	*P-1*	*P-1*	*P21/c*	*P21/c*	*P21/n*
a (Å)	9.6045(10)	15.671(3)	10.685(3)	10.8421(17)	9.9698(7)
b (Å)	12.0456(12)	15.668(3)	29.093(3)	9.8845(12)	17.4017(12)
c (Å)	13.9271(14)	16.235(4)	20.488(4)	34.895(2)	21.2563(14)
α (°)	64.4480(10)	108.514(3)	90	90	90
β (°)	75.5590(10)	93.226(3)	111.271(15)	92.883(3)	92.159(8)
γ (°)	75.9930(10)	94.916(3)	90	90	90
V ($Å^3$)	1374.9(2)	3751.2(14)	5935(2)	3734.9(8)	3685.2(4)
Z	2	2	4	4	4
F(000)	660	1690	2220	1784	1672
ρ_{calcd} (g cm^{-1})	1.568	1.073	1.033	1.405	1.457
μ (mm $^{-1}$)	0.902	0.643	0.394	0.756	0.624
data collected	(-12,-15,-17) to (12,15,18)	(-19,-20,-21) to(19,20,21)	(-7,-21,-14) to (7,21,14)	(-14,-12,-46) to (14,13,46)	(-13,-23,-28) to (13,23,28)
θ range (°)	1.663 to 28.12	1.309 to 28.200	2.162 to 14.973	2.164 to 28.885	1.513 to 28.527
Reflections collec.	15975	43841	15647	76565	43008
Independent refls.	6150	16840	2378	9432	8853
Refls.obsd. (I)>2σ(I)	5402	12698	2214	6899	7559
R_1[a] [(I)>2σ(I)]	0.0334	0.0551	0.0776	0.0535	0.0365
wR_2[b] (all refls)	0.0885	0.1497	0.1841	0.1265	0.0924
Largest diff. Peak and hole e$Å^{-3}$	0.809 and -0.524	1.265 and -0.676	0.697 and -0.472	1.620 and -1.301	1.112 and -1.003

[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$ [b] $wR_2 = \{\Sigma[w(F_O^2-F_C^2)^2]/\Sigma[w(F_O^2)^2]\}^{1/2}$

II.2.3. ACTIVATION OF C-H BONDS - ***THE REACTION OF [Rh(nbd)Cl]$_2$ WITH QUINOLINE-8-CARBALDEHYDE AND PYRAZOLE. REACTIVITY AND CATALYTIC APPLICATIONS***

Compound	**33b**	**36a**
Empirical formula	$C_{40}H_{38}N_6O_2Cl_2Rh_2$	$C_{32}H_{30}N_3O_2PClRh$
M	911.48	657.93
T (K)	100	100
crystal system	Triclinic	Orthorhombic
space group	*P-1*	*P b c n*
a (Å)	8.5060(4)	16.7366(9)
b (Å)	11.7521(5)	18.6235(10)
c (Å)	14.1406(6)	17.5642(9)
α (°)	112.075(2)	90
β (°)	99.886(2)	90
γ (°)	100.293(2)	90
V (Å^3)	1243.9(8)	5474.6(6)
Z	1	8