Electronic Supporting Information for:

Synthesis and group 9 complexes of macrocyclic PCP and POCOP pincer ligands

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1. Additional experimental details

1.1. Attempted reaction of mesylate of 3 with disodium resorcinolate

Triethylamine (19 µL, 0.14 mmol) was added dropwise to a solution of **3** (20.0 mg, 92.5 µmol) and methanesulfonic anhydride (16.1 mg, 92.5 µmol) in dichloromethane (1 mL) at -20 °C and the resulting solution stirred at this temperature for 1 h. A suspension of resorcinol (3.4 mg, 31 µmol) and sodium hydride (1.6 mg, 67 µmol) in dichloromethane (1 mL), which had been stirred at RT for 30 minutes, was added and the solution stirred at -20 °C for 2 days. Analysis of an aliquot by ESI-MS and ^{1}H and ^{31}P NMR spectroscopy was consistent with no reaction having taken place.

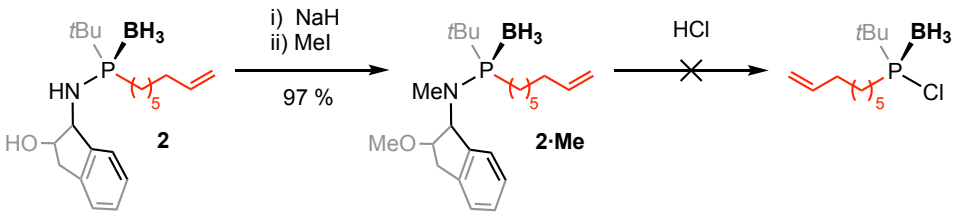
1.2. Attempted reaction of conjugate base of 3 with 1,3-difluorobenzene

A solution of **3** (30.0 mg, 139 µmol) and KHMDS (27.7 mg, 139 µmol) in anhydrous DMF (2 mL) was stirred at RT for 1 h. To this solution 1,3-difluorobenzene (7 µL, 71 µmol) was added, the flask sealed, and heated at 150 °C overnight. Analysis of the reaction mixture by ^{31}P NMR spectroscopy was consistent with no reaction having taken place.

1.3. Attempted acidolysis of 2 with HCl

A solution of HCl (1M in Et_2O, 0.06 mL, 0.06 mmol) was added to a solution of **2** (10.4 mg, 28.8 µmol) in C_6D_6 (0.5 mL) within J Young's valve NMR tube. Storage at RT followed by heating at 60 °C gave ^{1}H and ^{31}P{^{1}H} NMR spectra consistent with a mixture of the two reactants.

1.4. Attempted acidolysis of an alkylated derivative of 2 with HCl



A suspension of **2** (226 mg, 625 µmol) and NaH (56 mg, 2.3 mmol) in THF (ca. 5 mL) was stirred at RT for 1 h. MeI (0.39 mL, 6.3 mmol) was added and the suspension stirred at RT overnight. The reaction was exposed to air, quenched with saturated aqueous NH_4Cl (20 mL), and the aqueous phase extracted with EtOAc (3 x 15 mL). The combined organic fractions were dried ($MgSO_4$), filtered and volatiles removed under reduced pressure to afford **2·Me** as a colourless oil, which was dried *in vacuo* and used without further purification. Yield: 235 mg (97%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.31 (m, 1H, Ar), 7.20 – 7.26 (m, 3H, Ar), 5.81 (ddt, $^{3}J_{HH}$ = 16.9, 10.2, 6.7, 1H, C<u>H</u>=CH$_2$), 5.10 (dd, $^{3}J_{PH}$ = 9.9, $^{3}J_{HH}$ = 5.7, 1H, NC<u>H</u>), 4.99 (app dq, $^{3}J_{HH}$ = 17, J_{HH} = 2, 1H, CH=C<u>H</u>$_2$), 4.93 (br d, $^{3}J_{HH}$ = 10.1, 1H, CH=C<u>H</u>$_2$), 4.27 (app td, $^{3}J_{HH}$ = 5, $^{3}J_{HH}$ = 1.5, 1H, OCH),

3.33 (s, 3H, OCH_3), 2.97 (dd, $^2J_{HH}$ = 16.5, $^3J_{HH}$ = 1.5, 1H, OCHC$\underline{H}_2$), 2.88 (dd, $^2J_{HH}$ = 16.5, $^3J_{HH}$ = 5.2, 1H, OCHC$\underline{H}_2$), 2.64 (d, $^3J_{PH}$ = 6.1, 3H, NCH_3), 2.11 – 2.18 (m, 1H, PCH_2), 2.08 (app q, $^3J_{HH}$ = 7, 2H, C$\underline{H}_2$CH=CH_2), 1.75 – 1.91 (m, 1H, CH_2), 1.52 – 1.72 (m, 2H, CH_2), 1.34 – 1.52 (m, 6H, CH_2), 1.26 (d, $^3J_{PH}$ = 13.3, 9H, *t*Bu), 0.61 (partially collapsed quartet, fwhm = 310 Hz, 3H, BH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 140.68 (d, $^3J_{PC}$ = 6, Ar{C}), 140.65 (s, Ar{C}), 139.1 (s, $\underline{C}$H=CH_2), 127.7 (s, Ar), 126.6 (s, Ar), 125.9 (s, Ar), 124.7 (s, Ar), 114.5 (s, CH=$\underline{C}H_2$), 86.4 (s, OCH), 67.2 (d, $^2J_{PC}$ = 10, NCH), 56.9 (s, OCH_3), 35.7 (s, OCH$\underline{C}H_2$), 34.4 (d, $^1J_{PC}$ = 35, *t*Bu{C}), 33.93 (d, $^2J_{PC}$ = 4, NCH_3), 33.87 (s, $\underline{C}H_2$CH=CH_2), 31.6 (d, $^2J_{PC}$ = 14, CH_2), 29.0 (s, CH_2), 28.9 (s, CH_2), 26.6 (d, $^2J_{PC}$ = 2, *t*Bu{CH_3}), 22.4 (s, CH_2), 20.6. (d, $^1J_{PC}$ = 39, PCH_2).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): *δ* 86.0 (partially collapsed quartet, fwhm = 215 Hz).

HR ESI-MS (positive ion, 4 kV): 412.2923, $[M+Na]^+$ (calcd 412.2915); 801.5956, $[2M+Na]^+$ (calcd 801.5945) *m/z*.

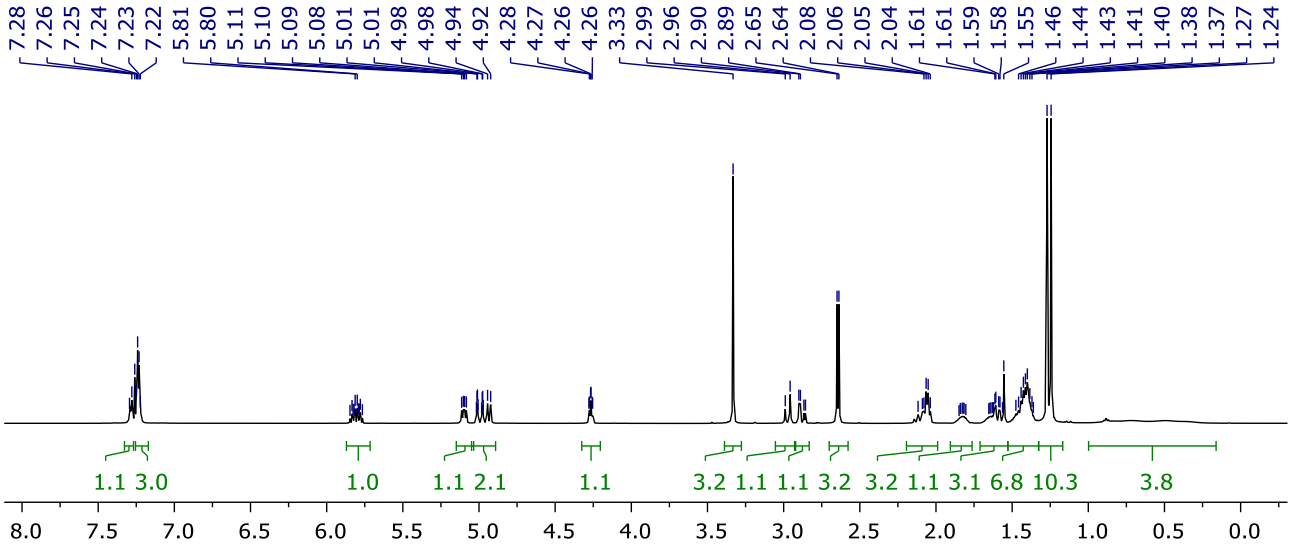


Figure S1. ^{1}H NMR spectrum of **2·Me** ($CDCl_3$, 500 MHz).

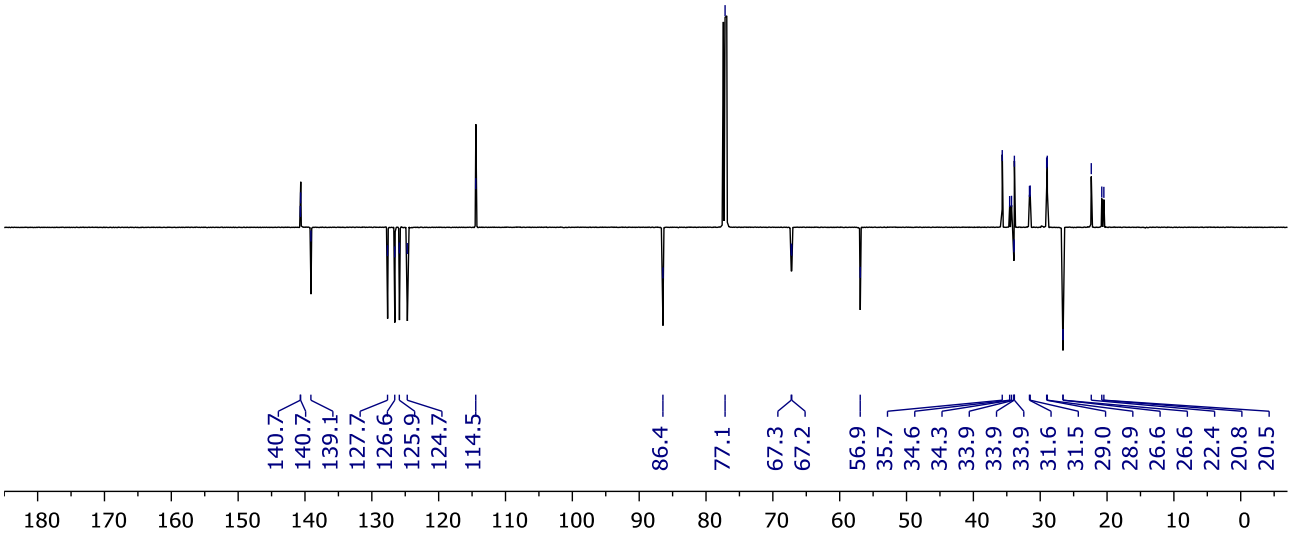


Figure S2. ^{13}C{^{1}H} APT NMR spectrum of **2·Me** ($CDCl_3$, 126 MHz).

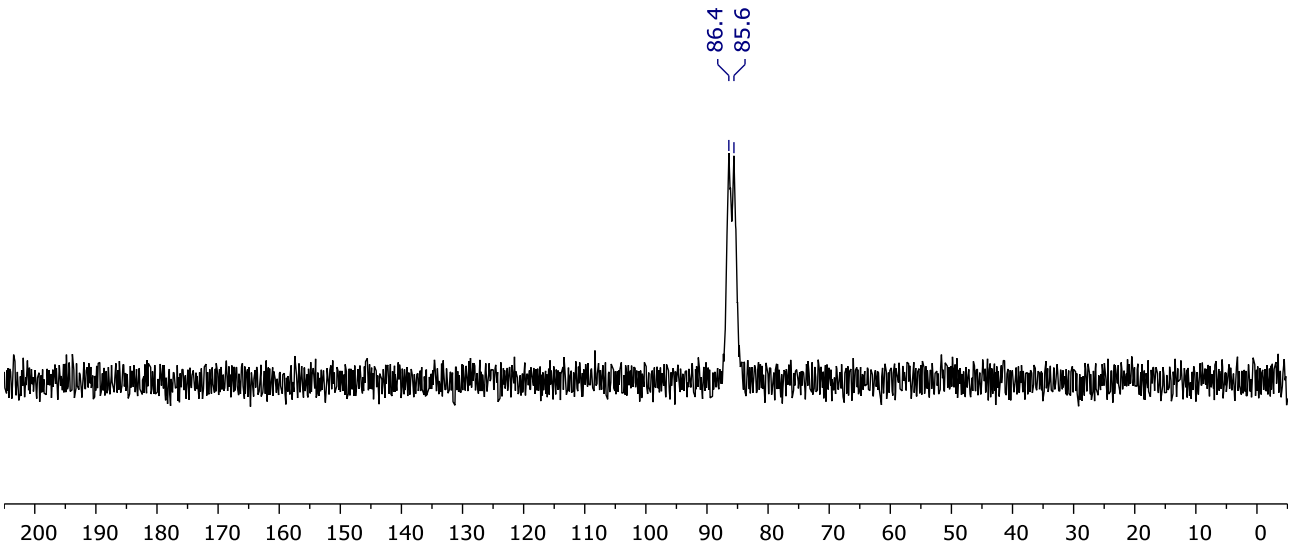


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **2·Me** ($CDCl_3$, 121 MHz).

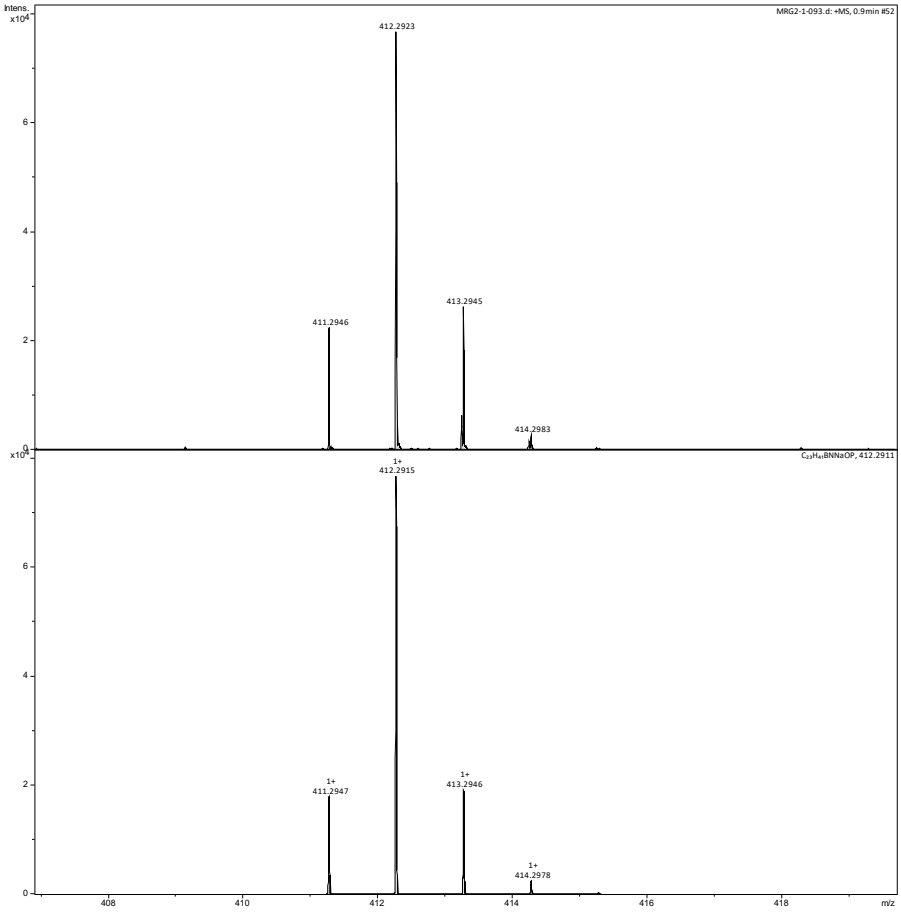


Figure S4. HR ESI-MS of **2·Me**.

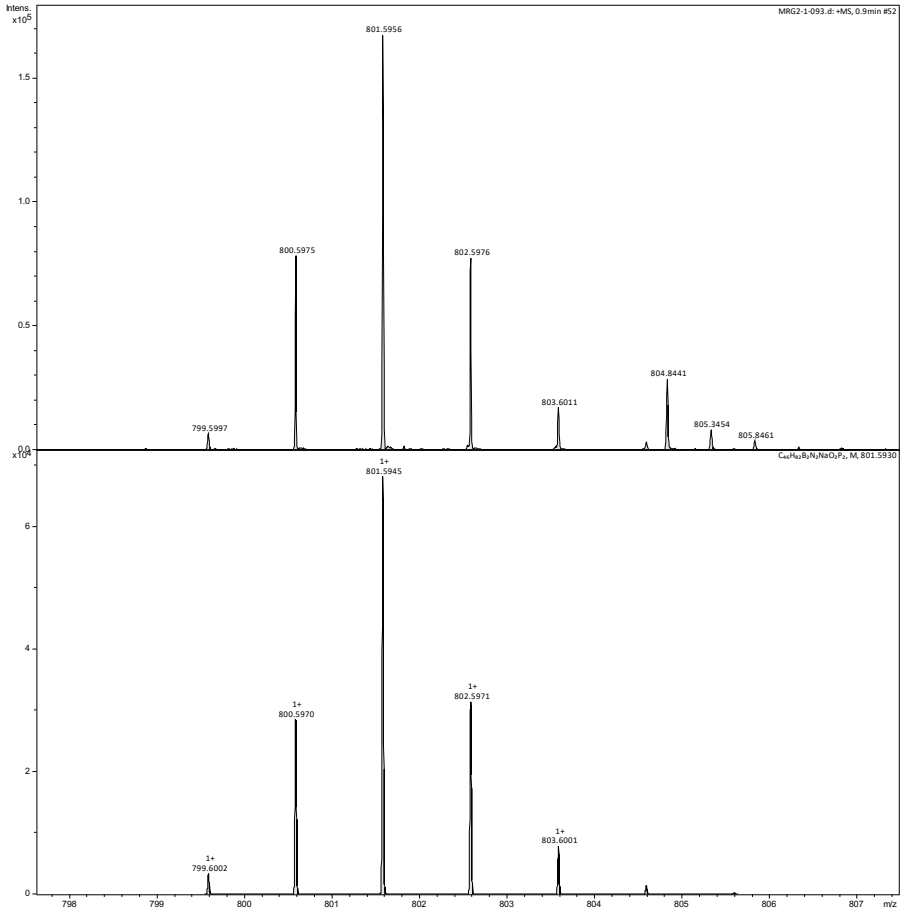


Figure S5. HR ESI-MS of **2·Me**.

A solution of HCl (1M in Et_2O, 0.2 mL, 0.2 μmol) was added to a solution of **2·Me** (40.3 mg, 104 μmol) in C_6D_6 (0.5 mL) within a J Young's valve NMR tube. Storage at room temperature followed by heating at 75 °C gave ^1H and $^{31}P\{^1H\}$ NMR spectra consistent with a mixture of the two reactants.

2. Selected NMR and HR ESI-MS spectra

2.1. Synthesis of PCP-14'

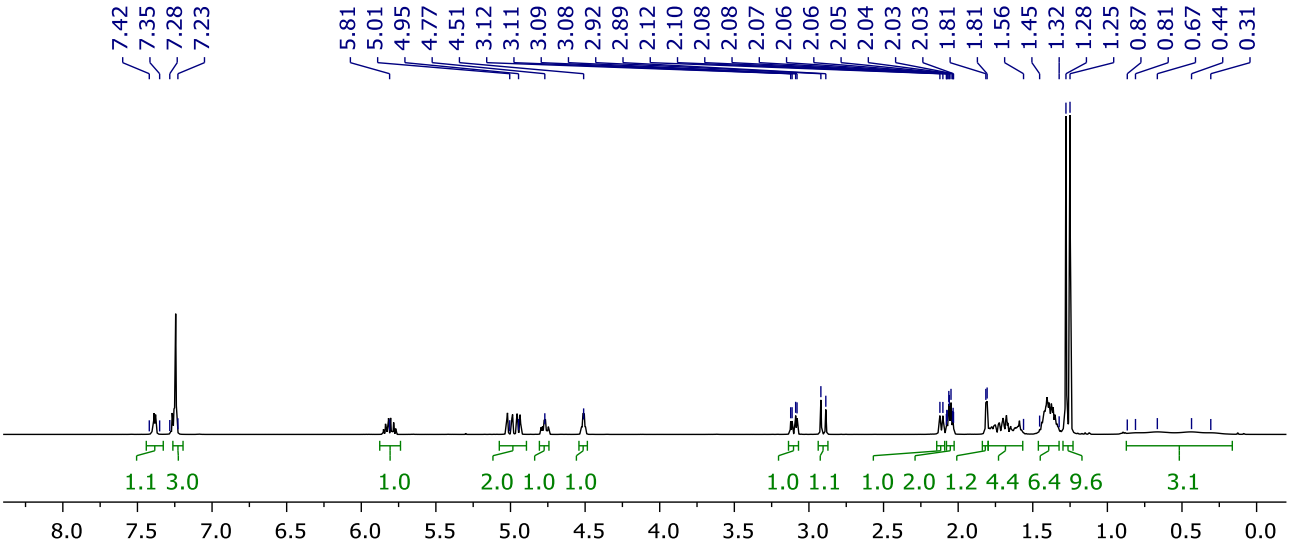


Figure S6. ^{1}H NMR spectrum of **2** ($CDCl_3$, 500 MHz).

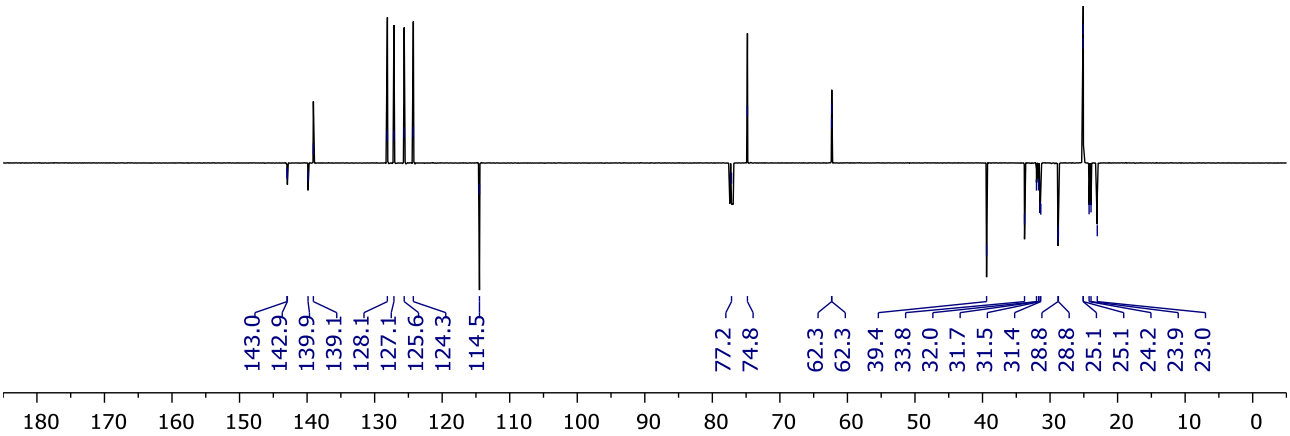


Figure S7. $^{13}C\{^{1}H\}$ APT NMR spectrum of **2** ($CDCl_3$, 126 MHz).

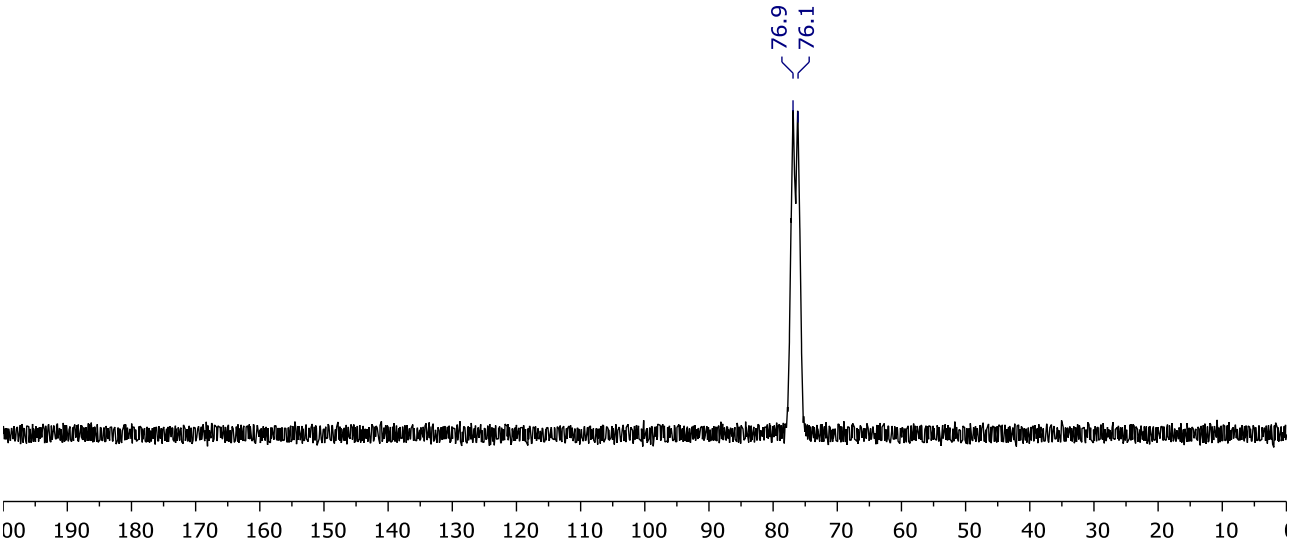


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **2** ($CDCl_3$, 121 MHz).

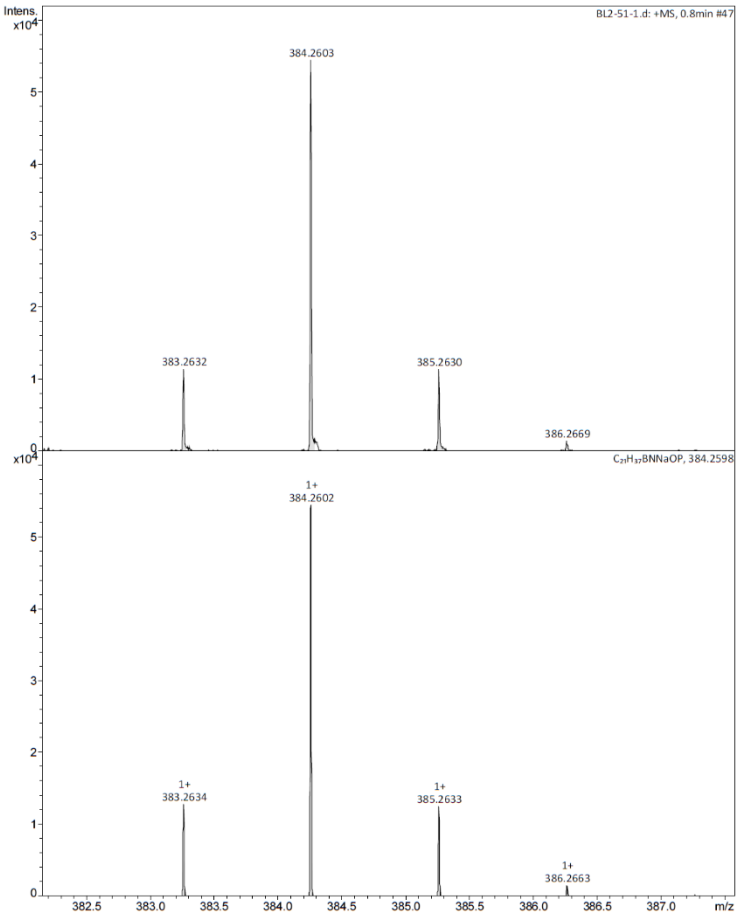


Figure S9. HR ESI-MS of **2**.

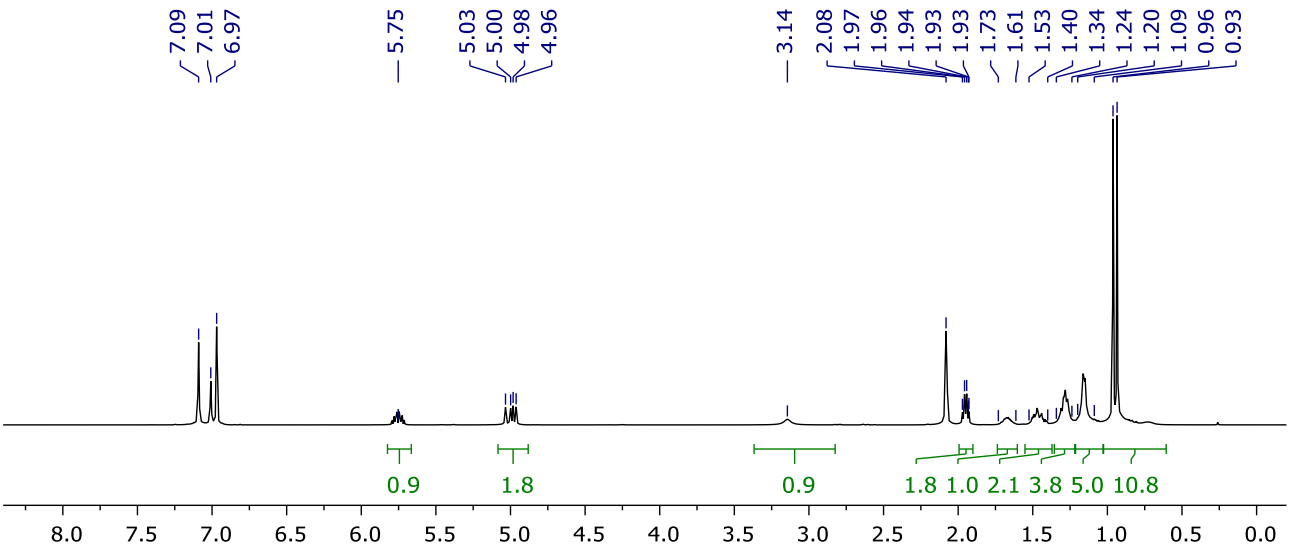


Figure S10. ^{1}H NMR spectrum of **3** (toluene-d_8, 500 MHz).

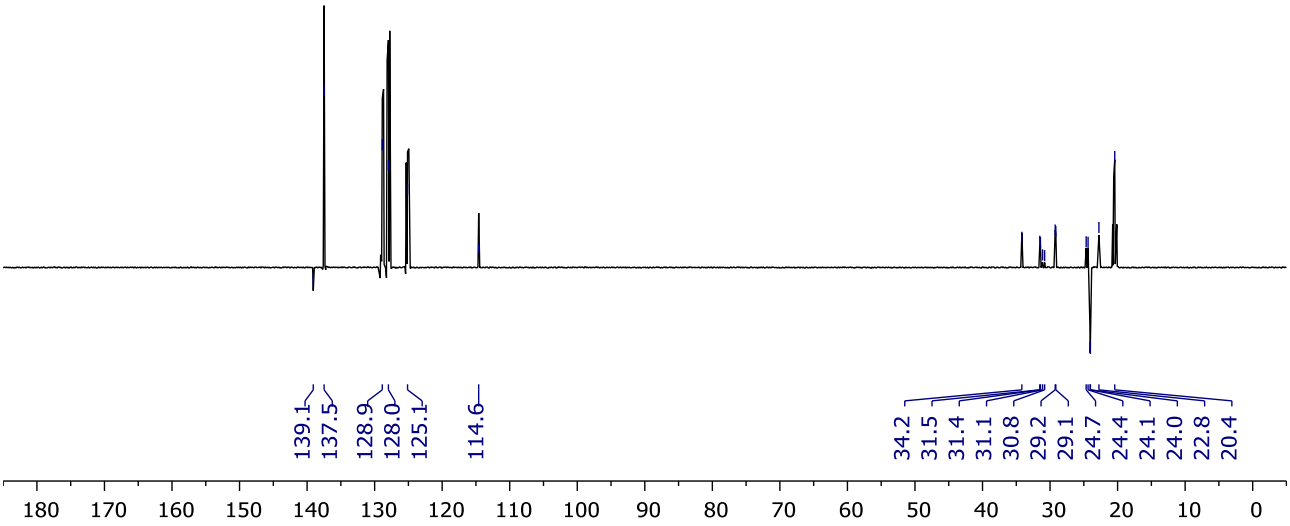


Figure S11. ^{13}C{^{1}H} APT NMR spectrum of **3** (toluene-d_8, 126 MHz).

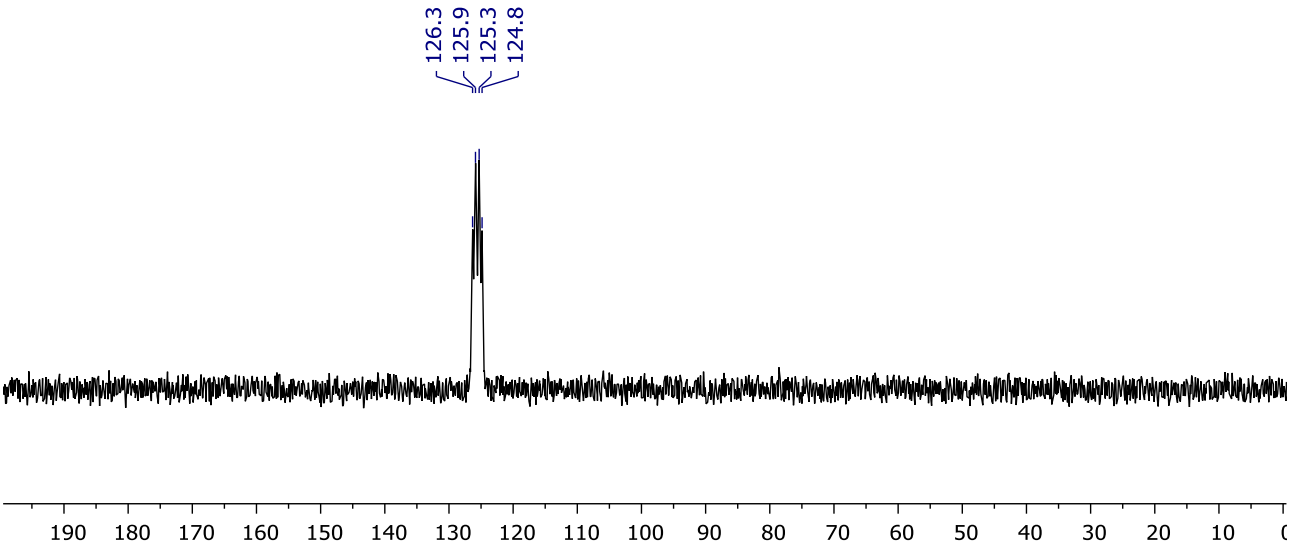


Figure S12. ^{31}P{^{1}H} NMR spectrum of **3** (toluene-d_8, 121 MHz).

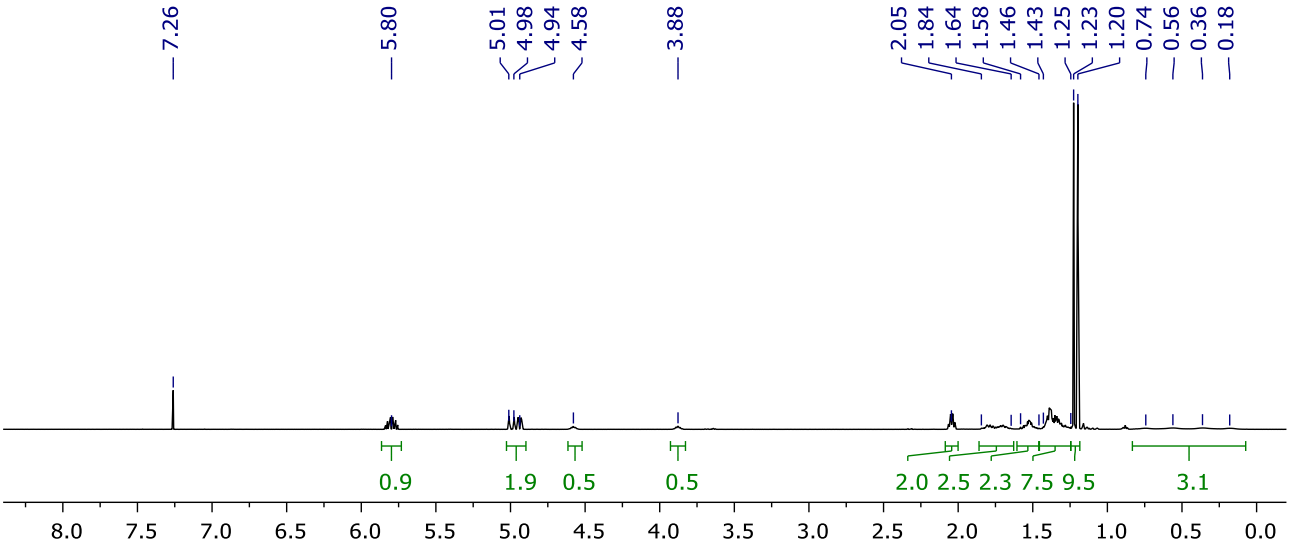


Figure S13. ^{1}H NMR spectrum of **4** ($CDCl_3$, 500 MHz).

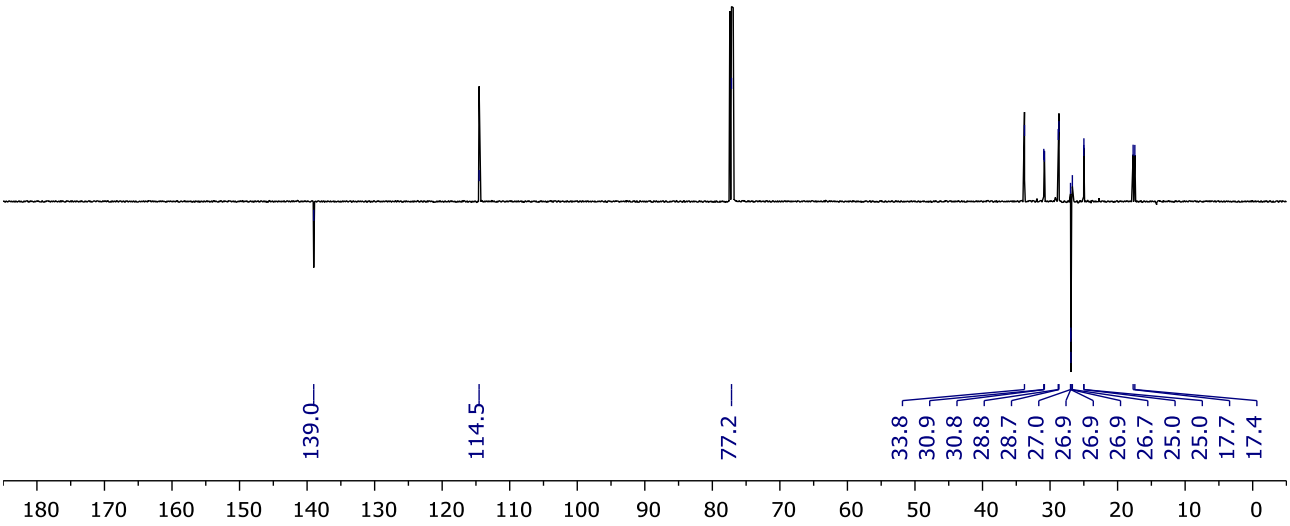


Figure S14. $^{13}C\{^{1}H\}$ APT NMR spectrum of **4** ($CDCl_3$, 126 MHz).

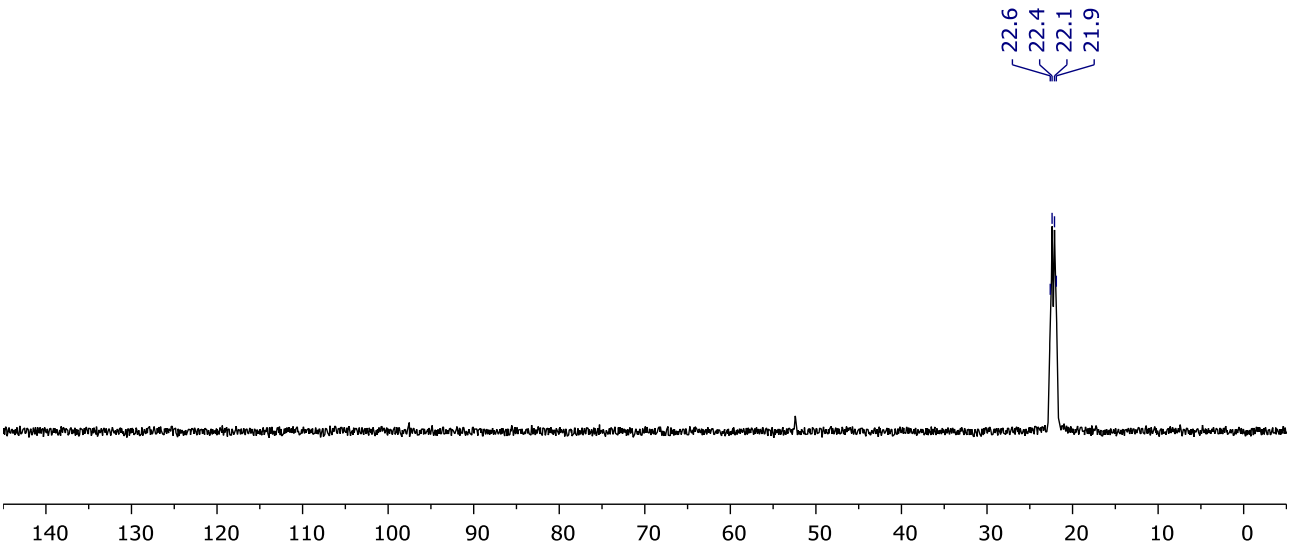


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **4** ($CDCl_3$, 202 MHz).

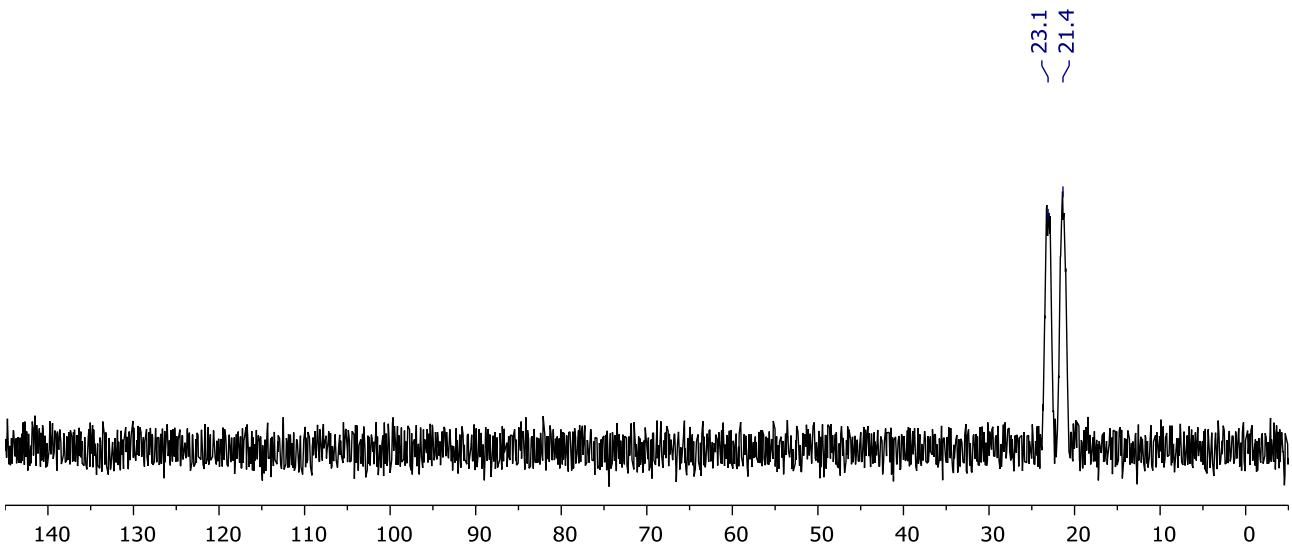


Figure S16. ^{31}P NMR spectrum of **4** ($CDCl_3$, 202 MHz).

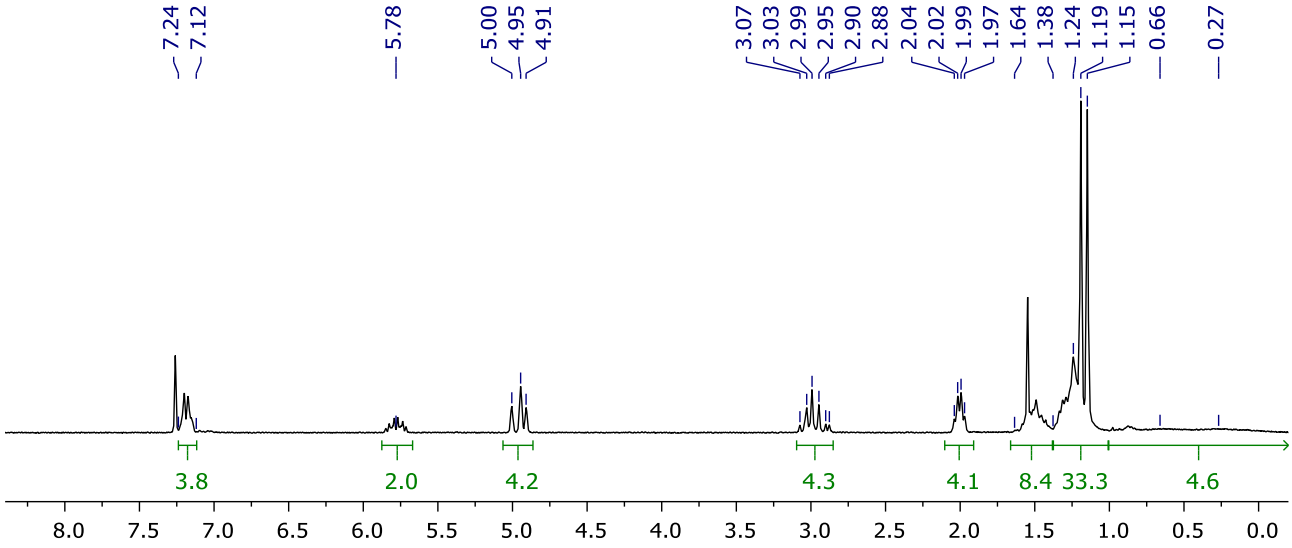


Figure S17. ^{1}H NMR spectrum of **5** ($CDCl_3$, 500 MHz).

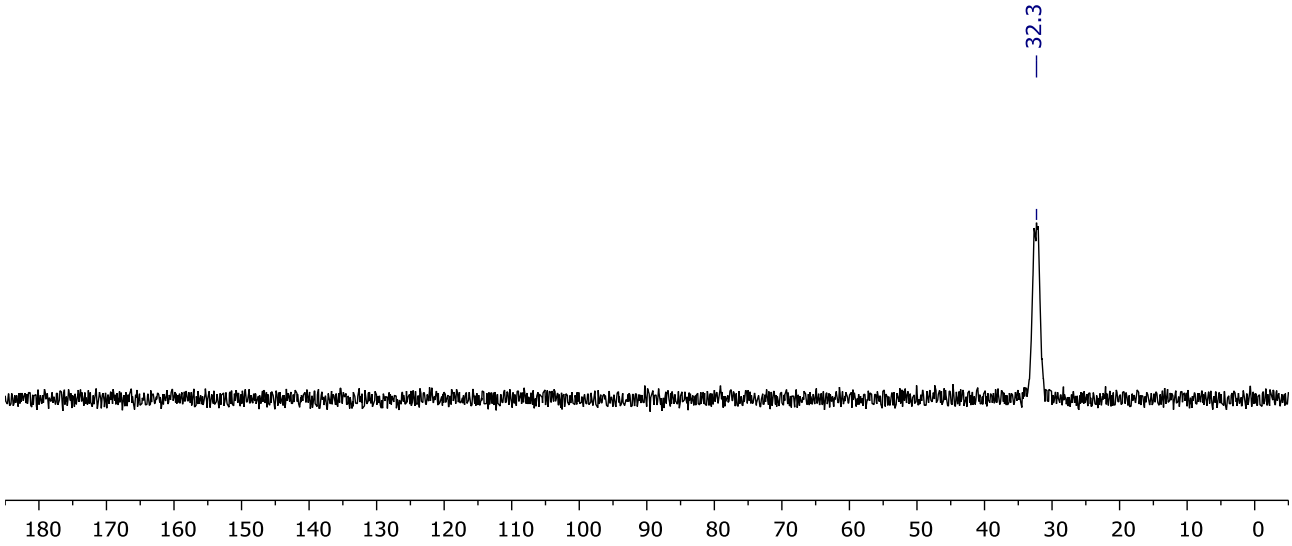


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$, 202 MHz).

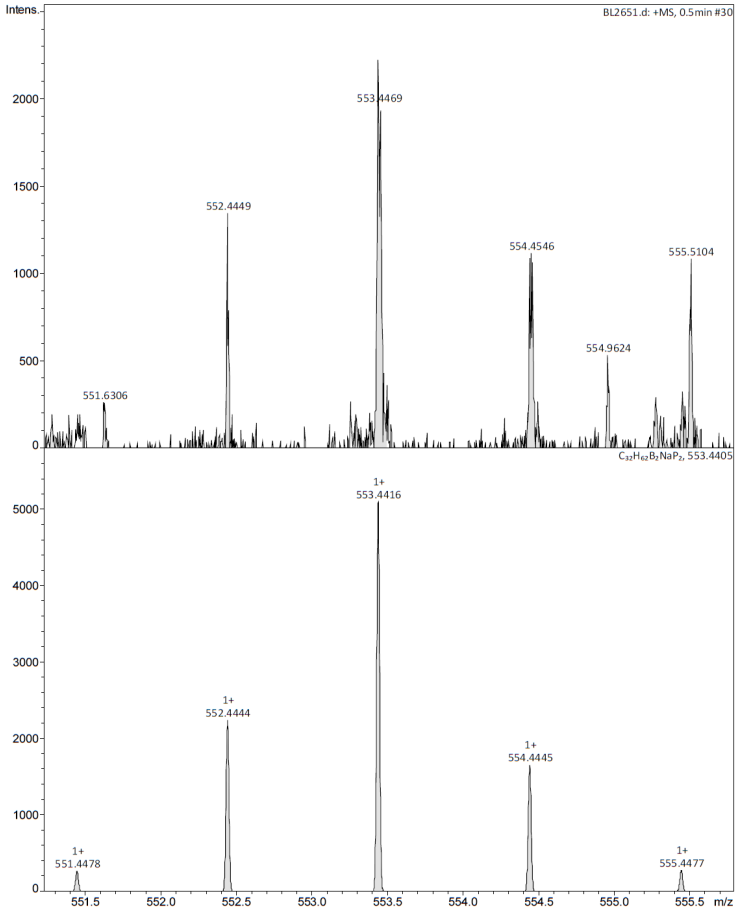


Figure S19. HR ESI-MS of **5**.

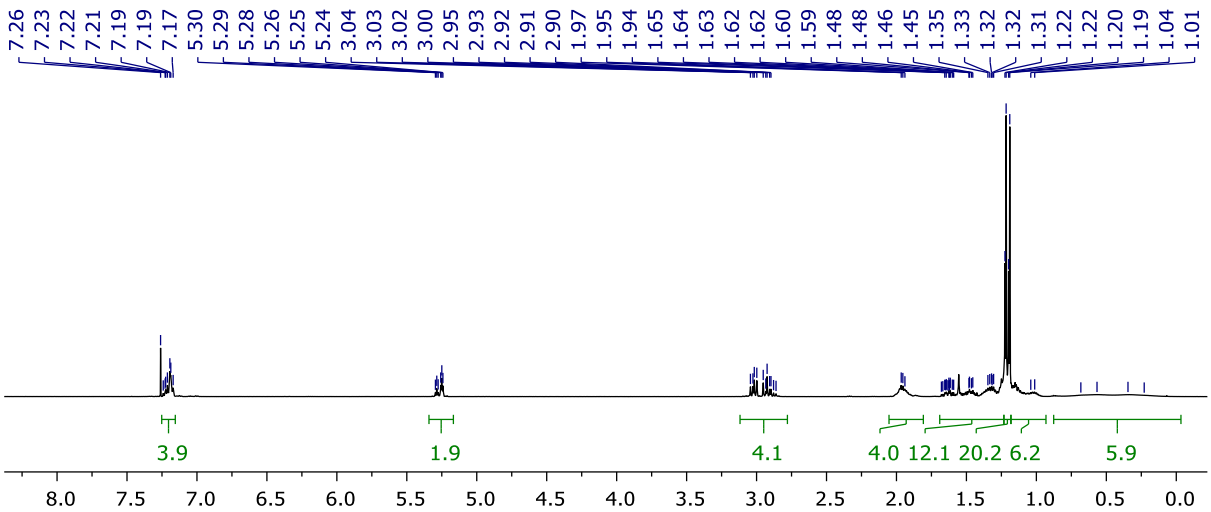


Figure S20. ^{1}H NMR spectrum of **6** ($CDCl_3$, 500 MHz).

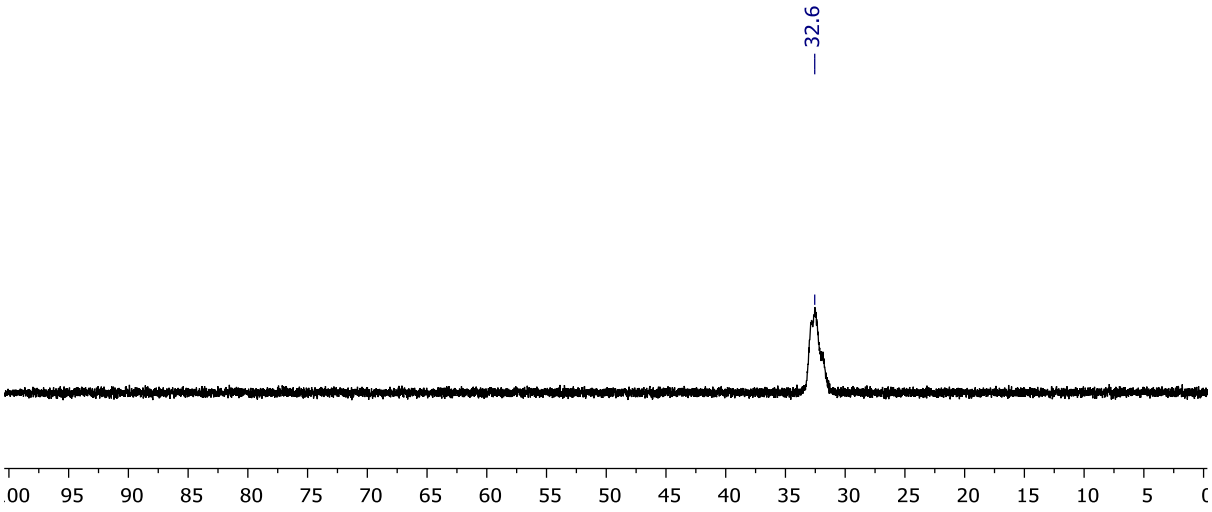


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **6** ($CDCl_3$, 202 MHz).

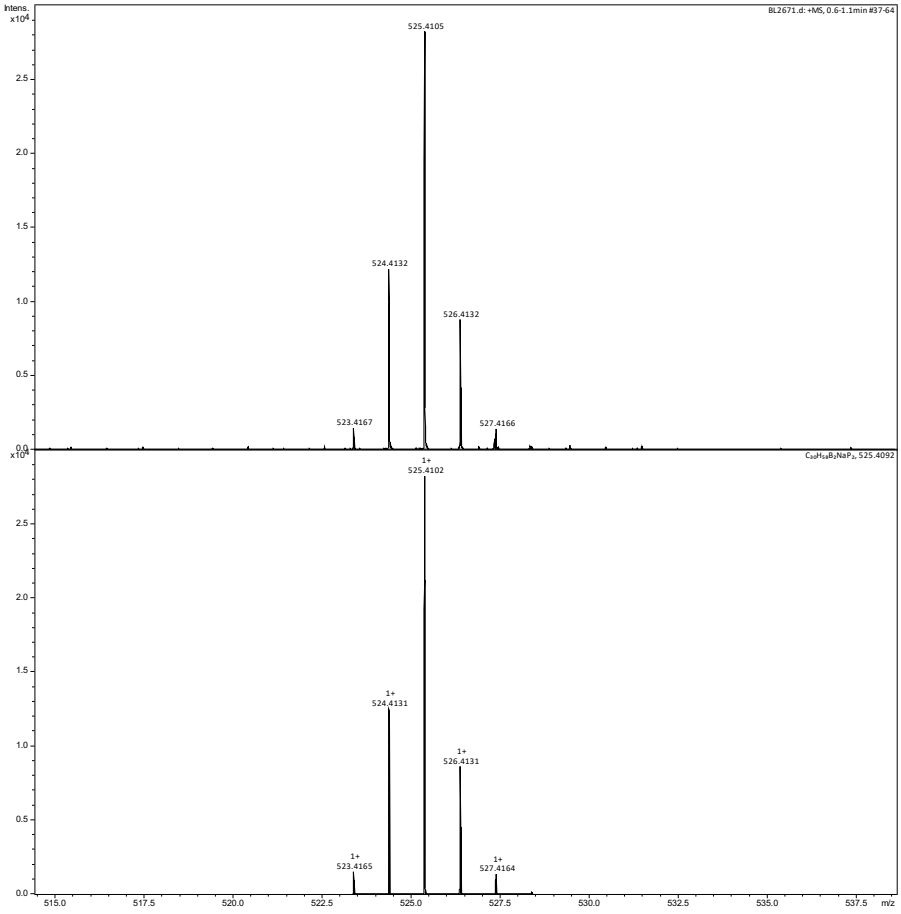


Figure S22. HR ESI-MS of **6**.

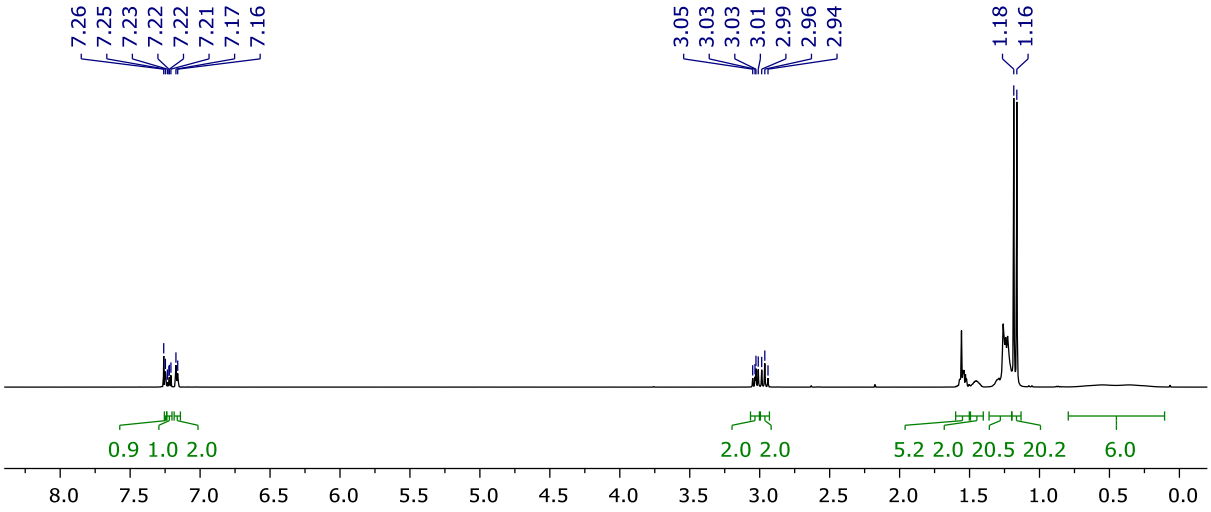


Figure S23. ^{1}H NMR spectrum of **7** ($CDCl_3$, 600 MHz).

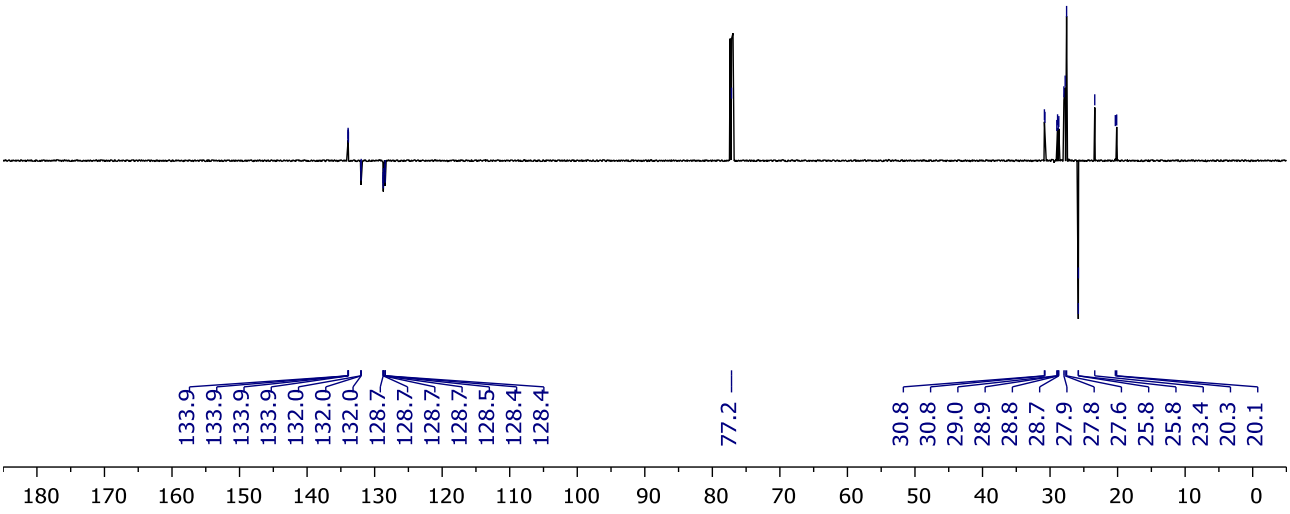


Figure S24. $^{13}C\{^{1}H\}$ APT NMR spectrum of **7** ($CDCl_3$, 151 MHz).

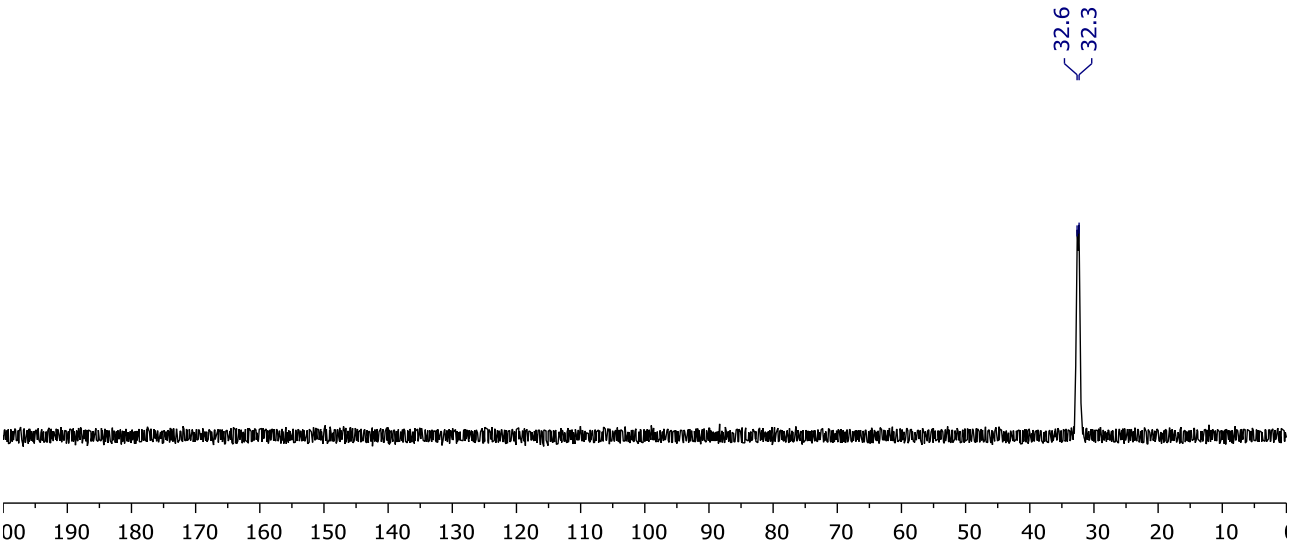


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **7** ($CDCl_3$, 243 MHz).

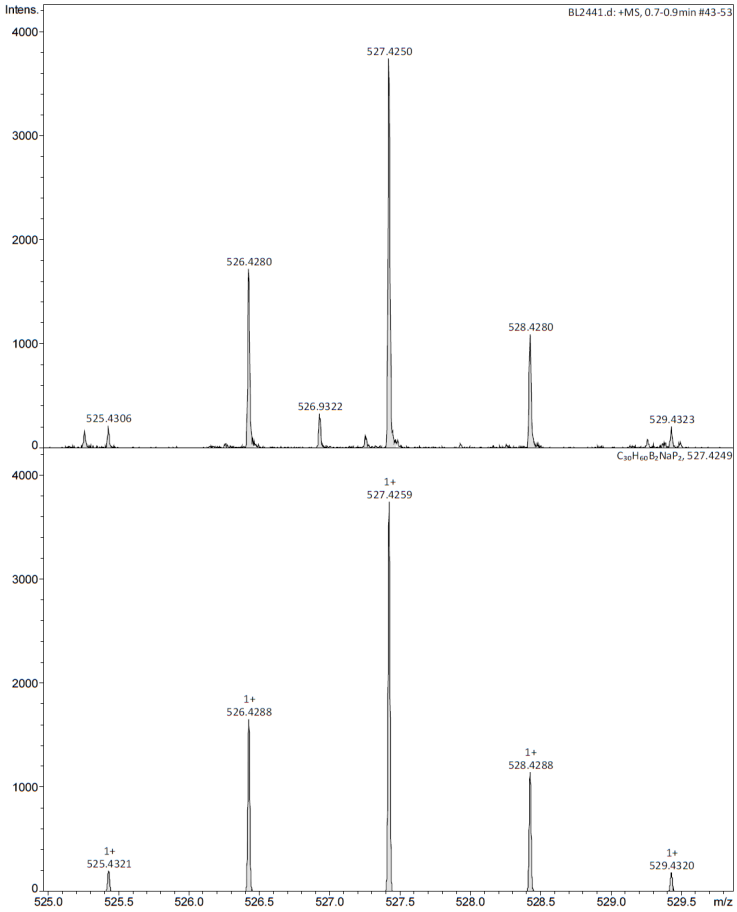


Figure S26. HR ESI-MS of **7**.

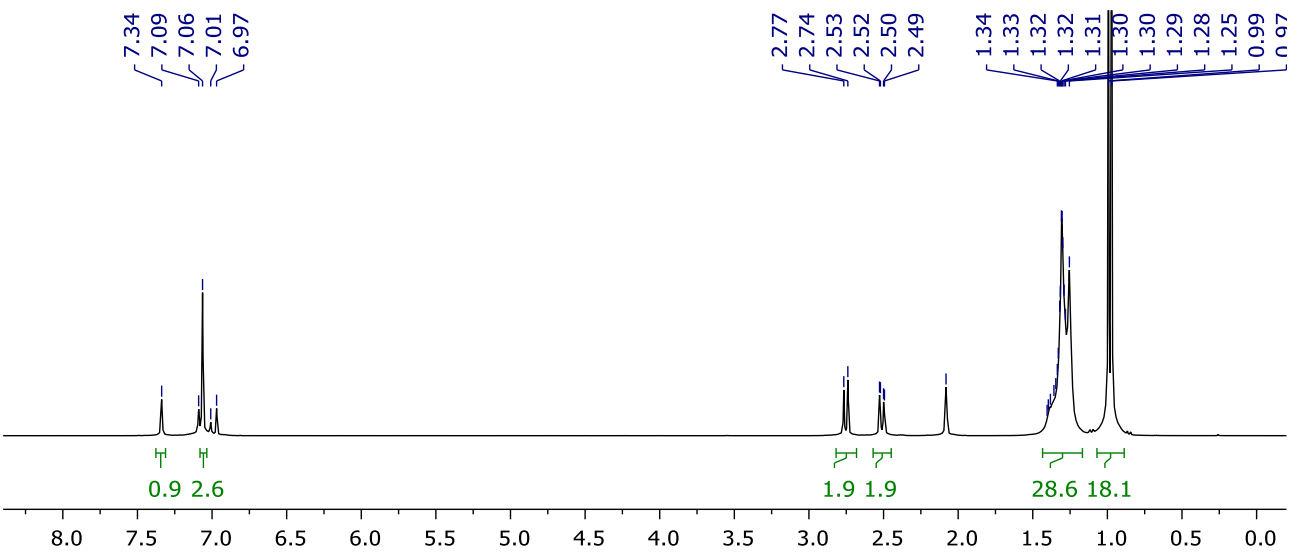


Figure S27. ^{1}H NMR spectrum of PCP-14' (toluene-d_8, 500 MHz).

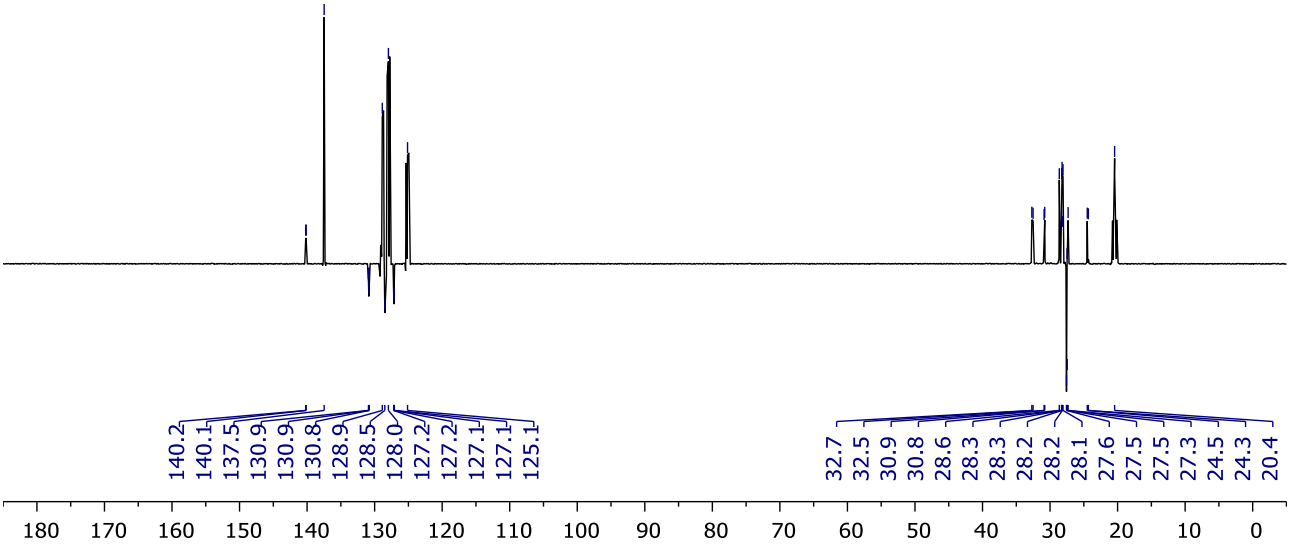


Figure S28. ^{13}C{^{1}H} APT NMR spectrum of PCP-14' (toluene-d_8, 126 MHz).

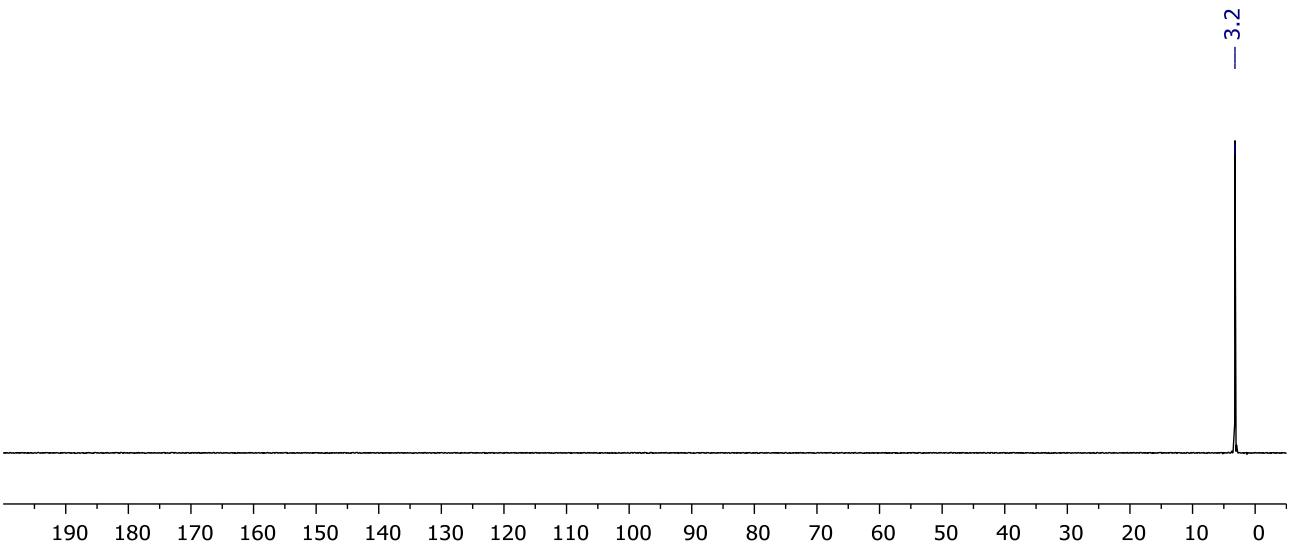


Figure S29. ^{31}P{^{1}H} NMR spectrum of PCP-14' (toluene-d_8, 121 MHz).

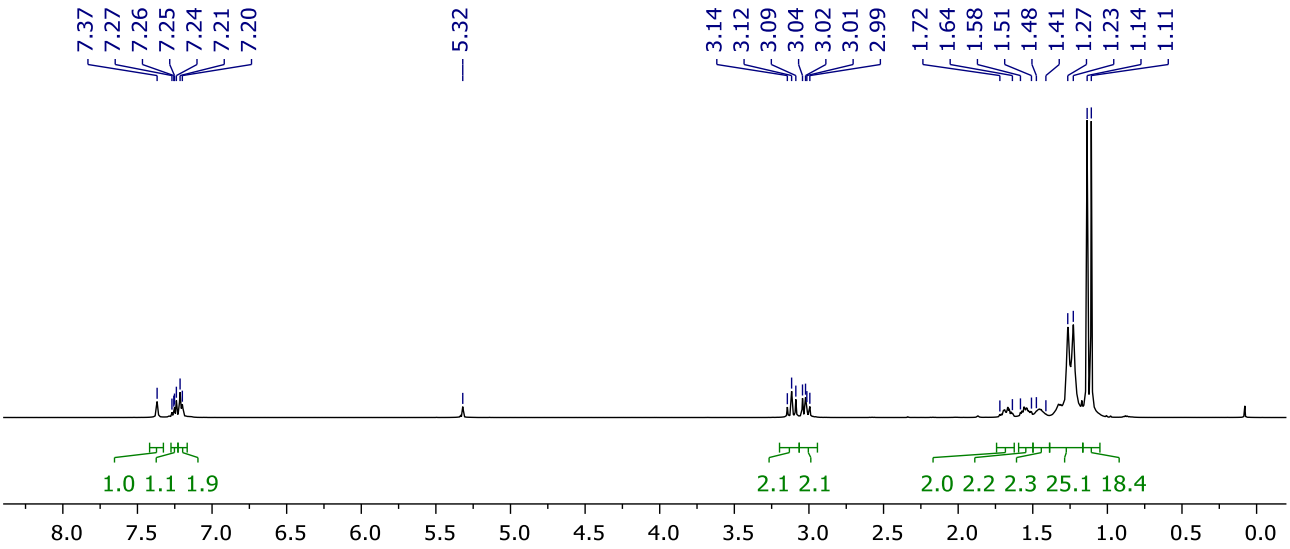


Figure S30. ^{1}H NMR spectrum of PCP-14'·O_2 (CD_2Cl_2, 500 MHz).

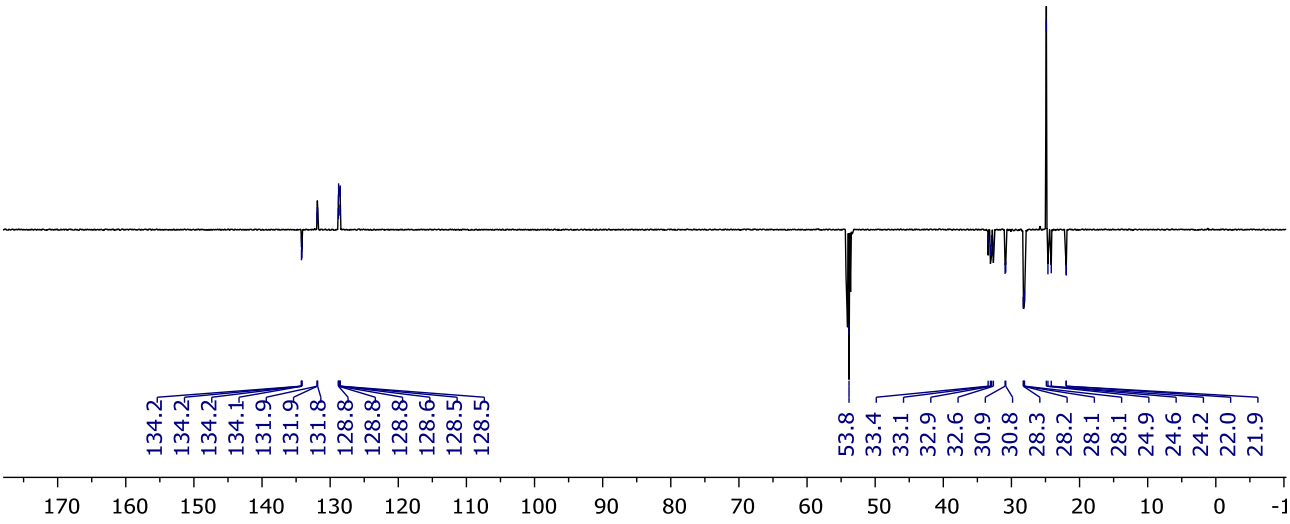


Figure S31. $^{13}C\{^{1}H\}$ APT NMR spectrum of PCP-14'·O_2 (CD_2Cl_2, 126 MHz).

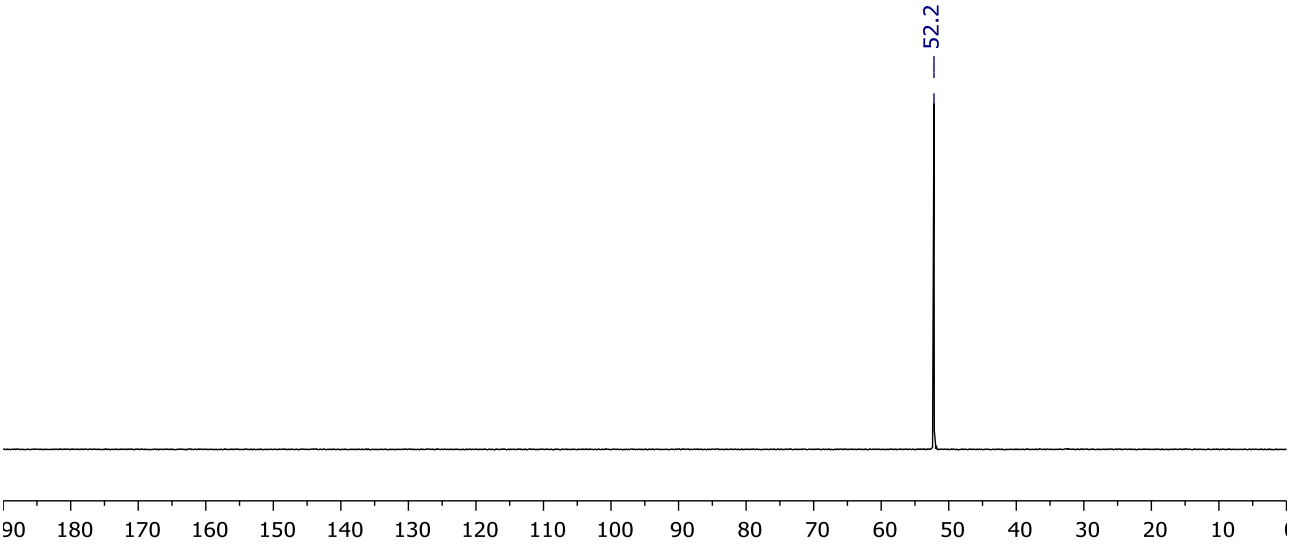


Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of PCP-14'·O_2 (CD_2Cl_2, 162 MHz).

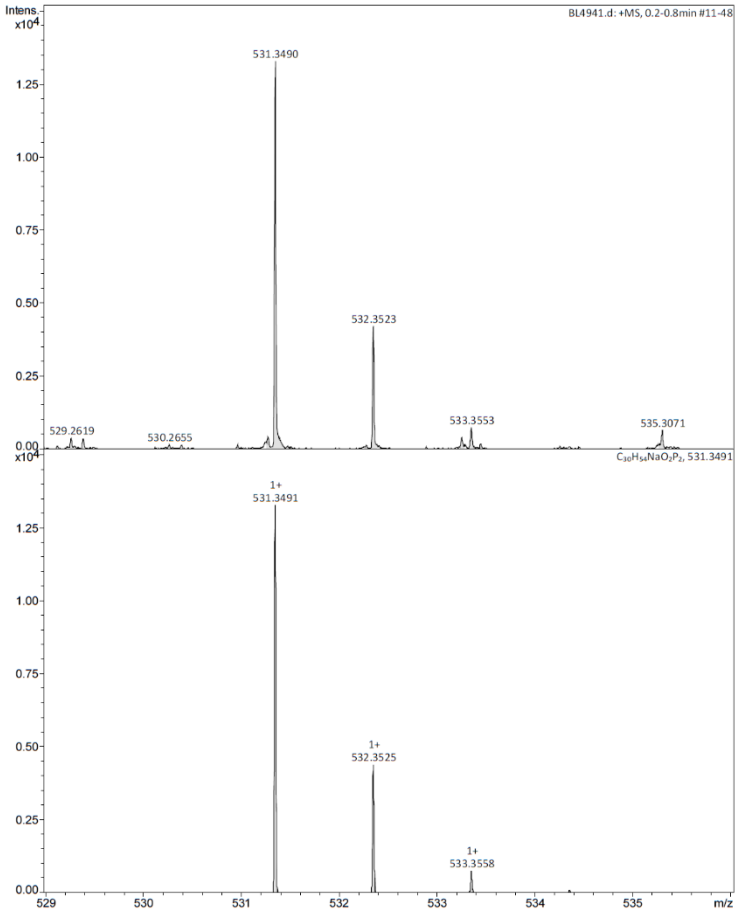


Figure S33. HR ESI-MS of PCP-14'·O_2.

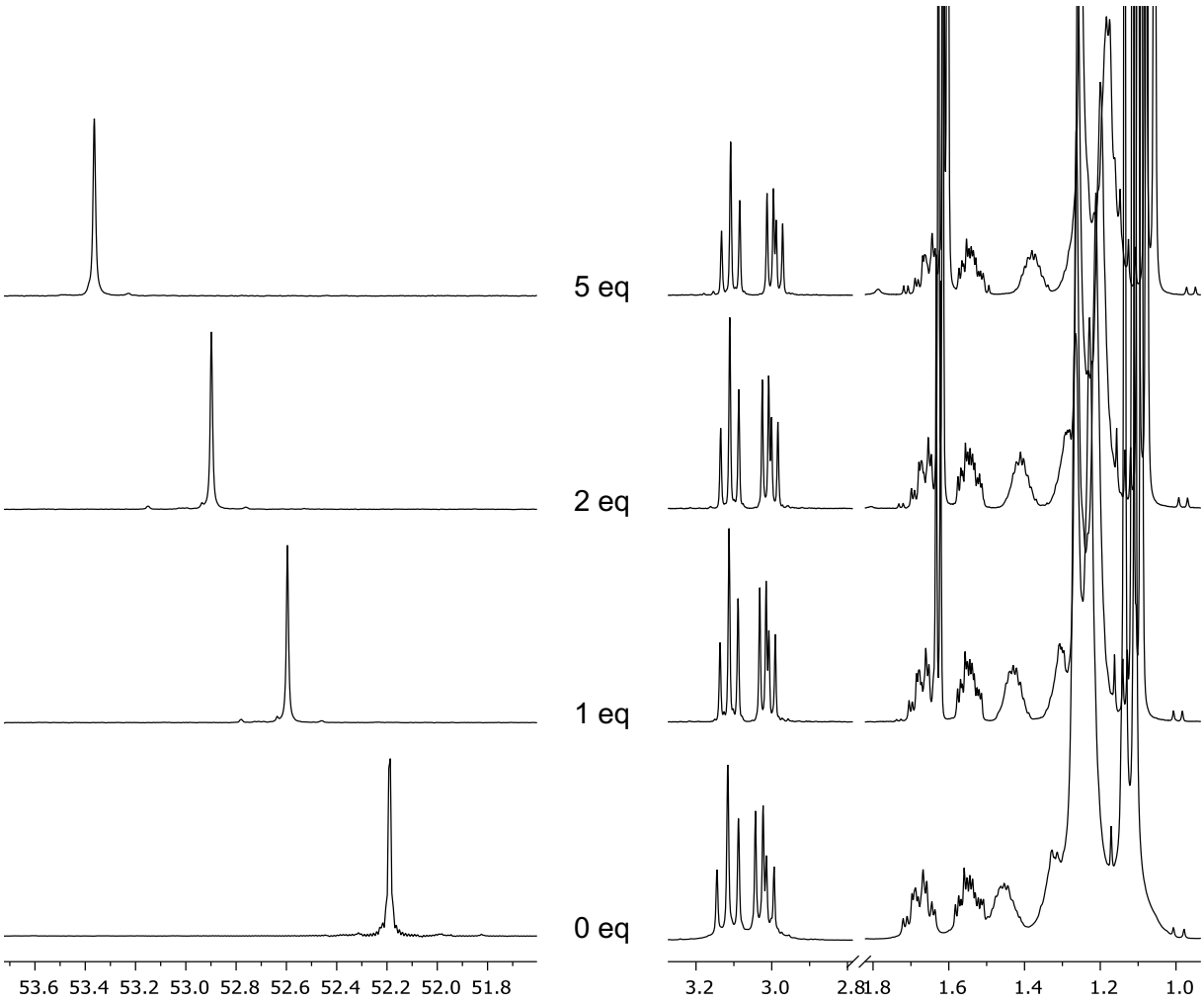


Figure S34. $^{31}P\{^{1}H\}$ (left) and ^{1}H (right) NMR spectra of PCP-14'·O_2 with 0, 1, 2 and 5 equiv. of chiral shift agent (CD_2Cl_2; 0 equiv.,162/500 MHz; 1, 2 and 5 equiv., 243/600 MHz).

2.2. Synthesis of POCOP-14’

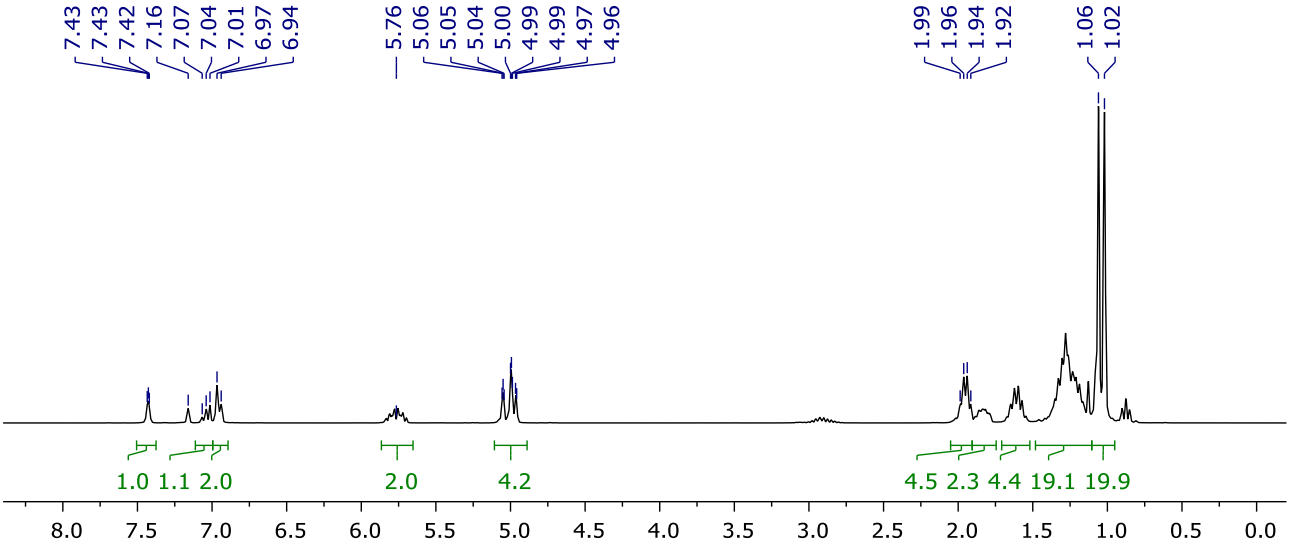


Figure S35. ^{1}H NMR spectrum of **9** (C_6D_6, 300 MHz).

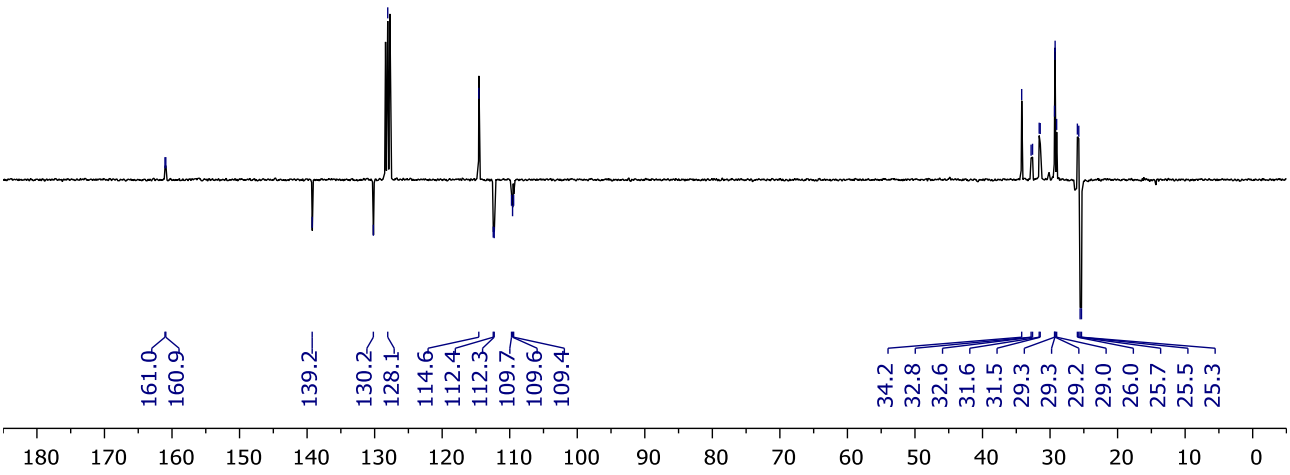


Figure S36. $^{13}C\{^{1}H\}$ APT NMR spectrum of **9** (C_6D_6, 75 MHz).

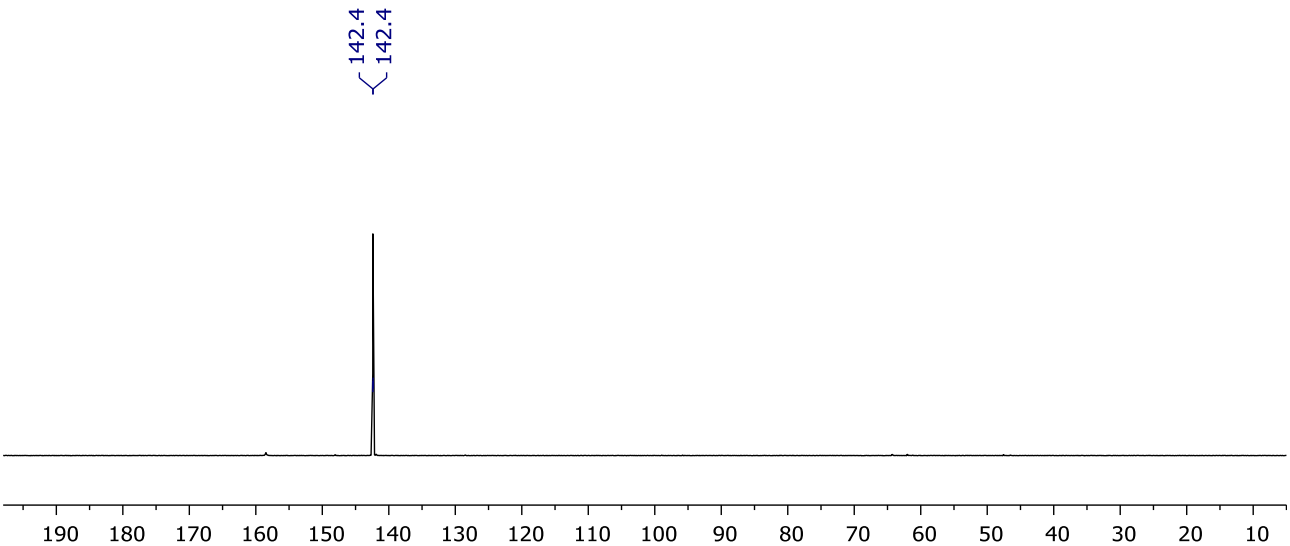


Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum of **9** (C_6D_6, 122 MHz).

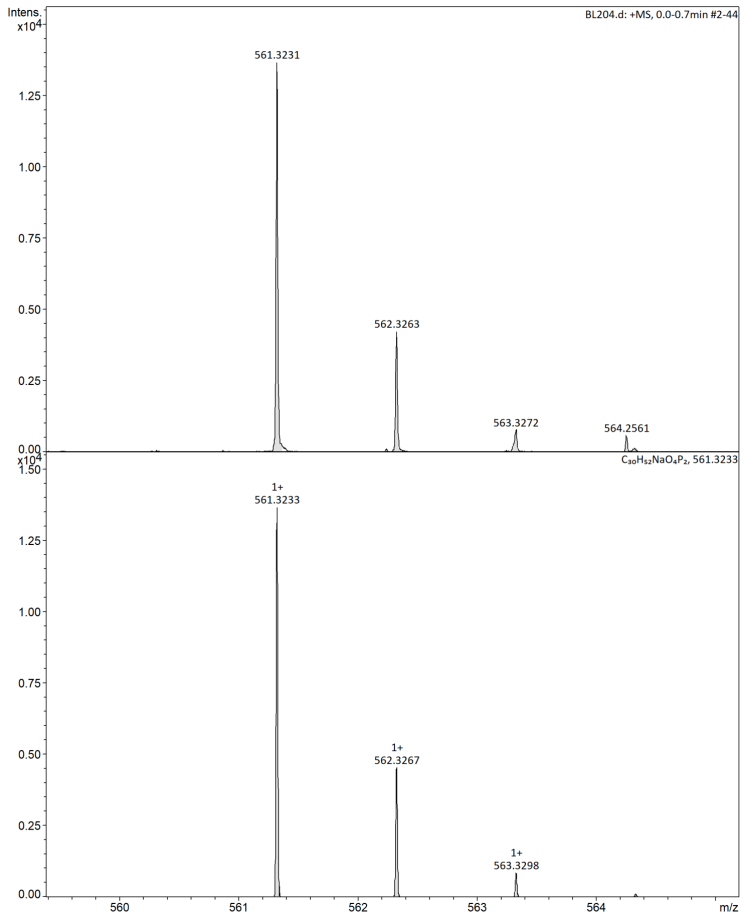


Figure S38. HR ESI-MS of **9.**

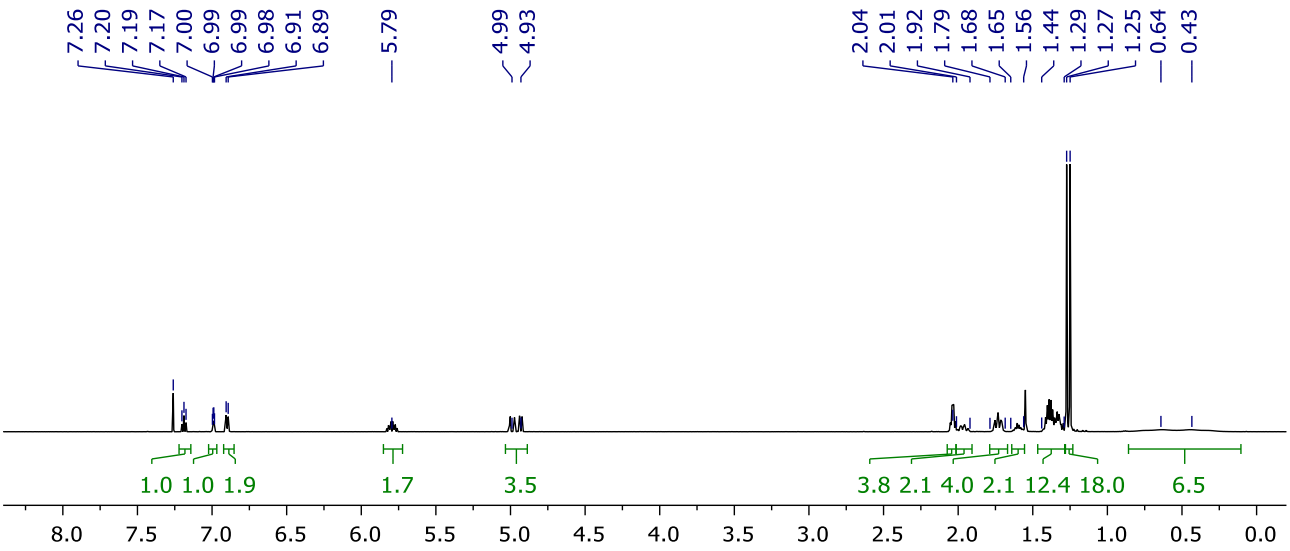


Figure S39. ^{1}H NMR spectrum of **10** ($CDCl_3$, 600 MHz).

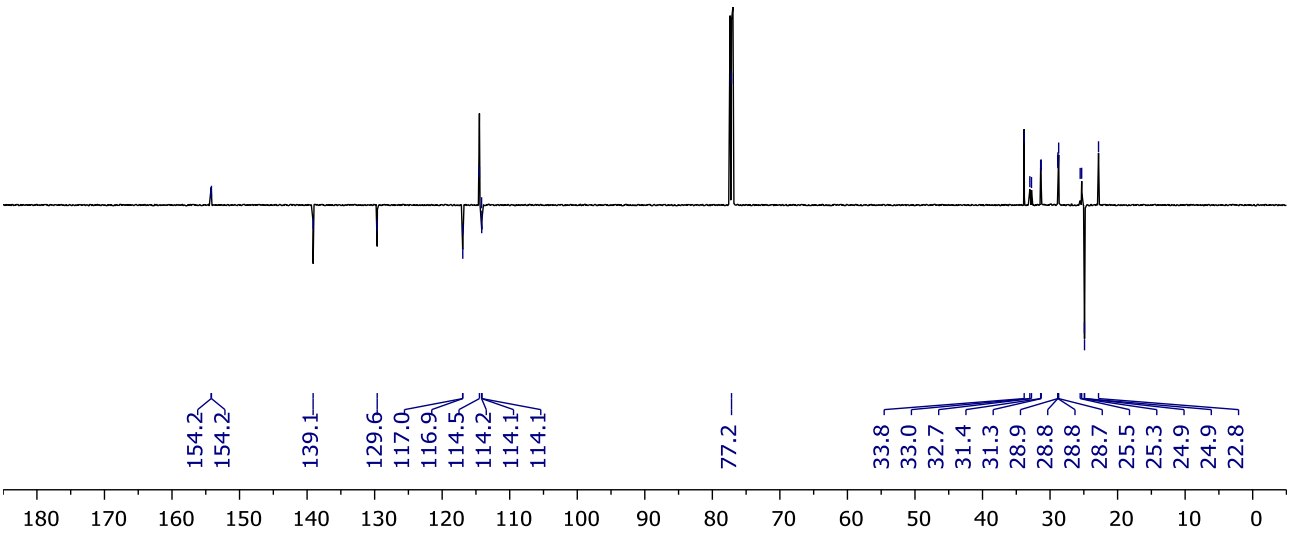


Figure S40. $^{13}C\{^{1}H\}$ APT NMR spectrum of **10** ($CDCl_3$, 151 MHz).

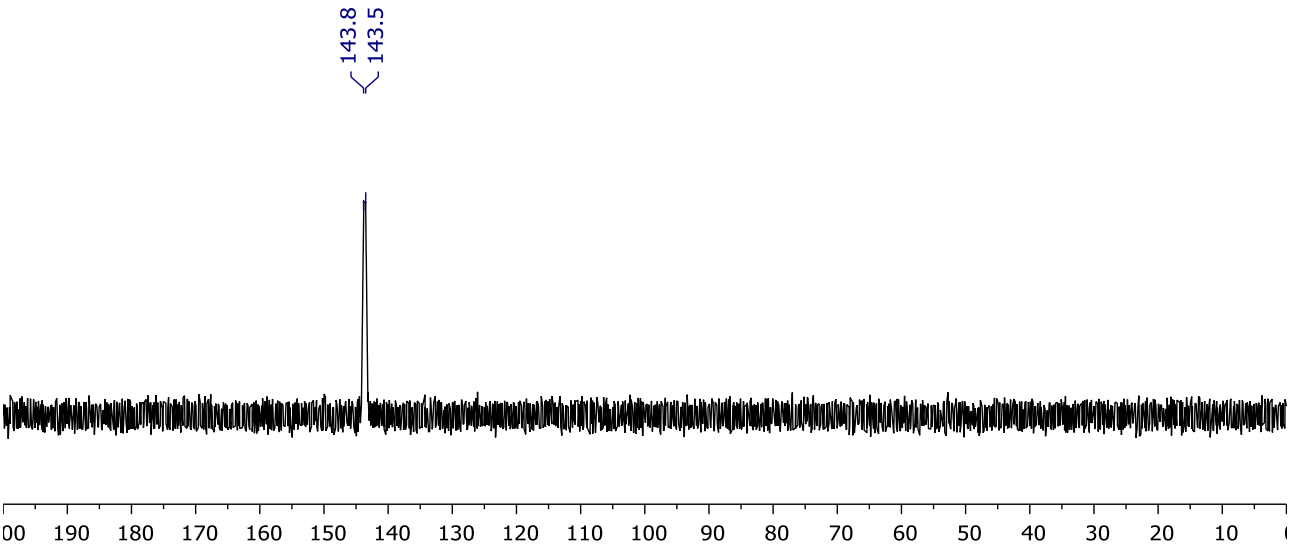


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of **10** ($CDCl_3$, 243 MHz).

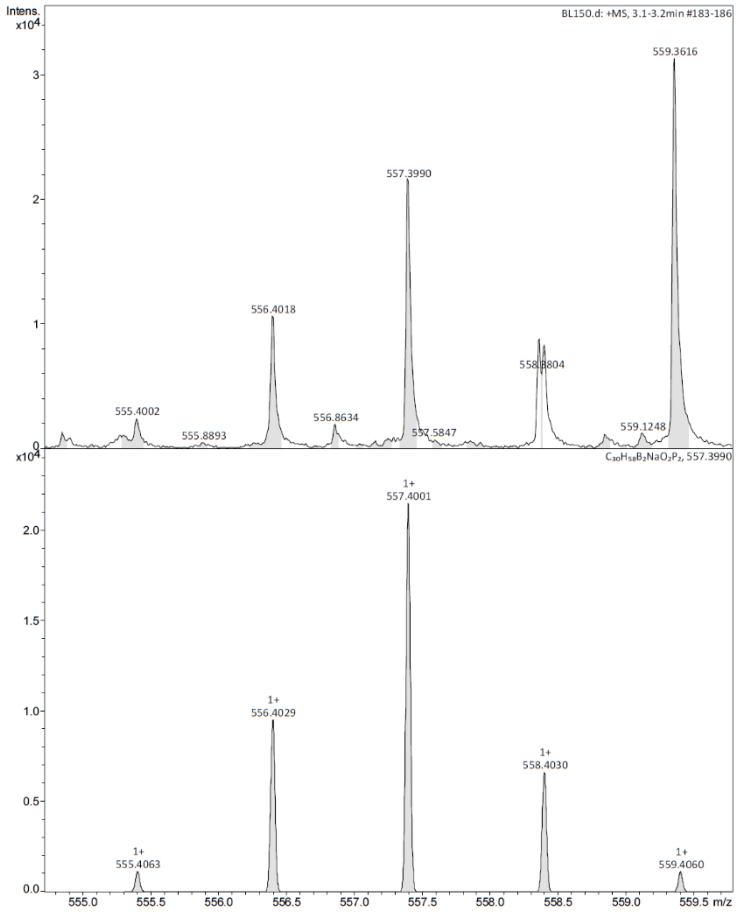


Figure S42. HR ESI-MS of **10.**

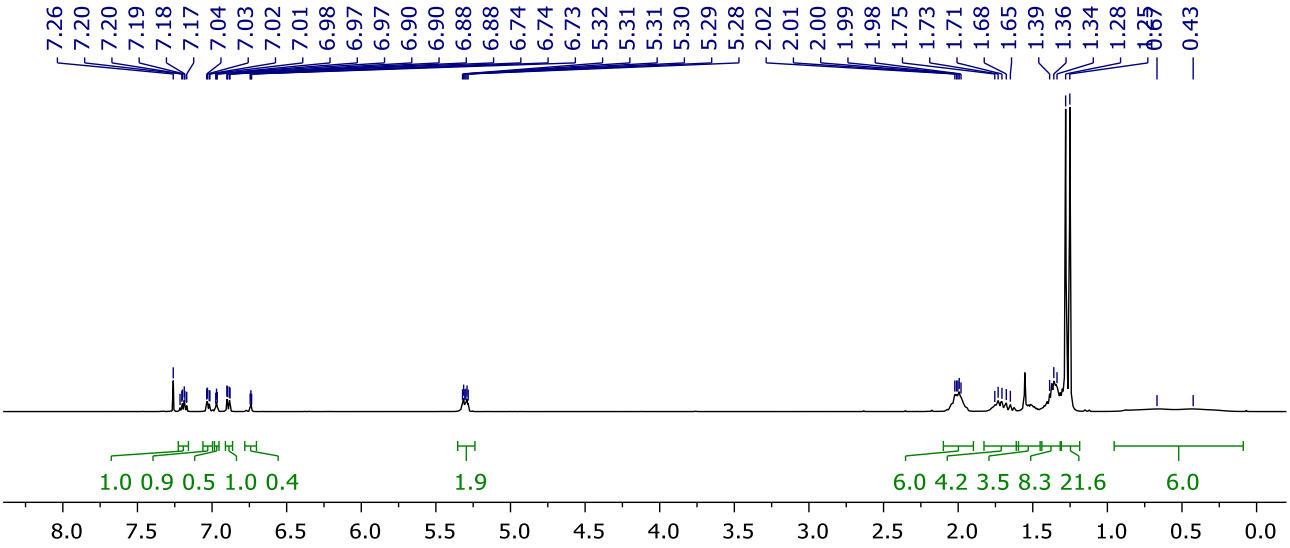


Figure S43. ^{1}H NMR spectrum of **11** ($CDCl_3$, 500 MHz).

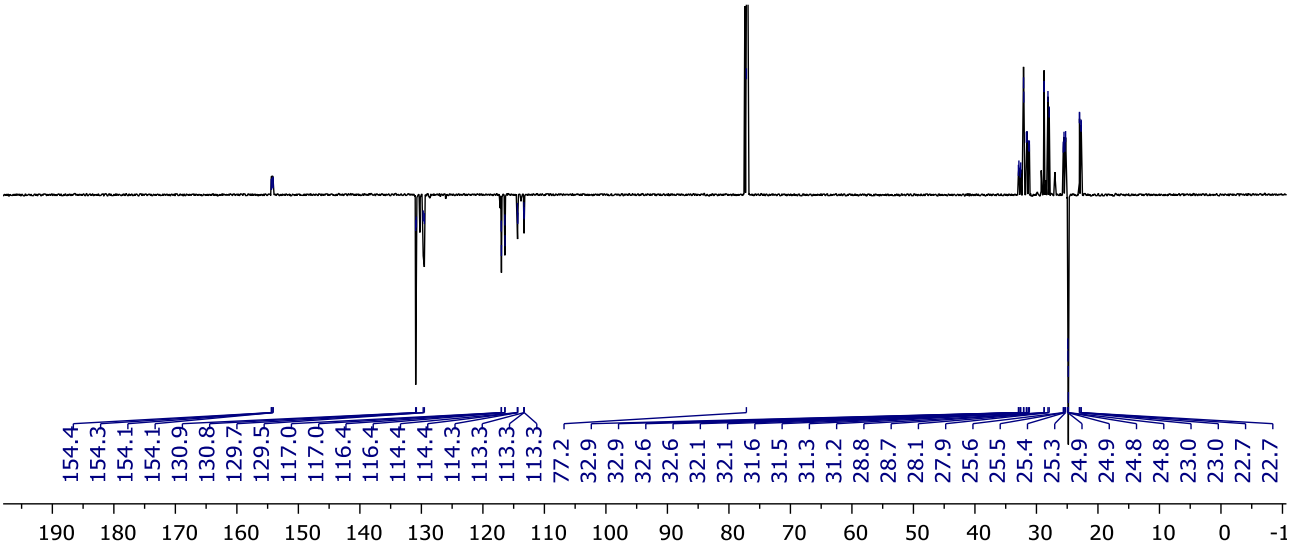


Figure S44. $^{13}C\{^{1}H\}$ APT NMR spectrum of **11** ($CDCl_3$, 126 MHz).

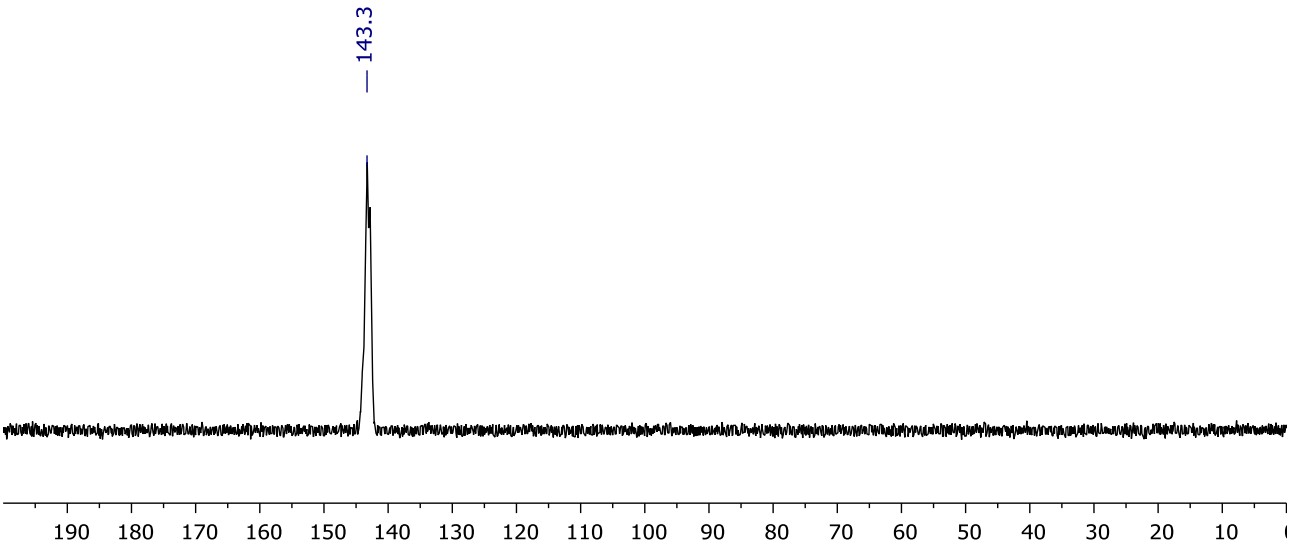


Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum of **11** ($CDCl_3$, 162 MHz).

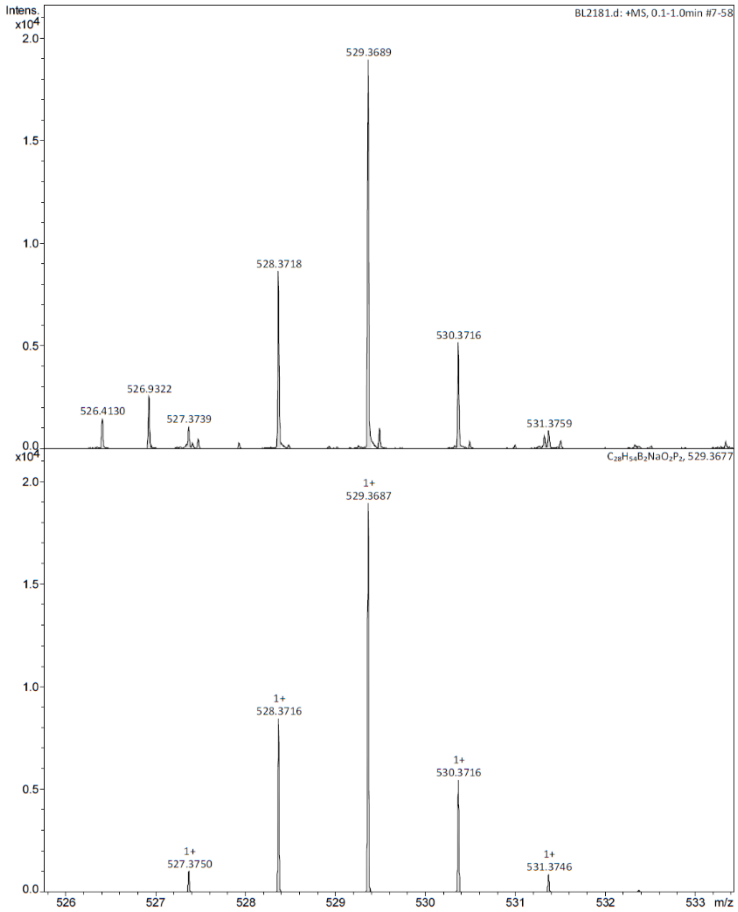


Figure S46. HR ESI-MS of **11.**

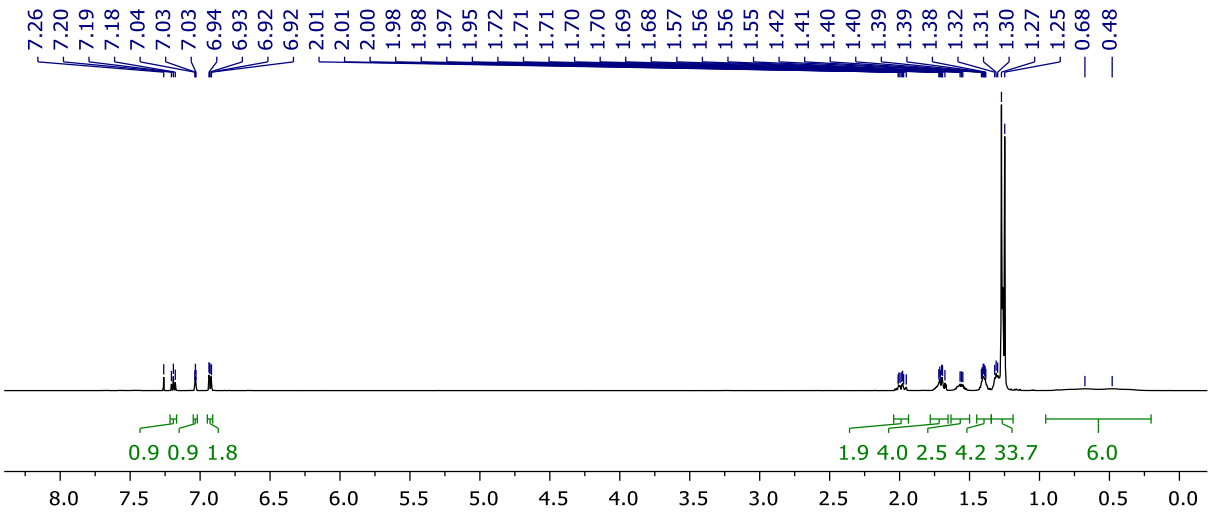


Figure S47. ^{1}H NMR spectrum of *trans*-**12** ($CDCl_3$, 600 MHz).

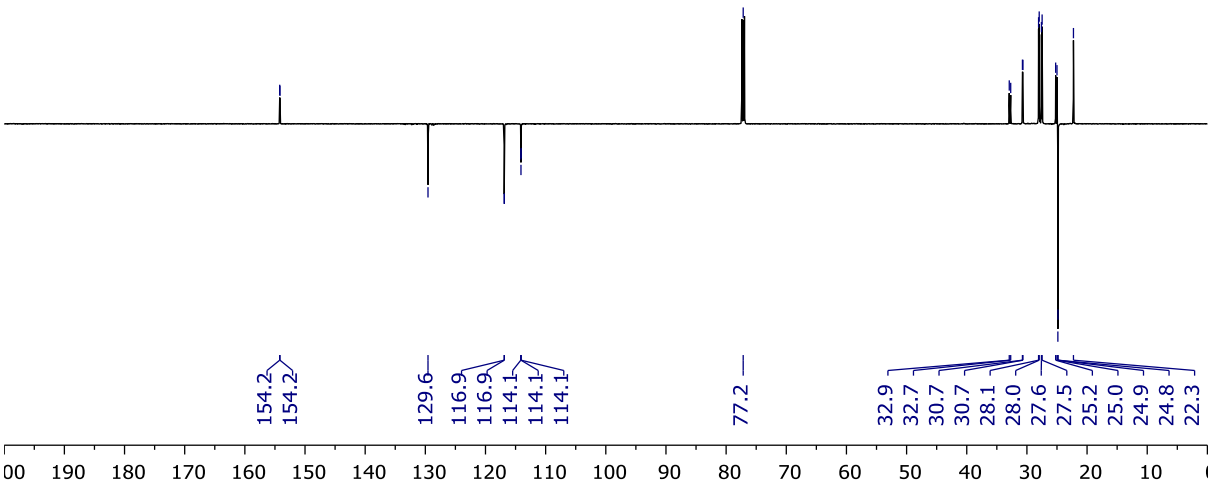


Figure S48. $^{13}C\{^{1}H\}$ APT NMR spectrum of *trans*-**12** ($CDCl_3$, 151 MHz).

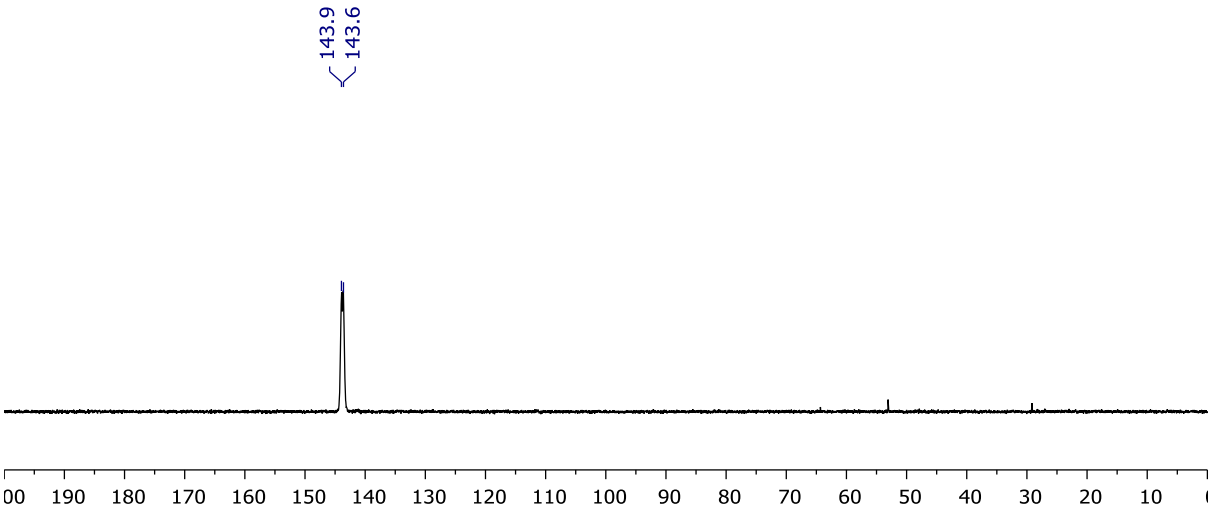


Figure S49. $^{31}P\{^{1}H\}$ NMR spectrum of *trans*-**12** ($CDCl_3$, 243 MHz).

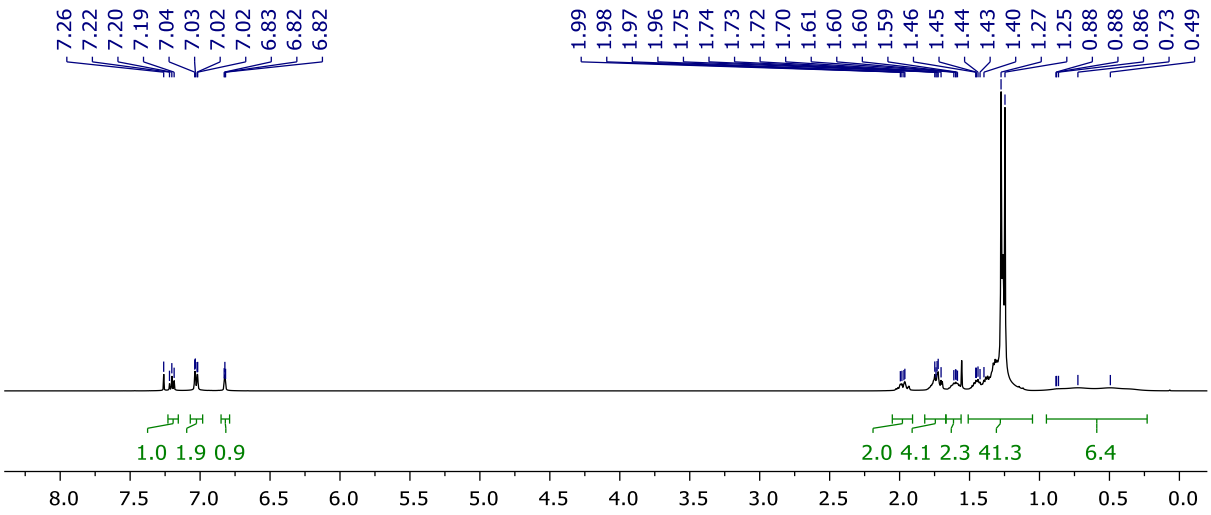


Figure S50. ^{1}H NMR spectrum of *cis*-**12** ($CDCl_3$, 500 MHz).

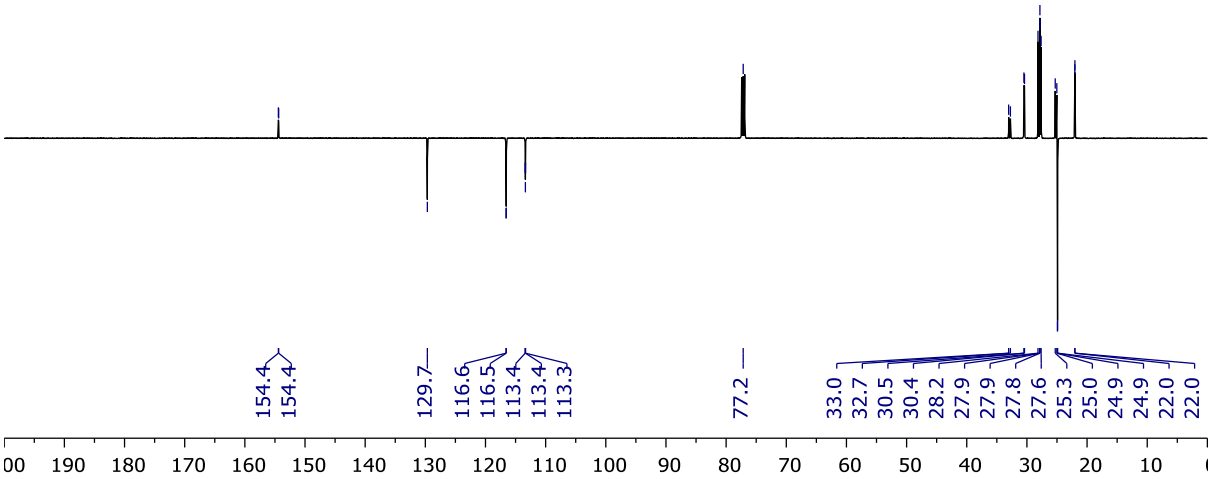


Figure S51. $^{13}C\{^{1}H\}$ APT NMR spectrum of *cis*-**12** ($CDCl_3$, 126 MHz).

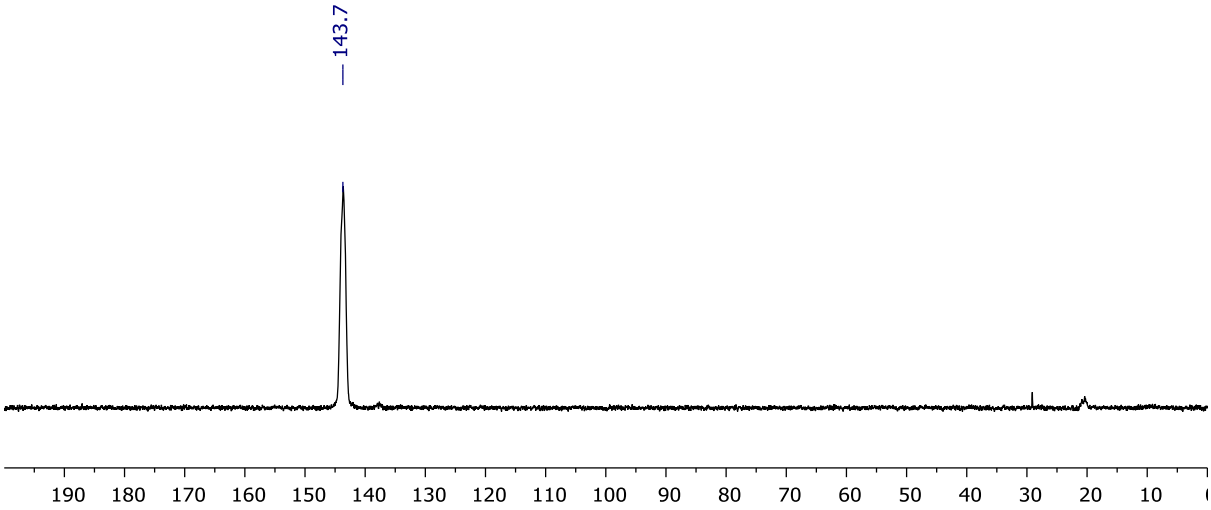


Figure S52. $^{31}P\{^{1}H\}$ NMR spectrum of *cis*-**12** ($CDCl_3$, 162 MHz).

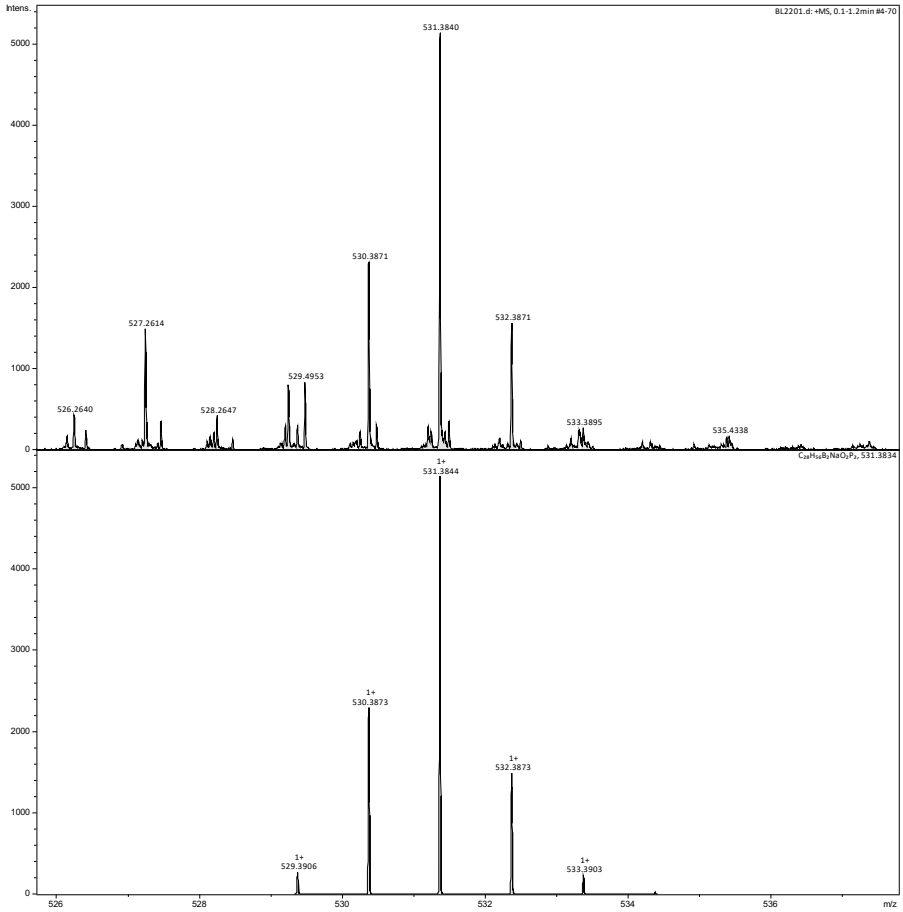


Figure S53. HR ESI-MS of *cis/trans*-**12**.

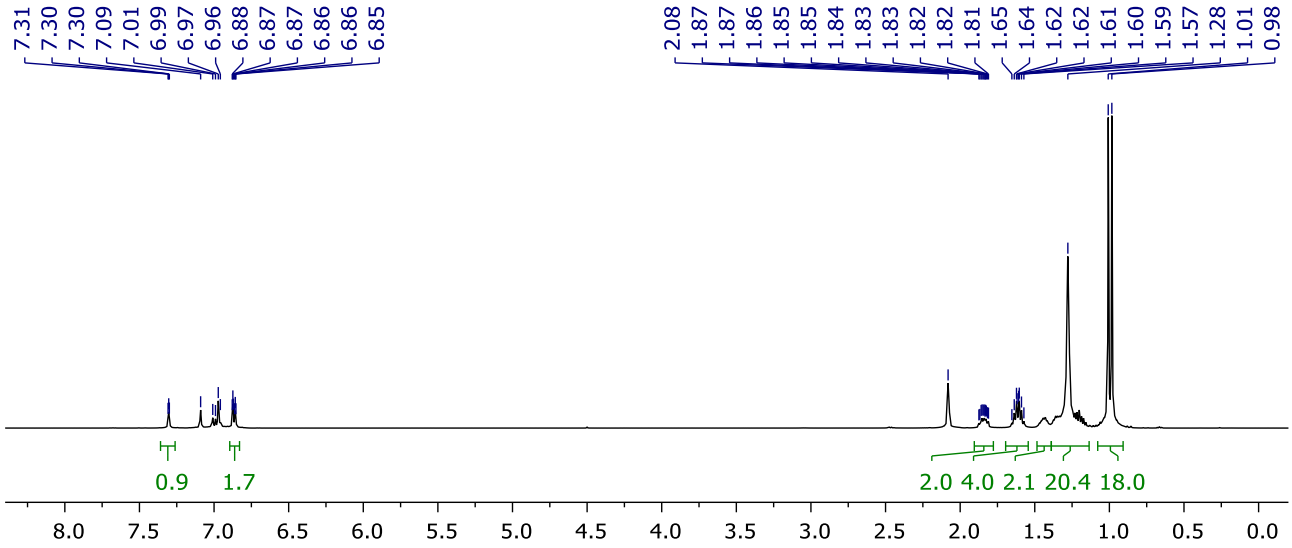


Figure S54. ^{1}H NMR spectrum of POCOP-14' (toluene-d_8, 500 MHz).

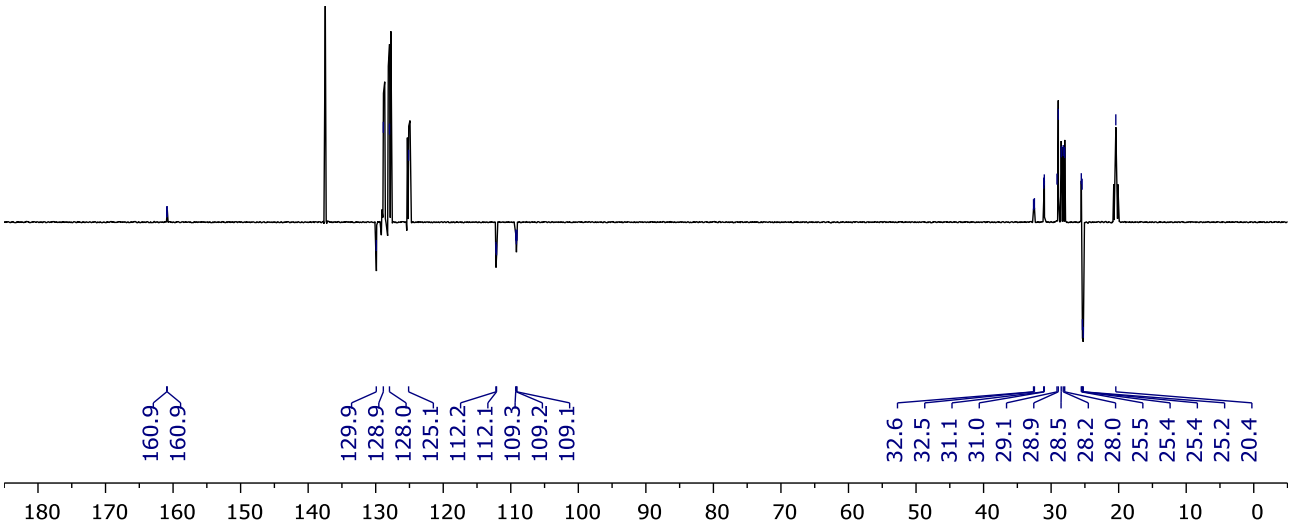


Figure S55. ^{13}C{^{1}H} APT NMR spectrum of POCOP-14' (toluene-d_8, 126 MHz).

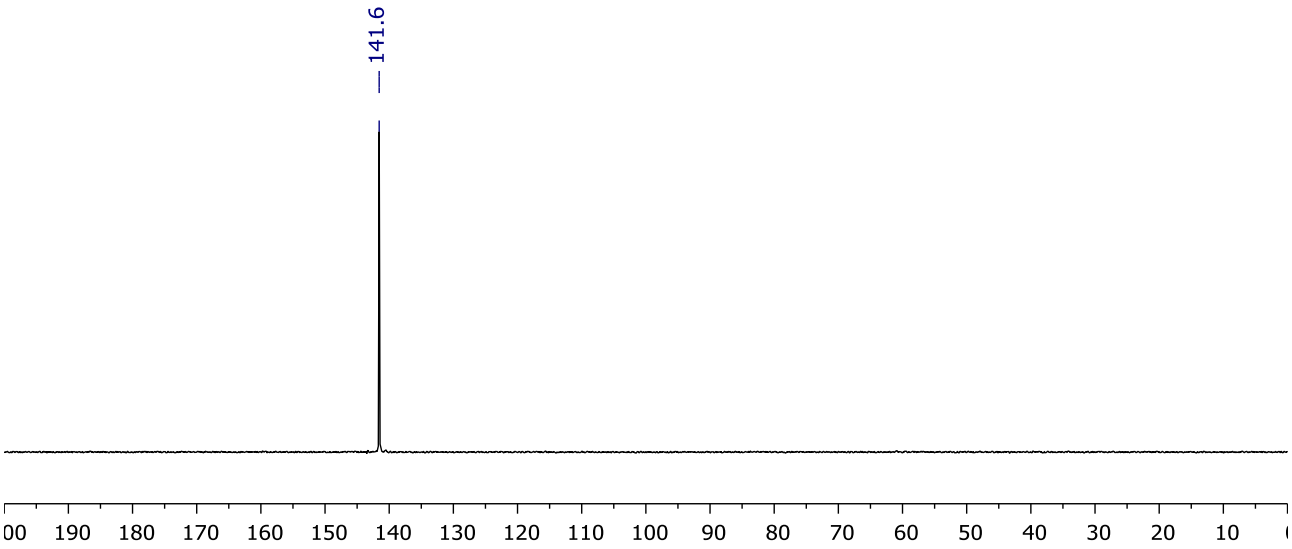


Figure S56. ^{31}P{^{1}H} NMR spectrum of POCOP-14' (toluene-d_8, 121 MHz).

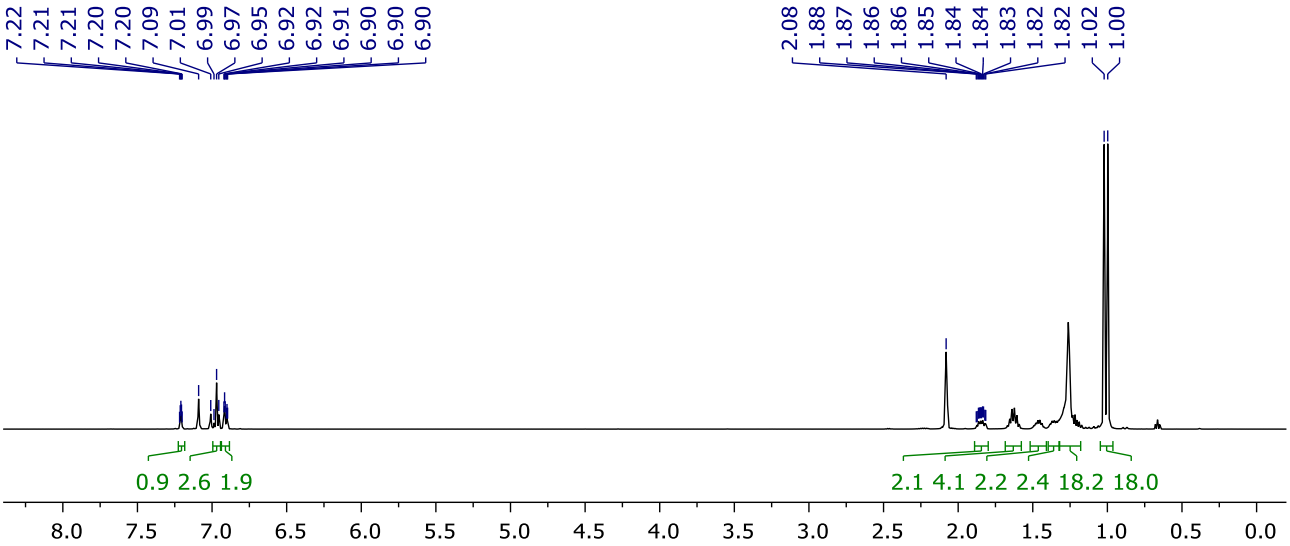


Figure S57. ^{1}H NMR spectrum of the *cis*-diastereoisomer of POCOP-14' (toluene-d_8, 500 MHz).

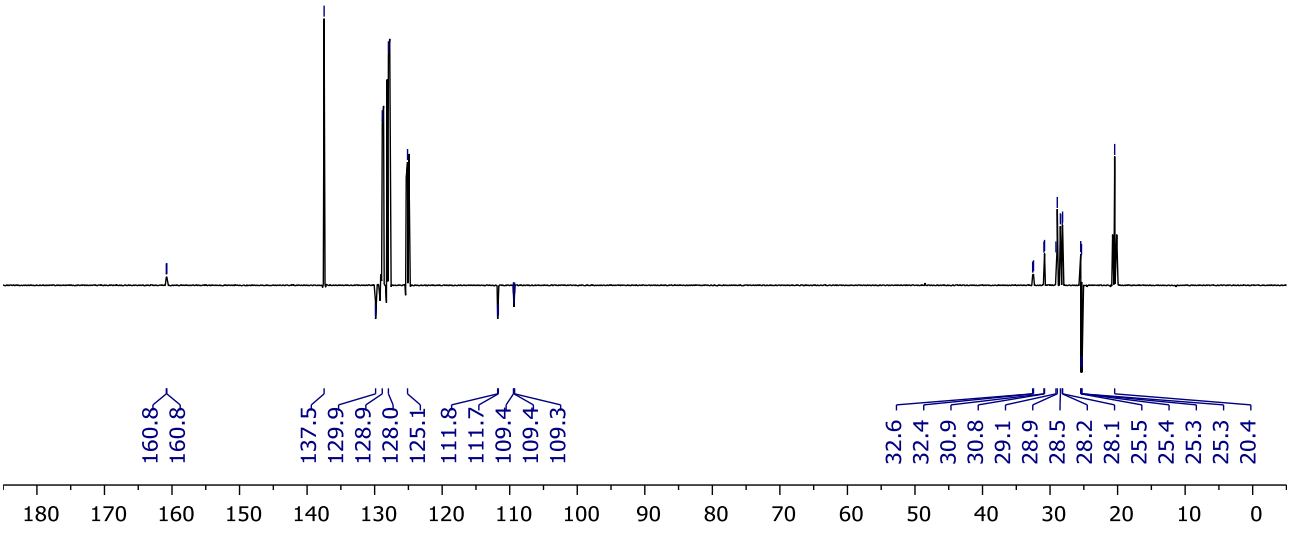


Figure S58. ^{13}C{^{1}H} APT NMR spectrum of the *cis*-diastereoisomer of POCOP-14' (toluene-d_8, 126 MHz).

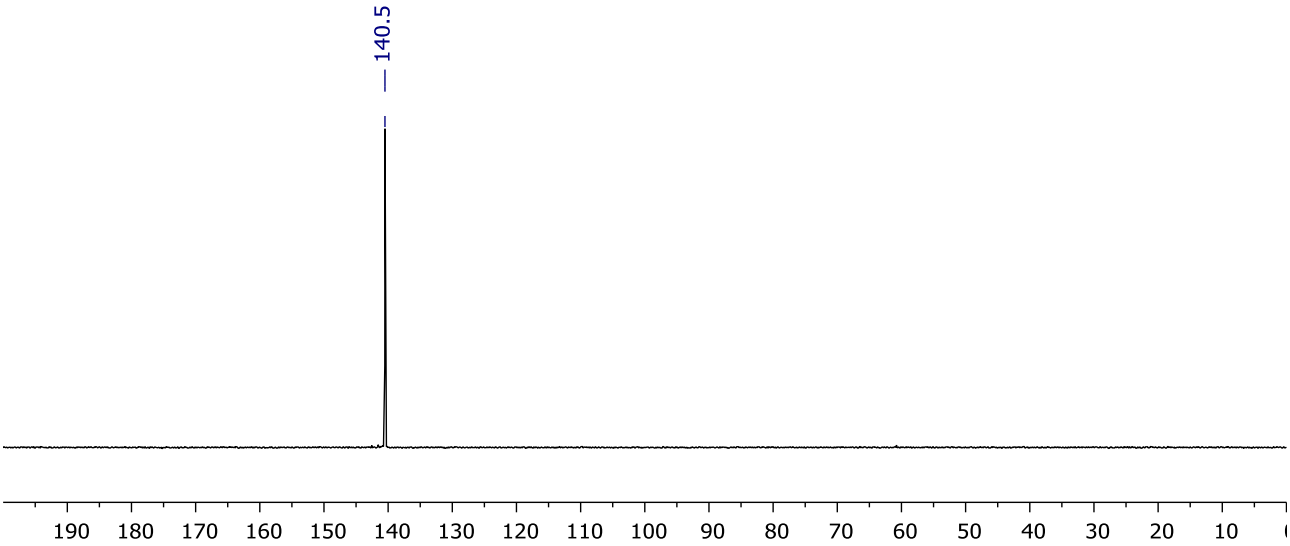


Figure S59. ^{31}P{^{1}H} NMR spectrum of the *cis*-diastereoisomer of POCOP-14' (toluene-d_8, 162 MHz).

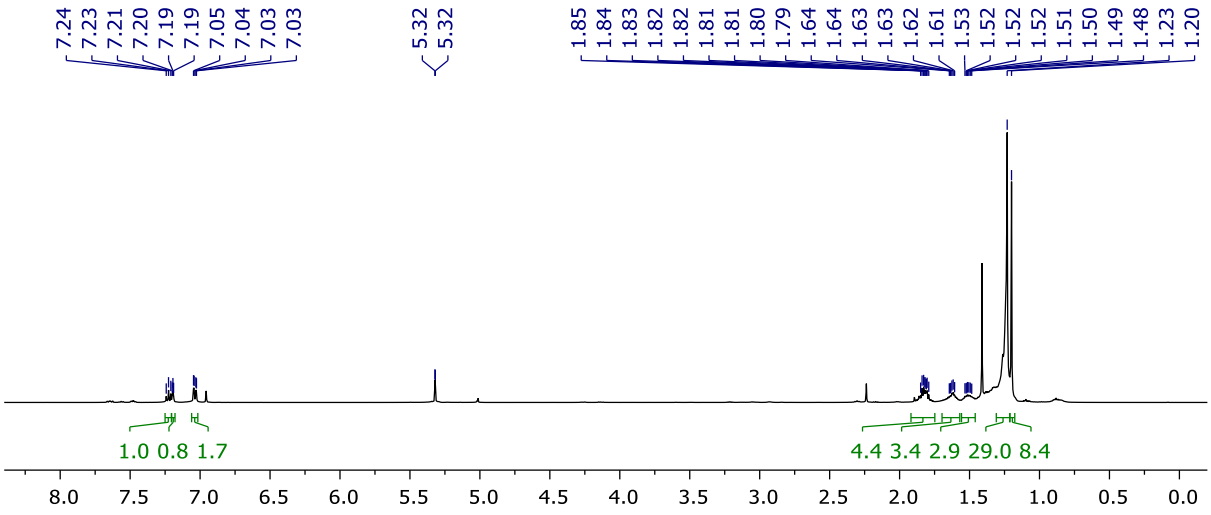


Figure S60. ^{1}H NMR spectrum of POCOP-14'·O_2 (CD_2Cl_2, 500 MHz).

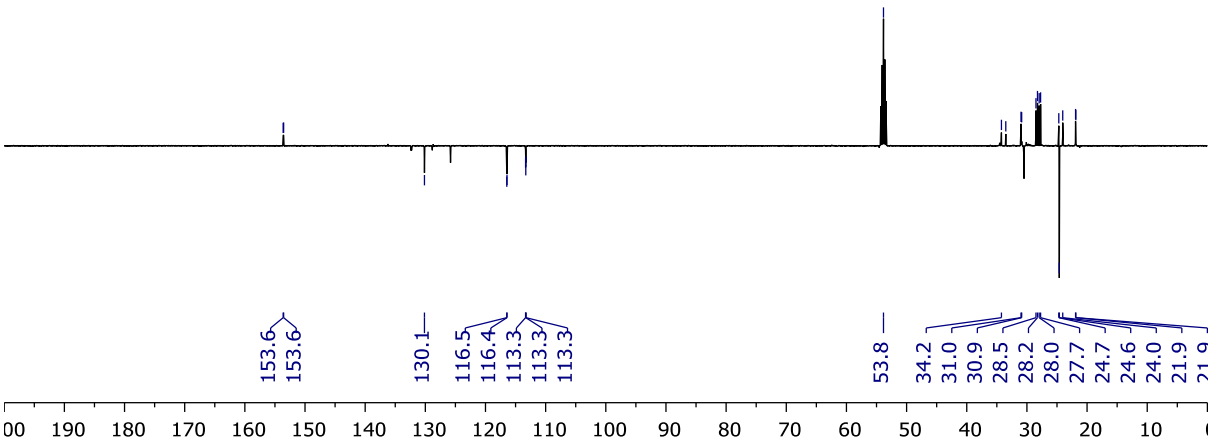


Figure S61. $^{13}C\{^{1}H\}$ APT NMR spectrum of POCOP-14'·O_2 (CD_2Cl_2, 126 MHz).

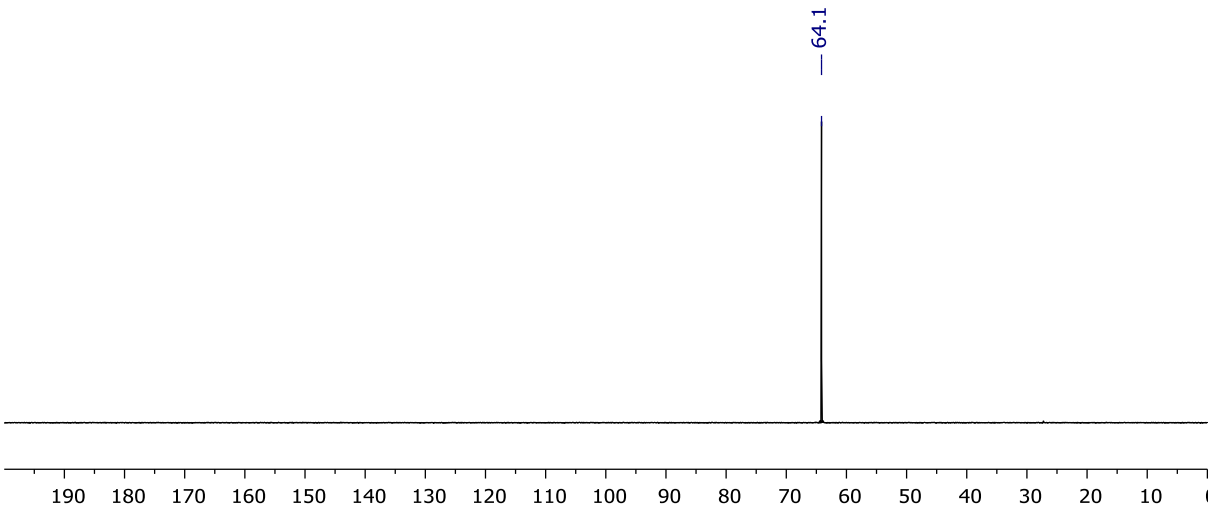


Figure S62. $^{31}P\{^{1}H\}$ NMR spectrum of POCOP-14'·O_2 (CD_2Cl_2, 162 MHz).

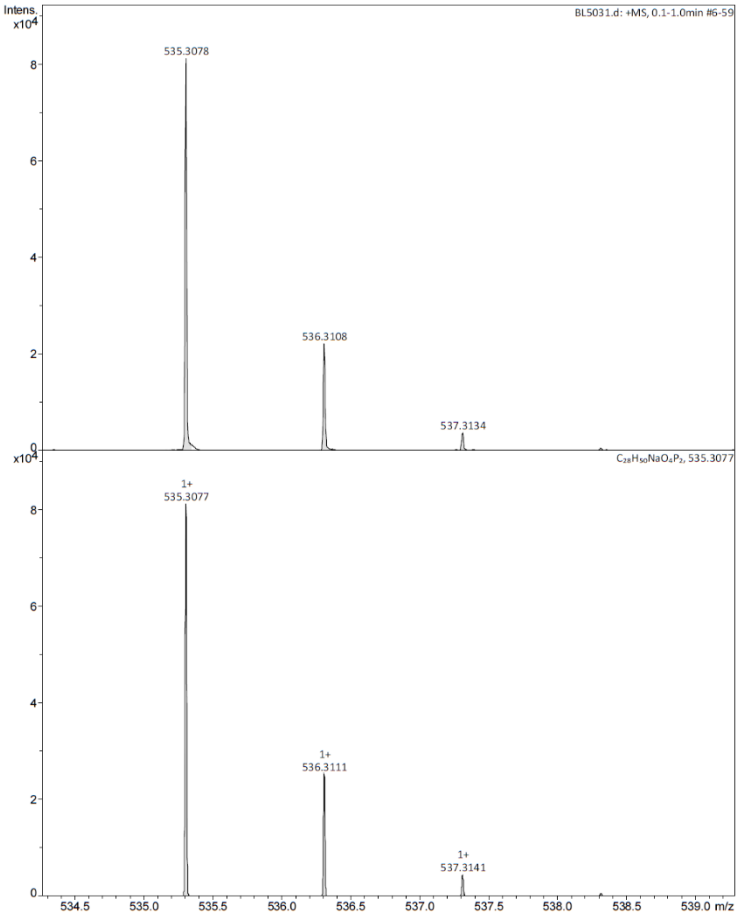


Figure S63. HR ESI-MS of POCOP-14'·O_2.

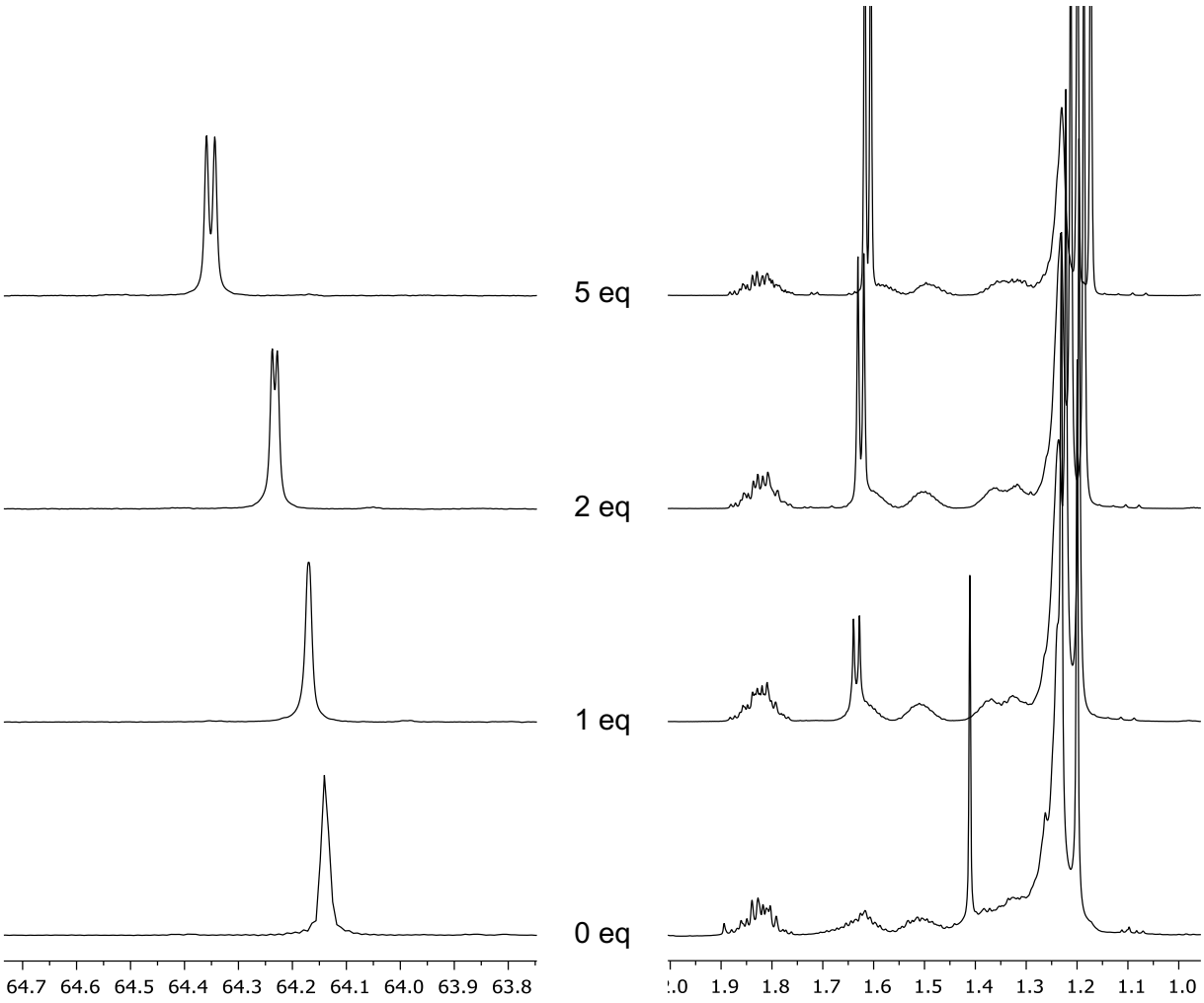


Figure S64. $^{31}P\{^{1}H\}$ (left) and ^{1}H (right) NMR spectra of POCOP-14'·O_2 with 0, 1, 2 and 5 equiv. of chiral shift agent (CD_2Cl_2; 0 equiv.,162/500 MHz; 1, 2 and 5 equiv., 243/600 MHz).

2.3. Synthesis of rhodium complexes of PCP-14

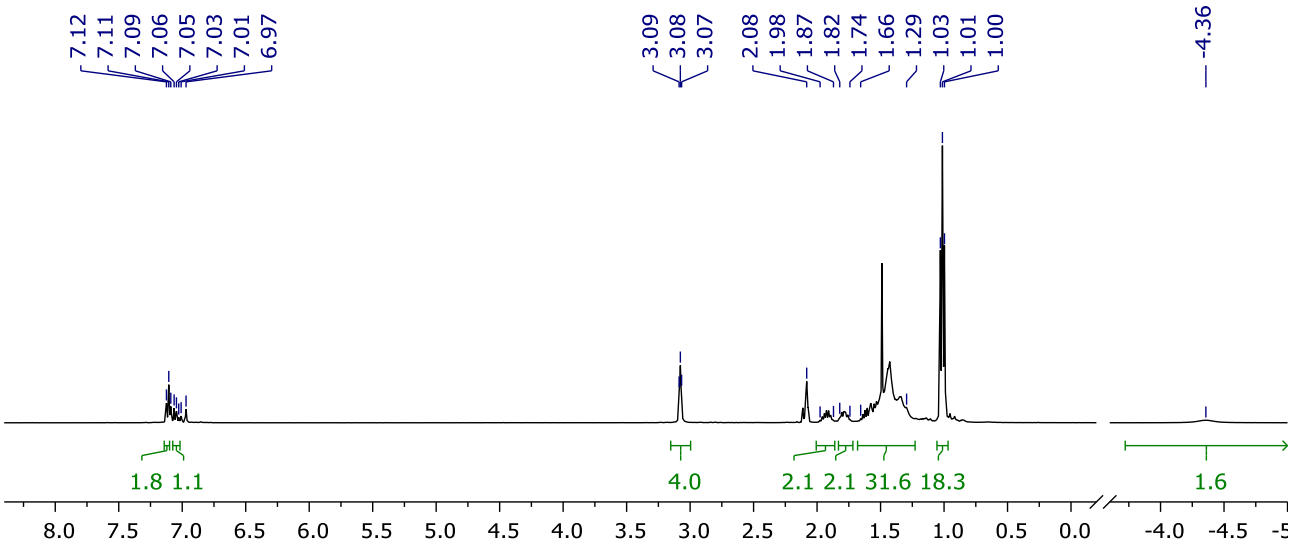


Figure S65. ^{1}H NMR spectrum of **13a** (toluene-d_8, 400 MHz, H_2).

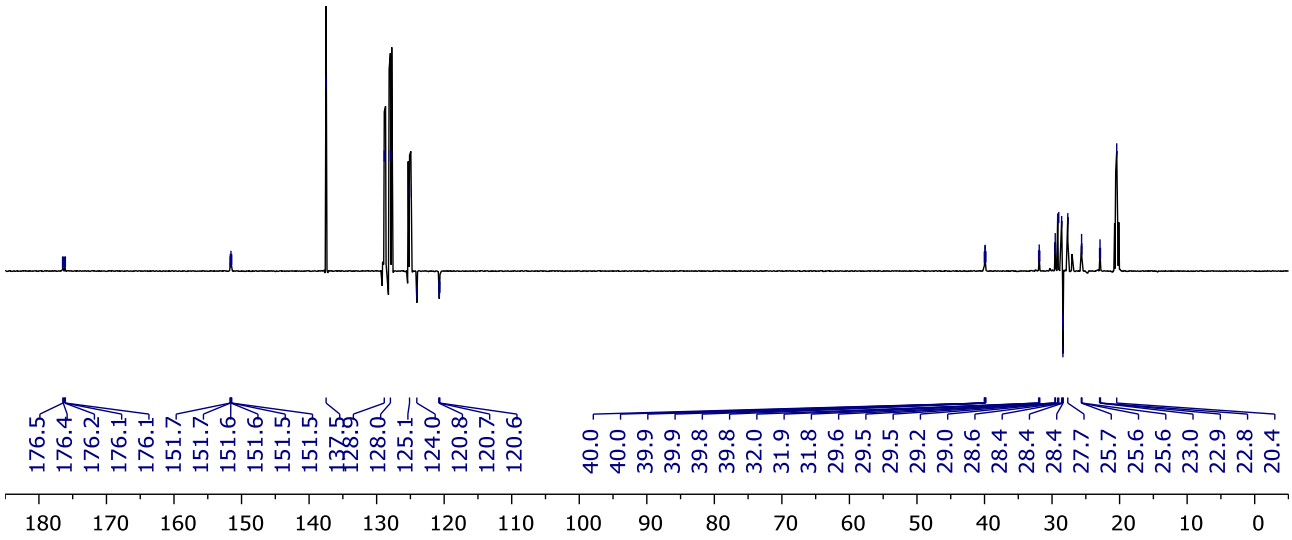


Figure S66. ^{13}C{^{1}H} APT NMR spectrum of **13a** (toluene-d_8, 126 MHz, H_2).

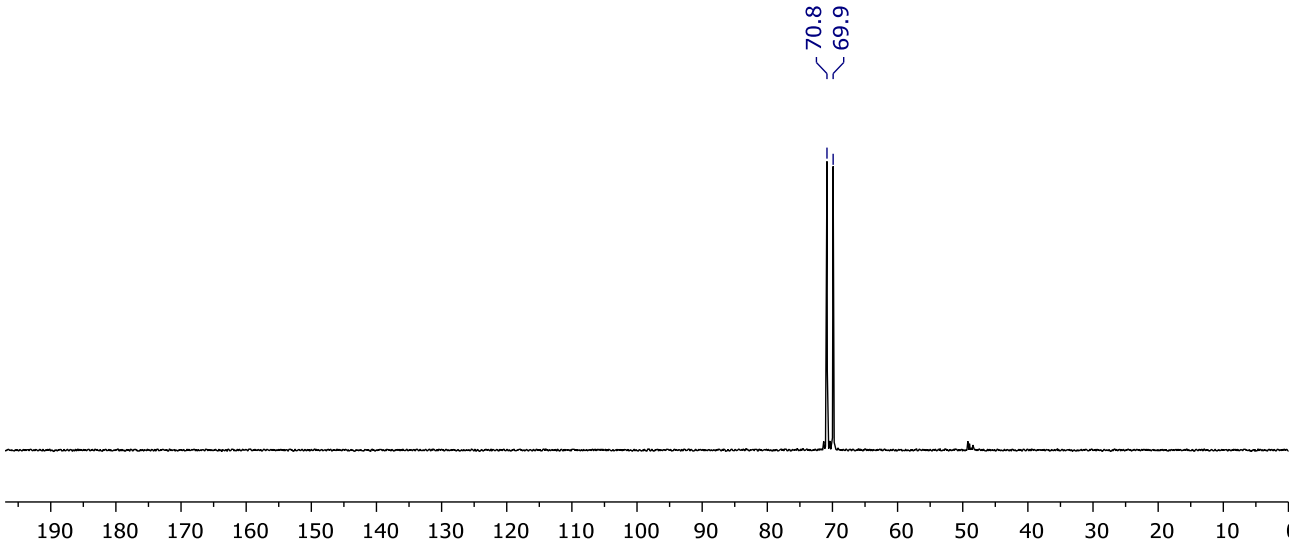


Figure S67. ^{31}P{^{1}H} NMR spectrum of **13a** (toluene-d_8, 162 MHz, H_2).

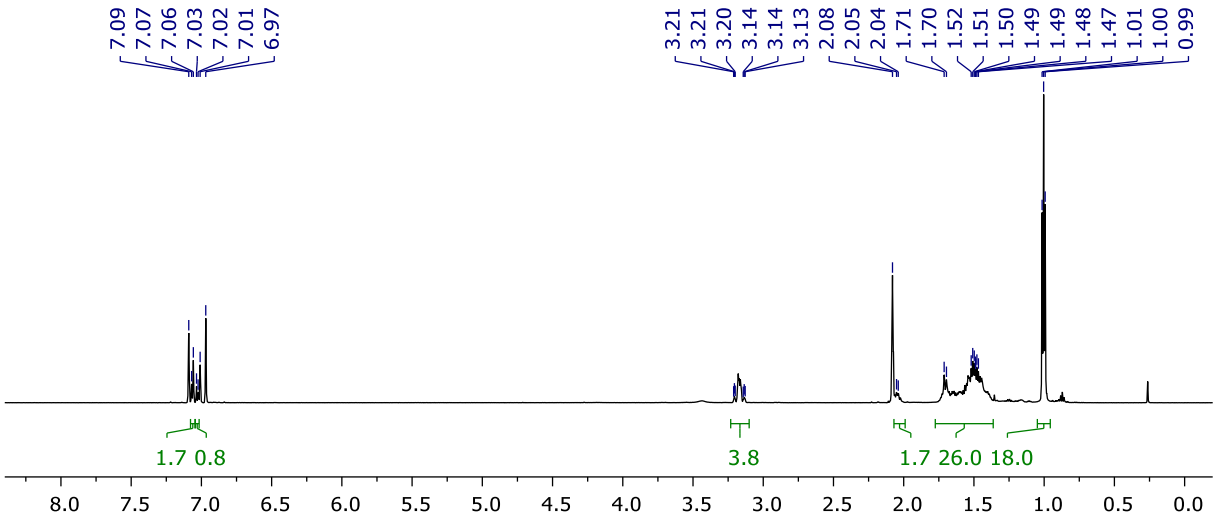


Figure S68. ^{1}H NMR spectrum of **14a** (toluene-d_8, 600 MHz).

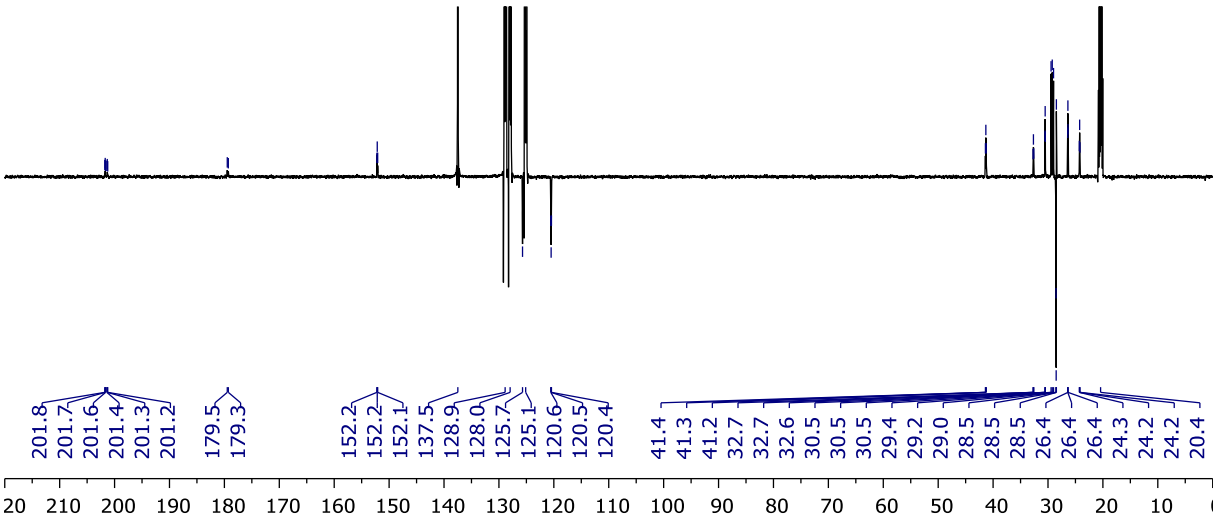


Figure S69. ^{13}C{^{1}H} APT NMR spectrum of **14a** (toluene-d_8, 151 MHz).

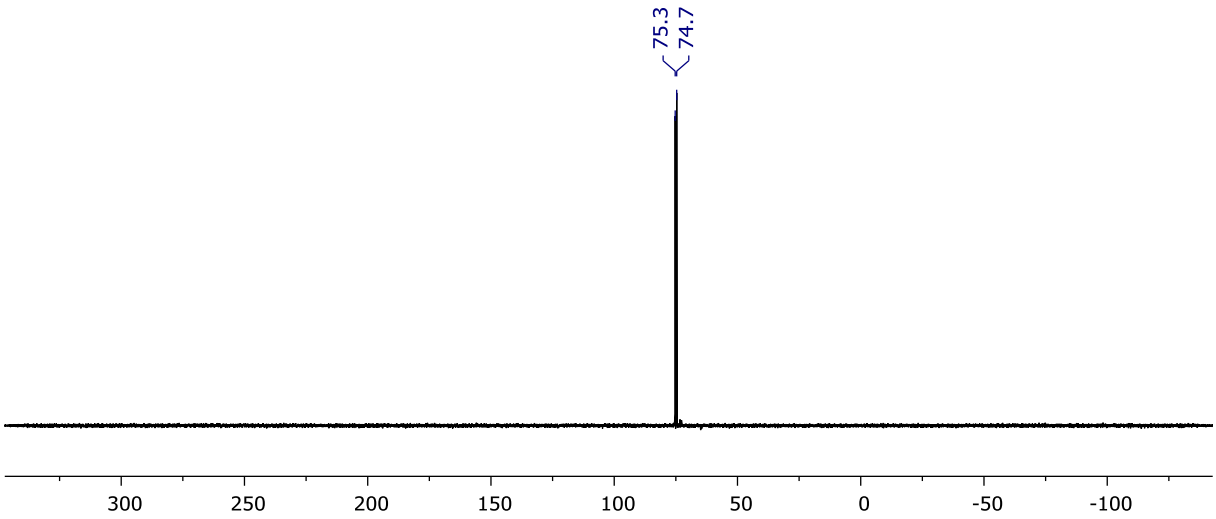


Figure S70. ^{31}P{^{1}H} NMR spectrum of **14a** (toluene-d_8, 243 MHz).

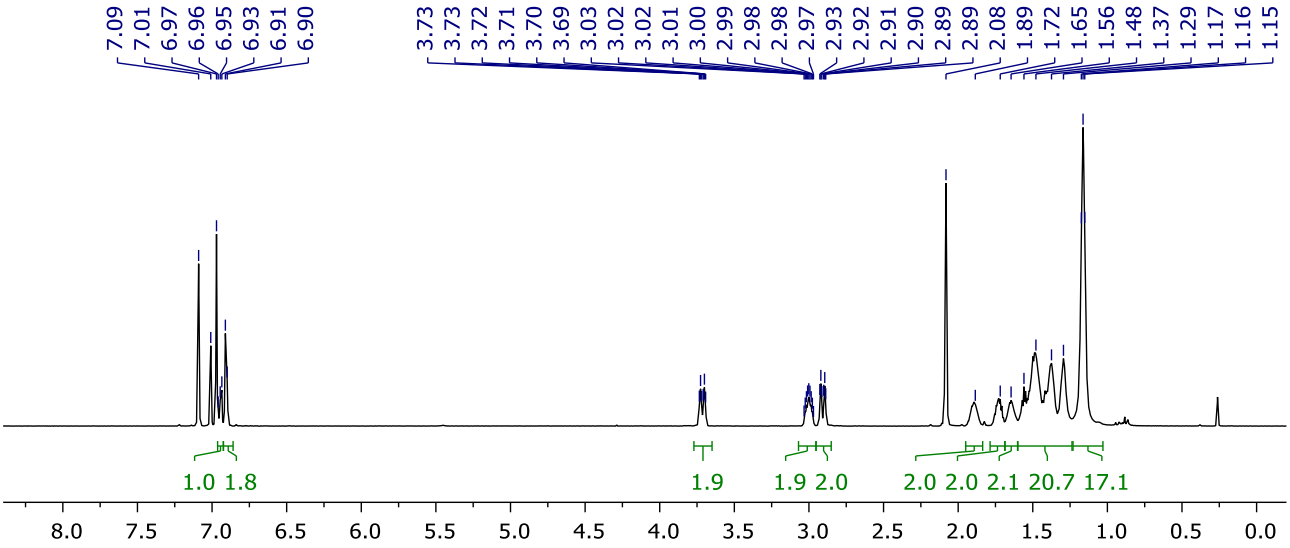


Figure S71. ^{1}H NMR spectrum of **15a** (toluene-d_8, 600 MHz, CO).

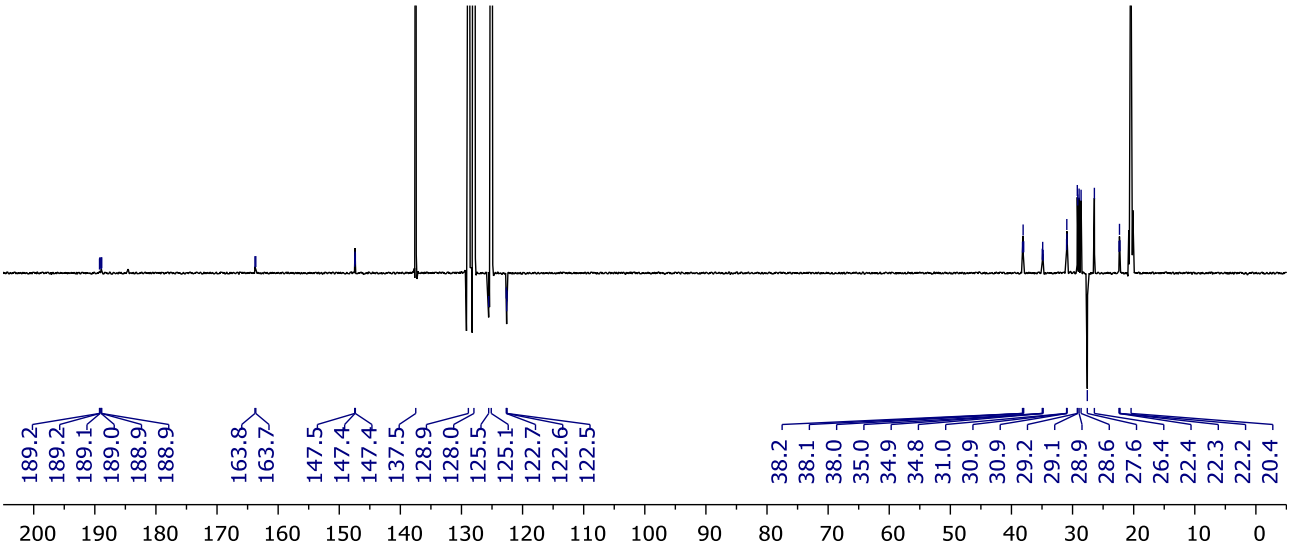


Figure S72. ^{13}C{^{1}H} APT NMR spectrum of **15a** (toluene-d_8, 151 MHz, CO).

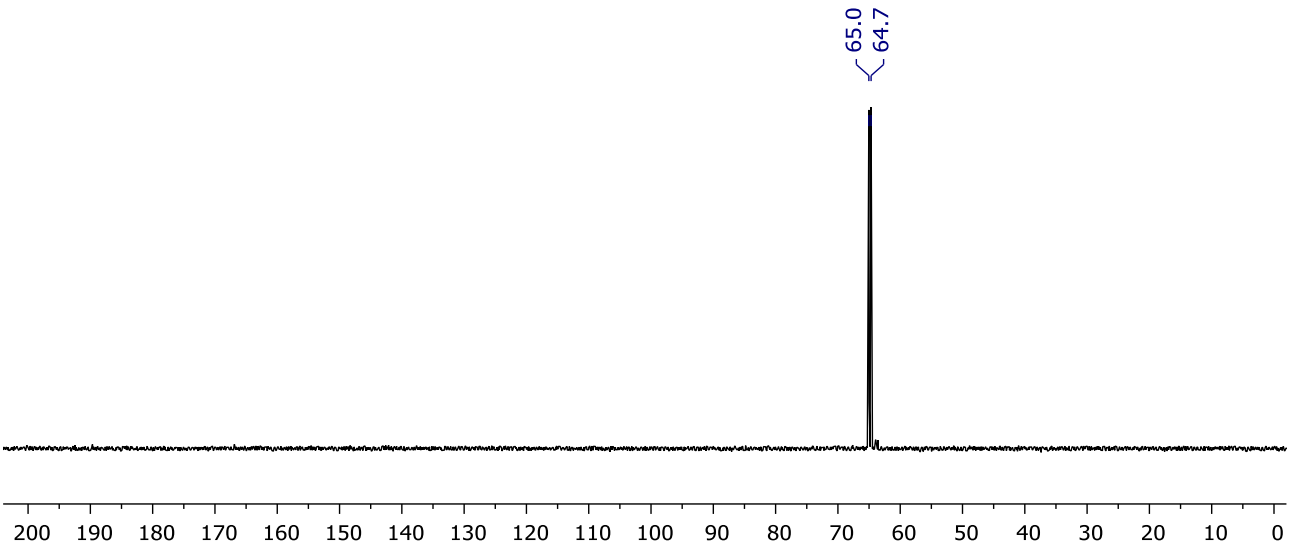


Figure S73. ^{31}P{^{1}H} NMR spectrum of 15a (toluene-d_8, 243 MHz, CO).

2.4. Synthesis of rhodium complexes of POCOP-14

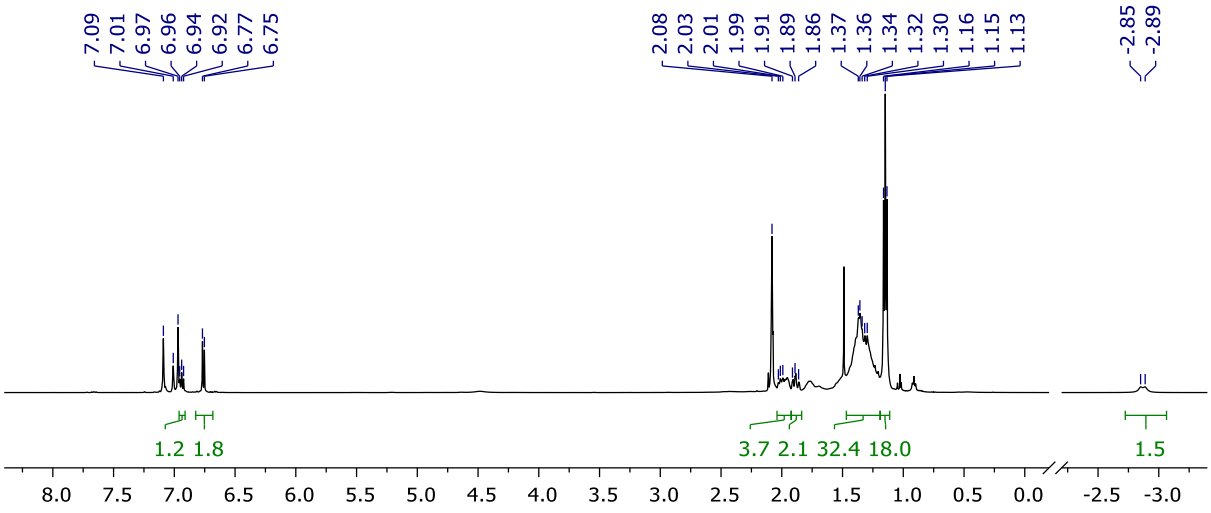


Figure S74. ^{1}H NMR spectrum of **13b** (toluene-d_8, 500 MHz, H_2).

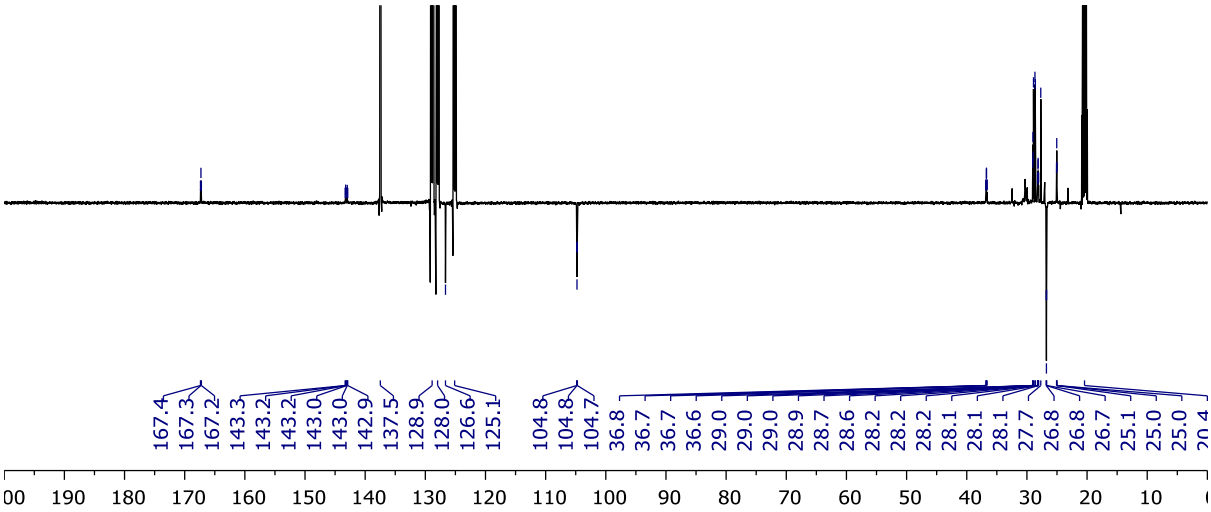


Figure S75. $^{13}C\{^{1}H\}$ APT NMR spectrum of **13b** (toluene-d_8, 126 MHz, H_2).

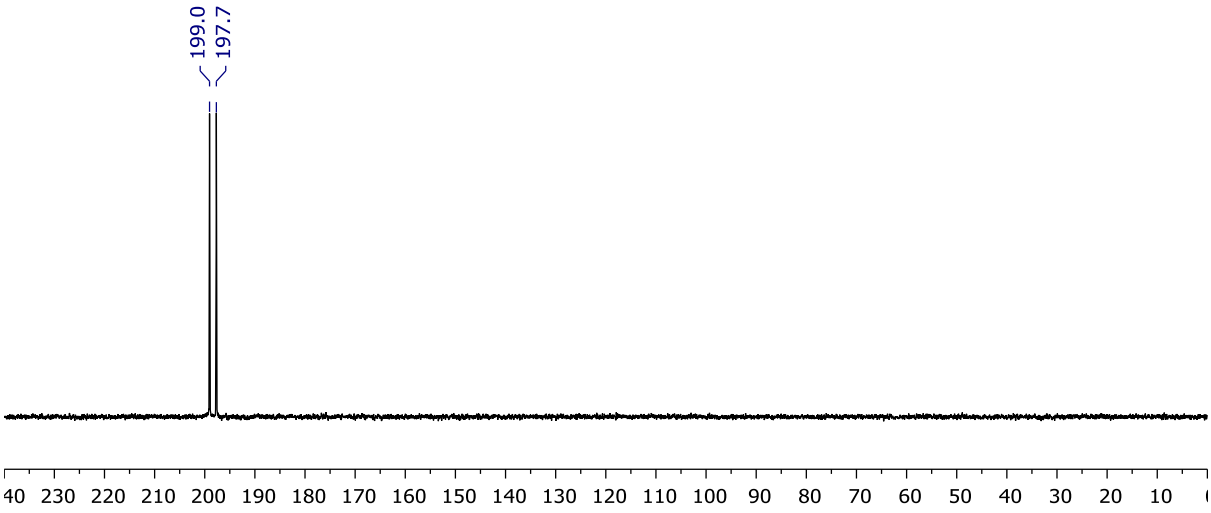


Figure S76. $^{13}C\{^{1}H\}$ APT NMR spectrum of **13b** (toluene-d_8, 162 MHz, H_2).

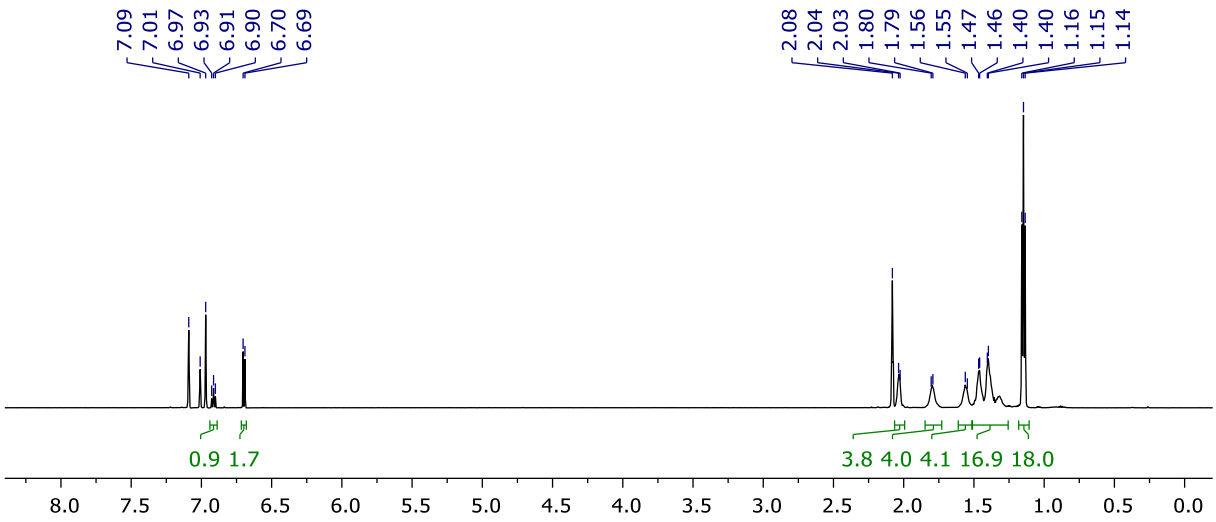


Figure S77. ^{1}H NMR spectrum of **14b** (toluene-d_8, 600 MHz).

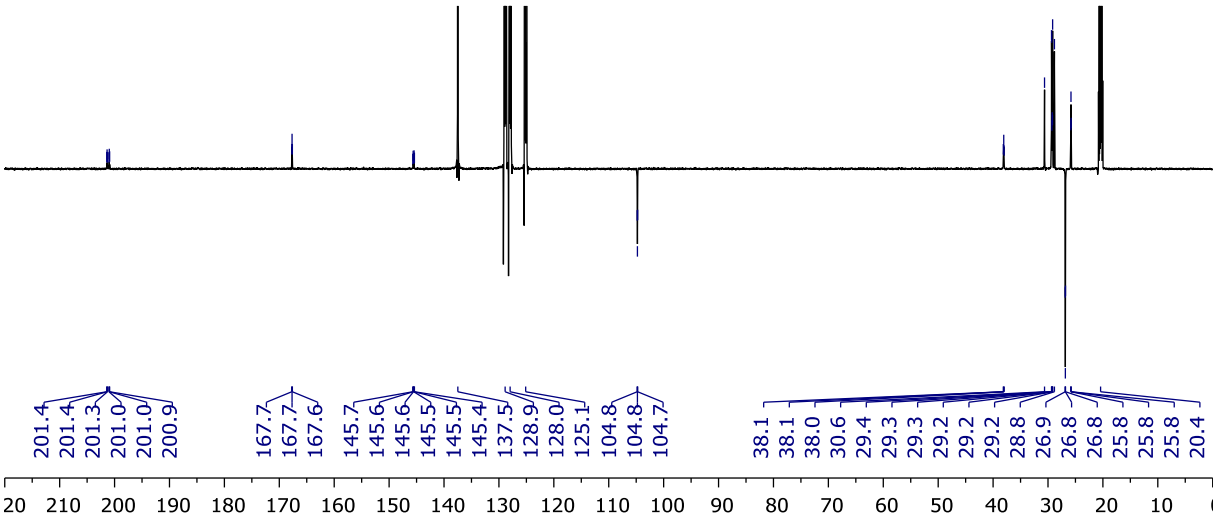


Figure S78. ^{13}C{^{1}H} APT NMR spectrum of **14b** (toluene-d_8, 151 MHz).

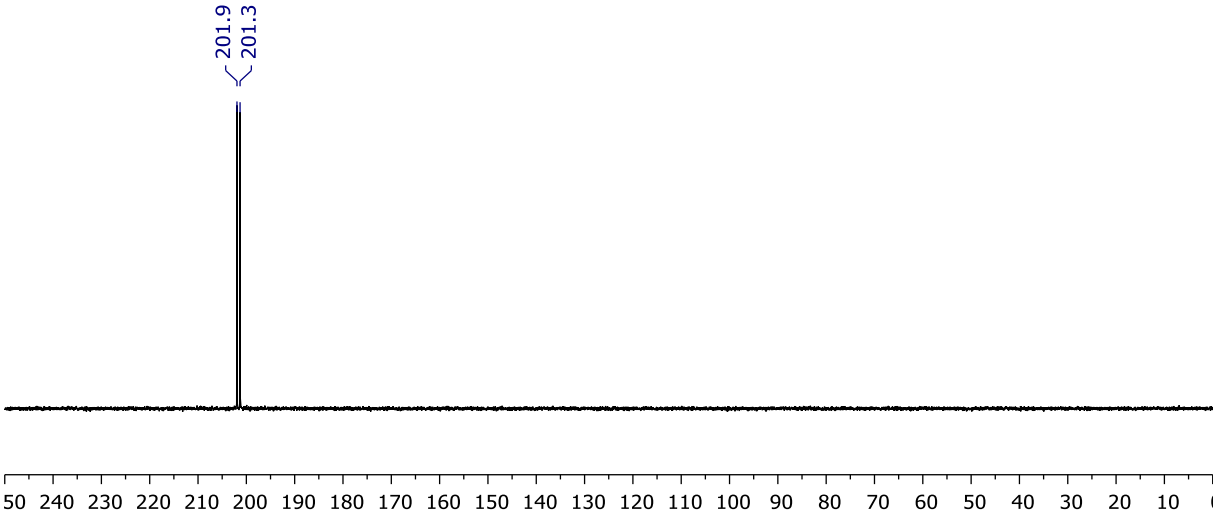


Figure S79. ^{31}P{^{1}H} NMR spectrum of **14b** (toluene-d_8, 243 MHz).

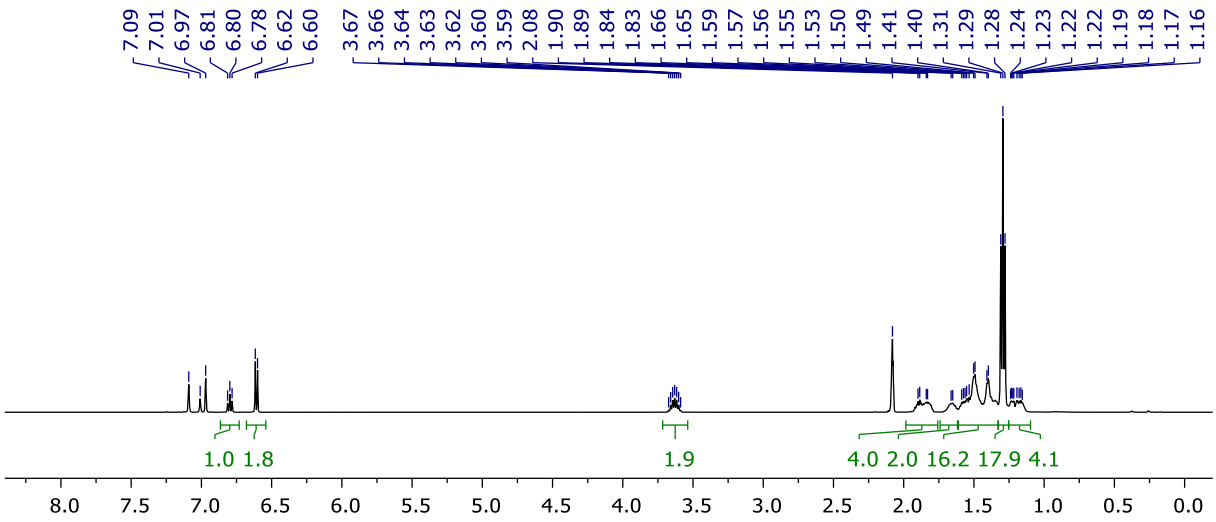


Figure S80. ^{1}H NMR spectrum of **15b** (toluene-d_8, 500 MHz, CO).

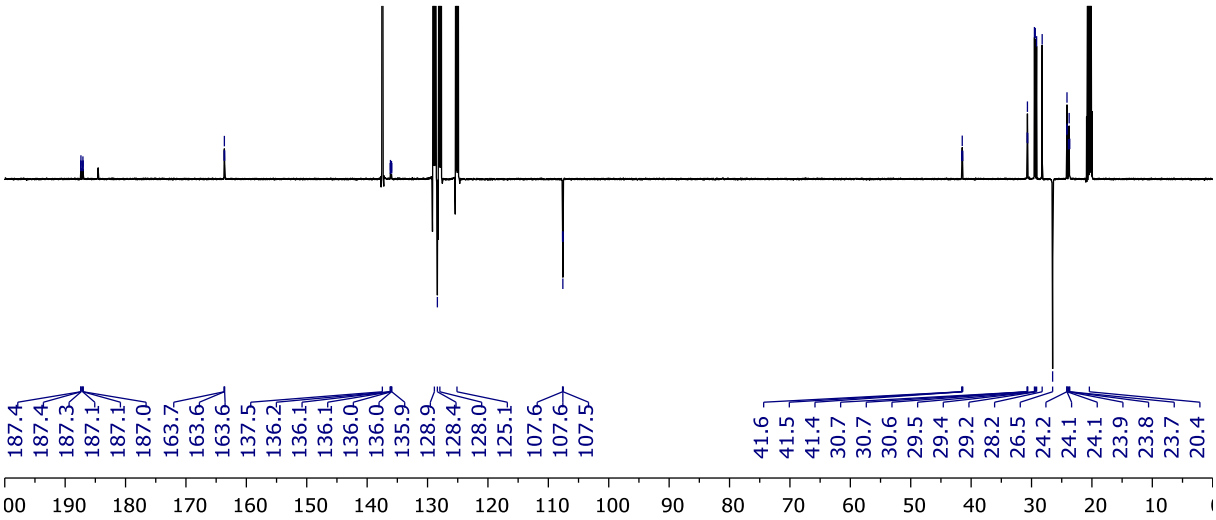


Figure S81. ^{13}C{^{1}H} APT NMR spectrum of **15b** (toluene-d_8, 126 MHz, CO).

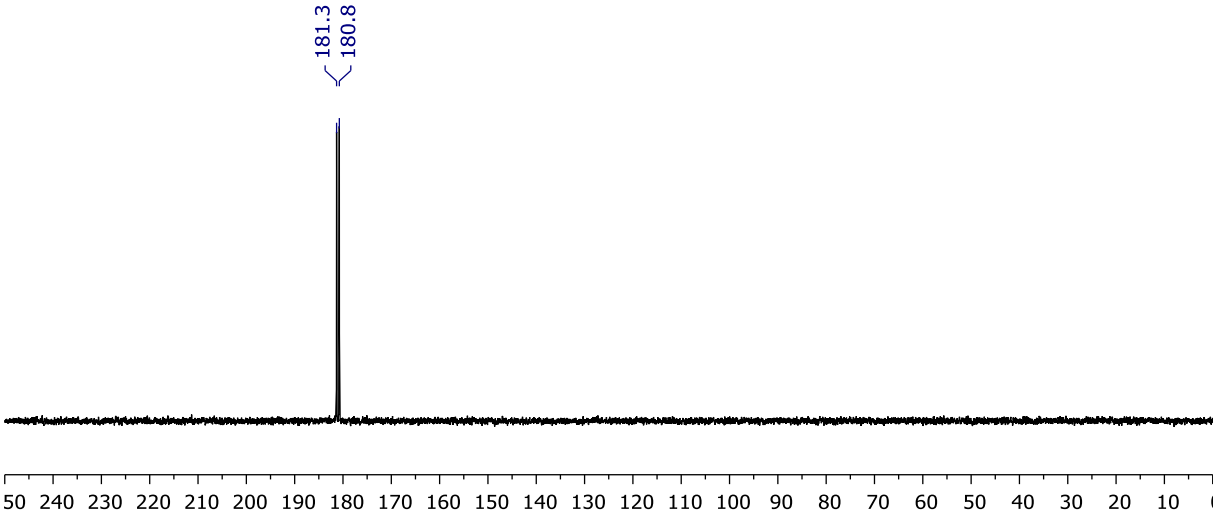


Figure S82. ^{31}P{^{1}H} NMR spectrum of **15b** (toluene-d_8, 162 MHz, CO).

2.5. Synthesis of iridium complexes of PCP-14

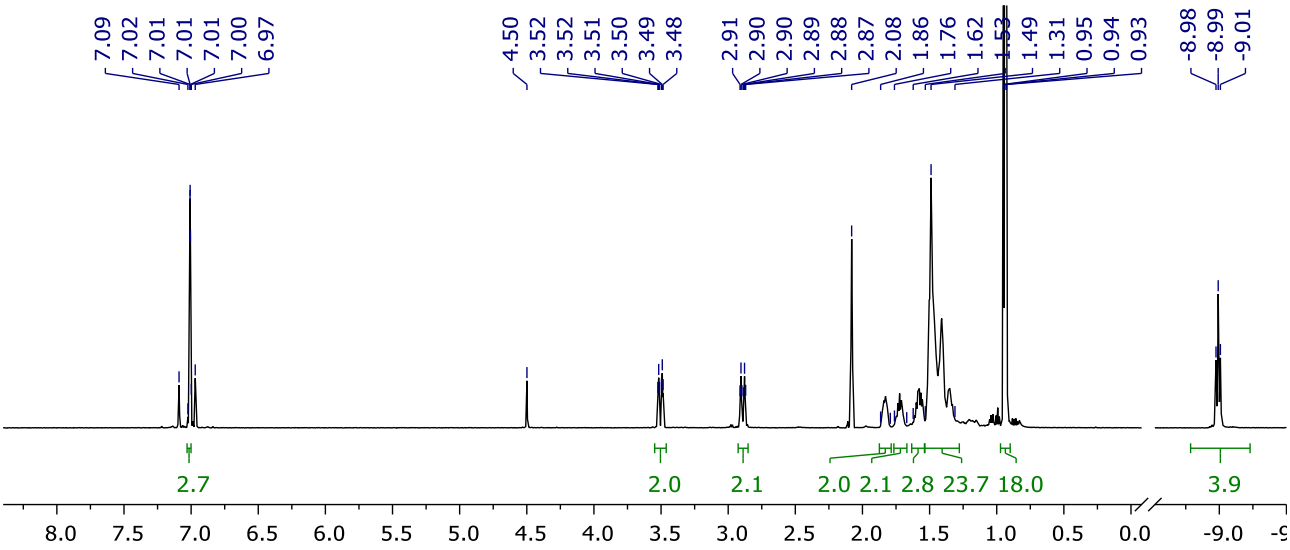


Figure S83. ^{1}H NMR spectrum of **16a** (toluene-d_8, 600 MHz, H_2).

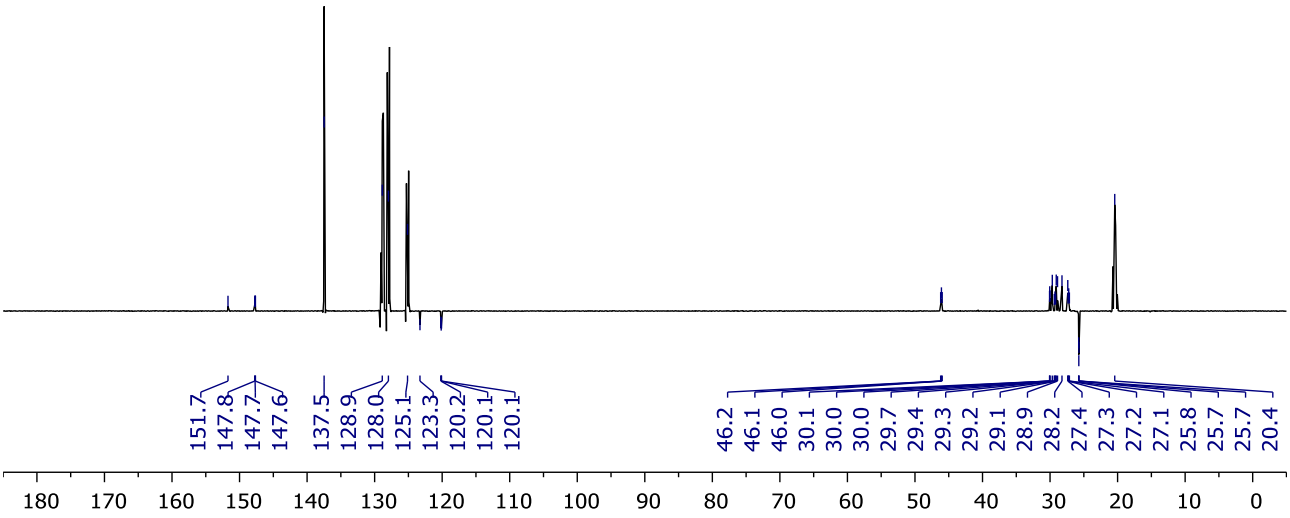


Figure S84. $^{13}C\{^{1}H\}$ APT NMR spectrum of **16a** (toluene-d_8, 151 MHz, H_2).

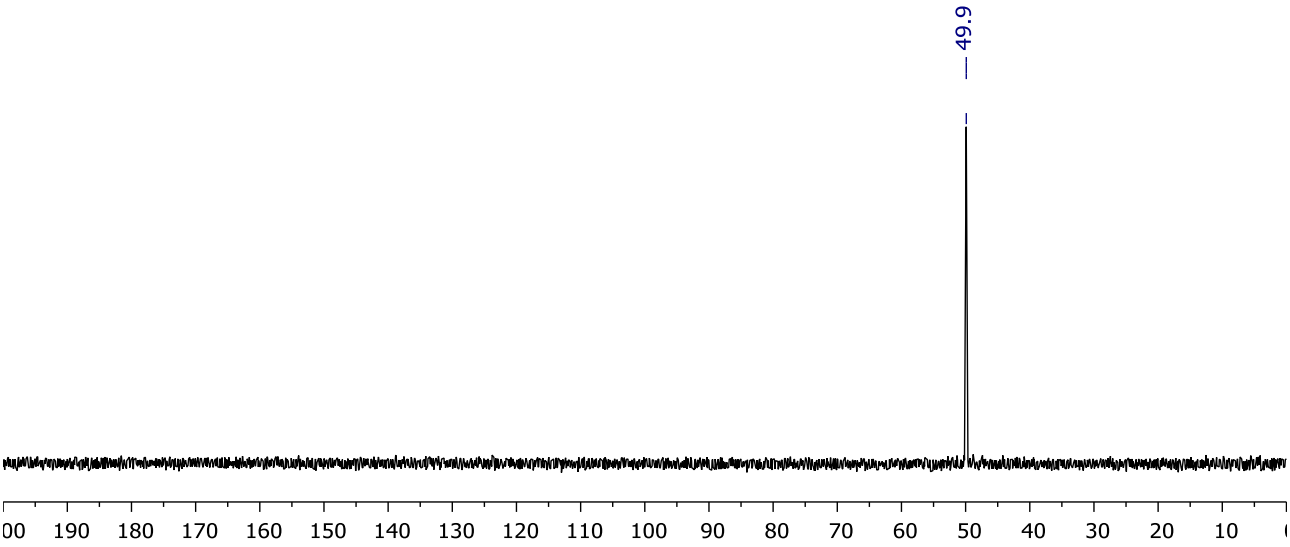


Figure S85. $^{31}P\{^{1}H\}$ NMR spectrum of **16a** (toluene-d_8, 243 MHz, H_2).

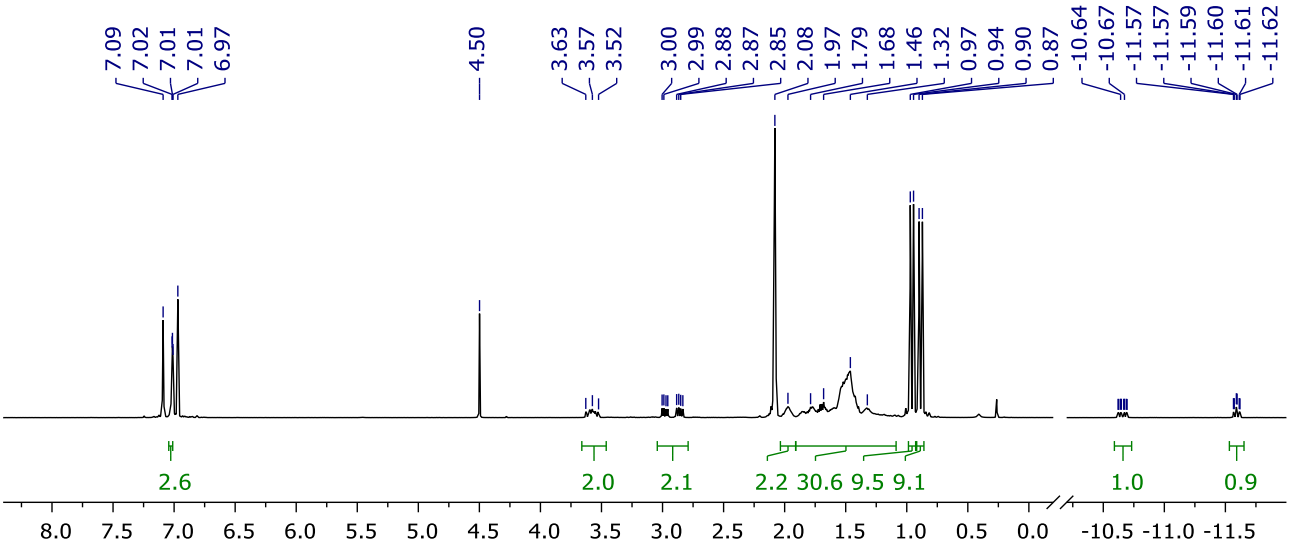


Figure S86. ^{1}H NMR spectrum of *cis*-**17a** (toluene-d_8, 500 MHz).

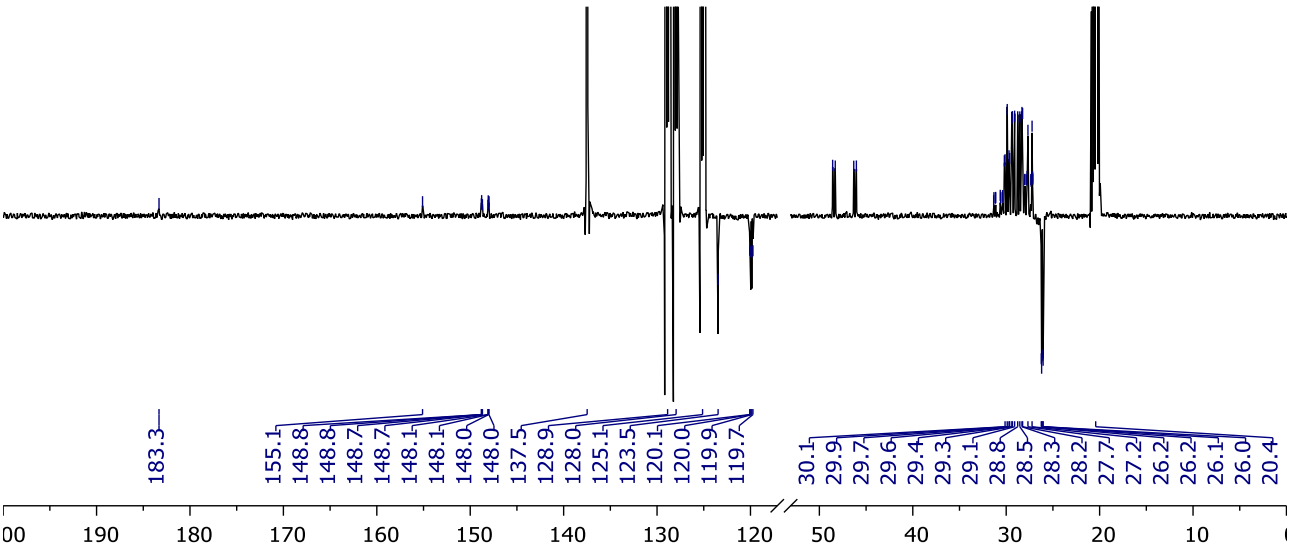


Figure S87. ^{13}C{^{1}H} APT NMR spectrum of *cis*-**17a** (toluene-d_8, 126 MHz).

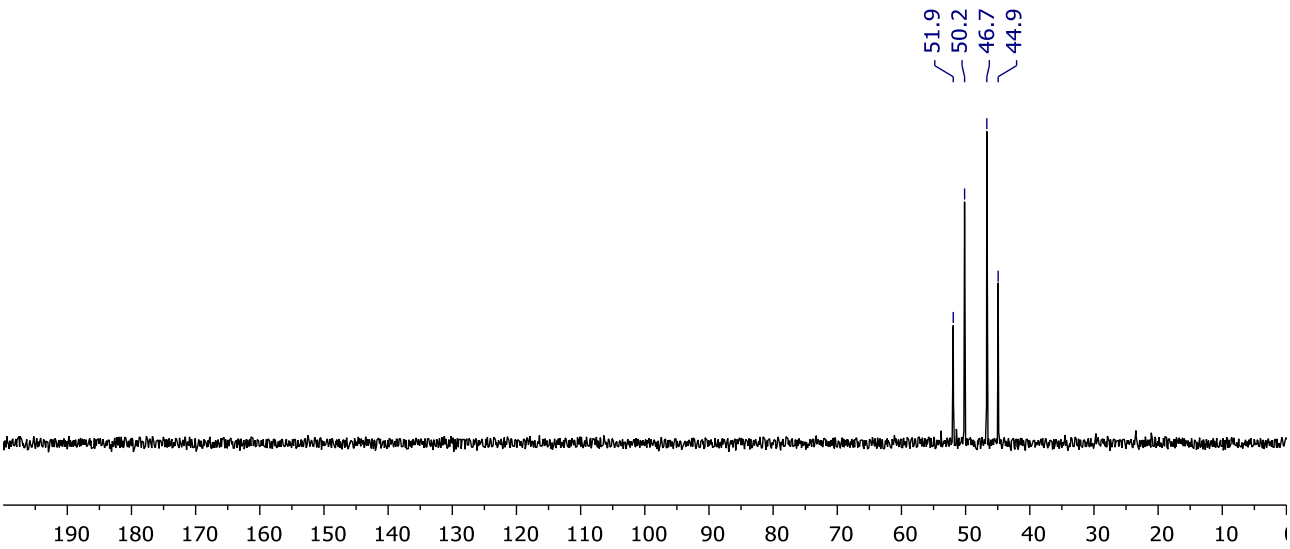


Figure S88. ^{31}P{^{1}H} NMR spectrum of *cis*-**17a** (toluene-d_8, 162 MHz).

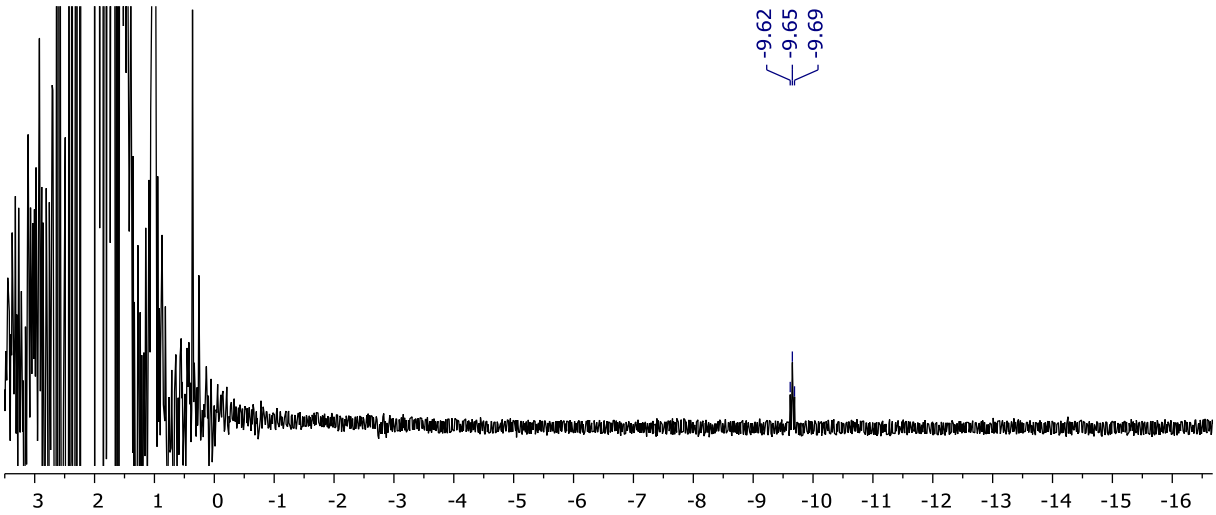


Figure S89. ^{1}H NMR spectrum of *trans*-**17a** (toluene-d_0, 400 MHz, CO).

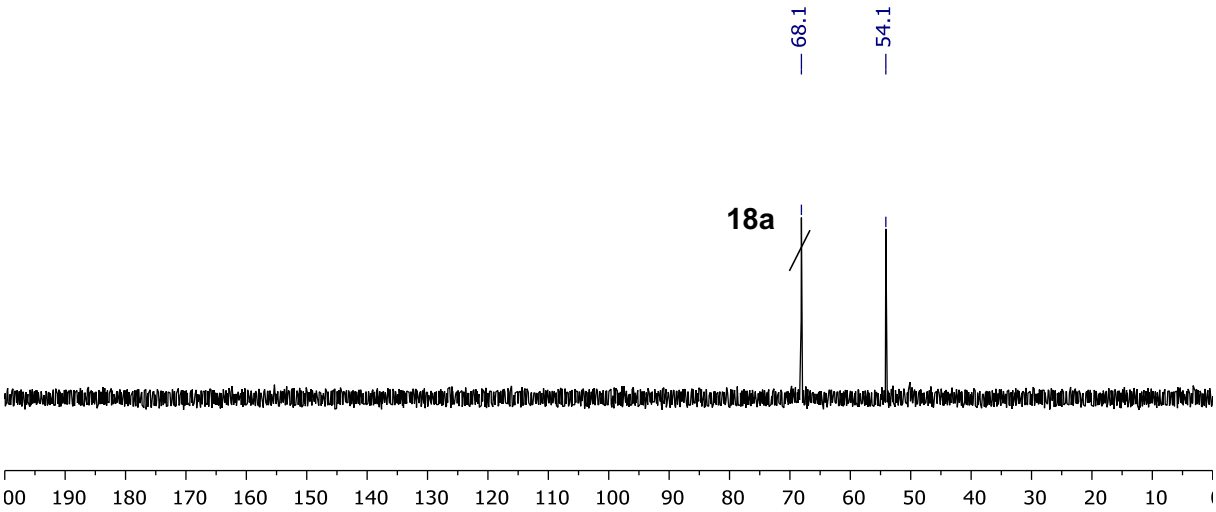


Figure S90. ^{31}P{^{1}H} NMR spectrum of *trans*-**17a** (toluene-d_0, 162 MHz, CO).

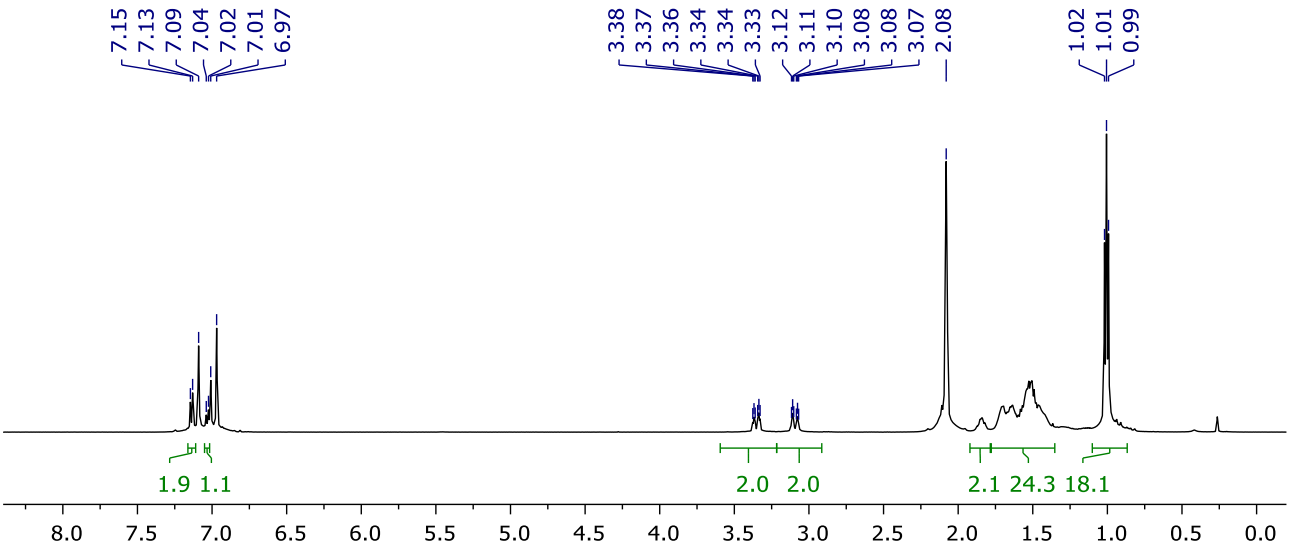


Figure S91. ^{1}H NMR spectrum of **18a** (toluene-d_8, 500 MHz).

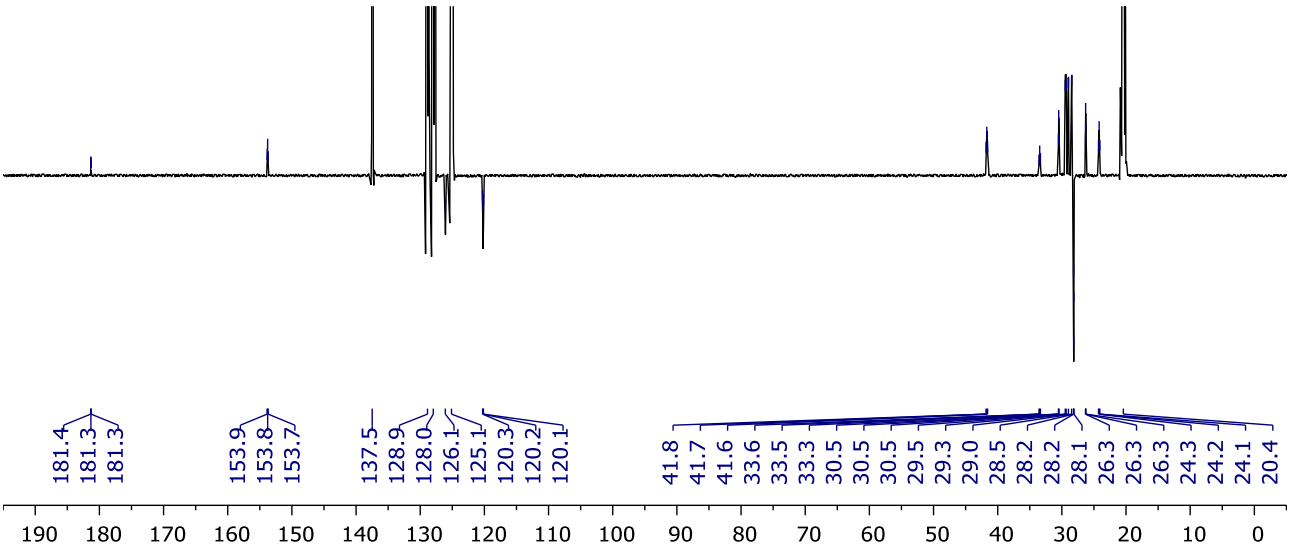


Figure S92. $^{13}C\{^{1}H\}$ APT NMR spectrum of **18a** (toluene-d_8, 126 MHz).

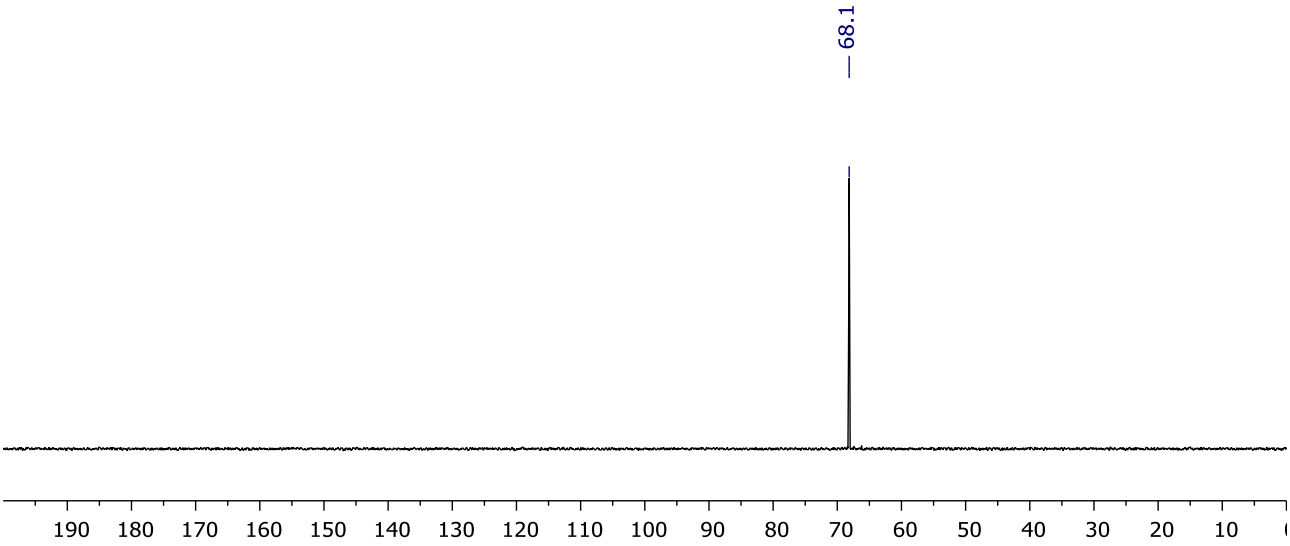


Figure S93. $^{31}P\{^{1}H\}$ NMR spectrum of **18a** (toluene-d_8, 162 MHz).

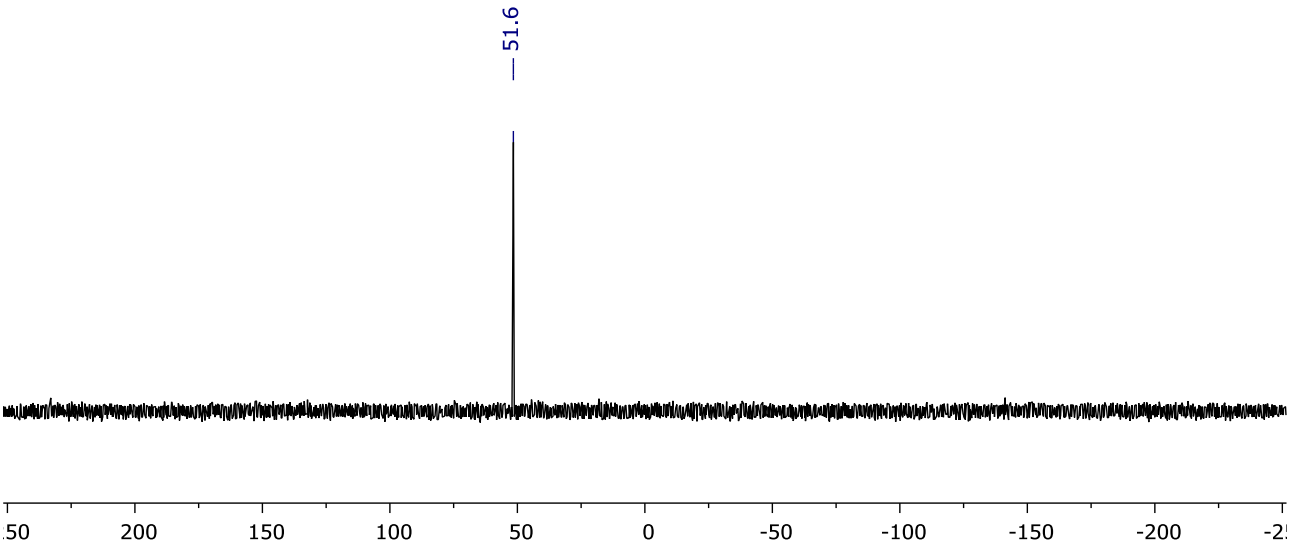


Figure S94. $^{31}P\{^{1}H\}$ NMR spectrum of [Ir(PCP-14)$(CO)_2$] (toluene-d_8, 162 MHz, CO).

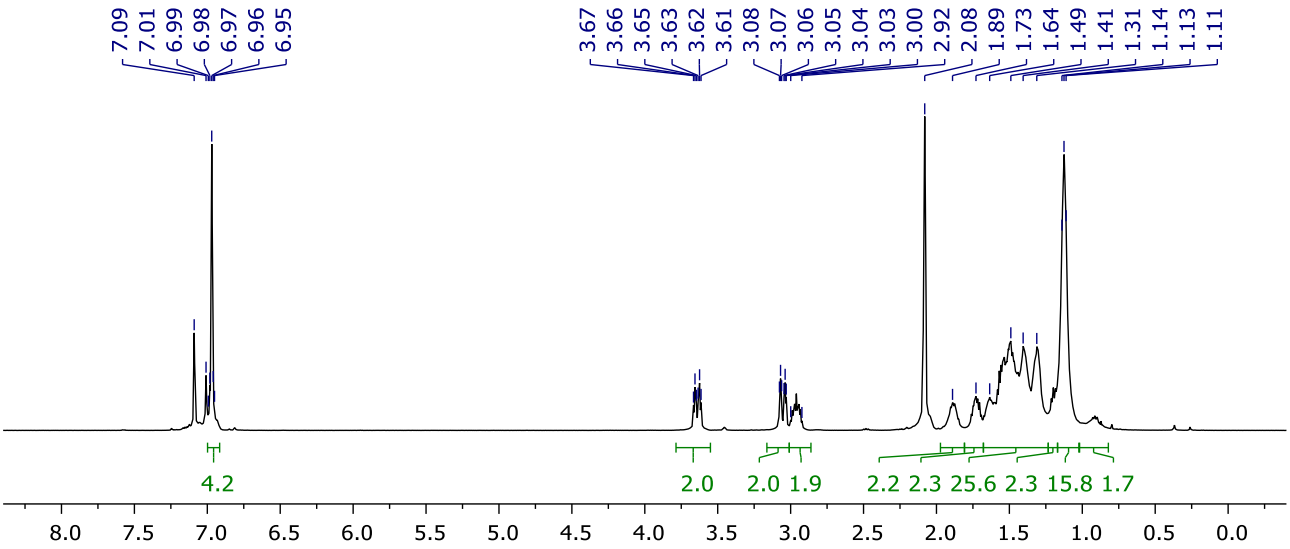


Figure S95. ^{1}H NMR spectrum of **19a** (toluene-d_8, 500 MHz).

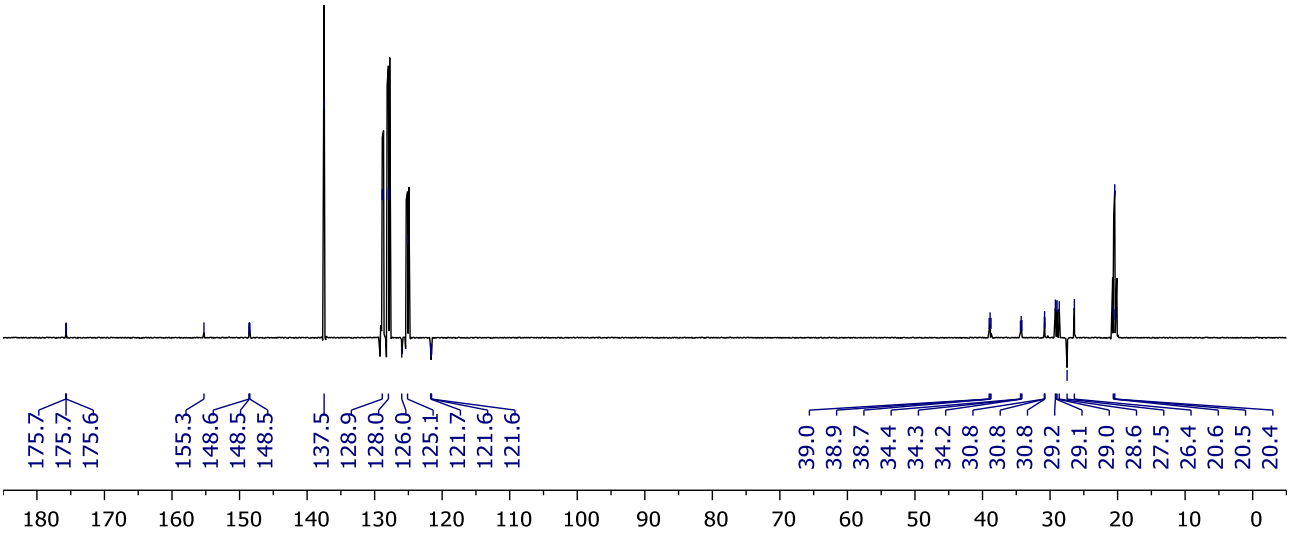


Figure S96. ^{13}C{^{1}H} APT NMR spectrum of **19a** (toluene-d_8, 126 MHz).

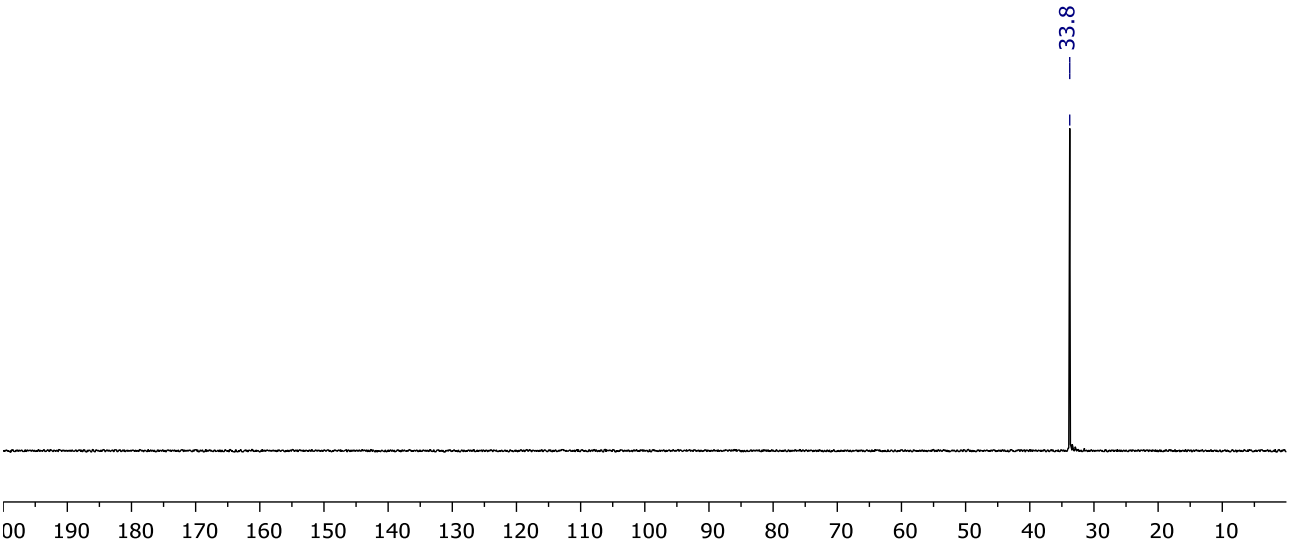


Figure S97. ^{31}P{^{1}H} NMR spectrum of **19a** (toluene-d_8, 162 MHz).

2.6. Synthesis of iridium complexes of POCOP-14

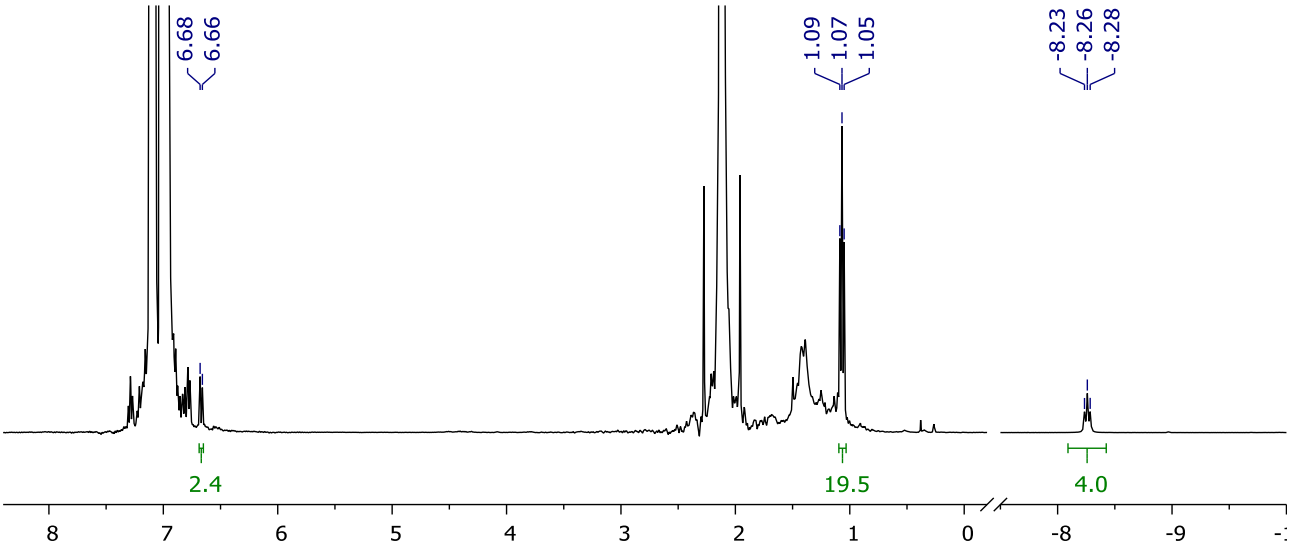


Figure S98. ^{1}H NMR spectrum of **16b** (toluene-d_0, 400 MHz, H_2).

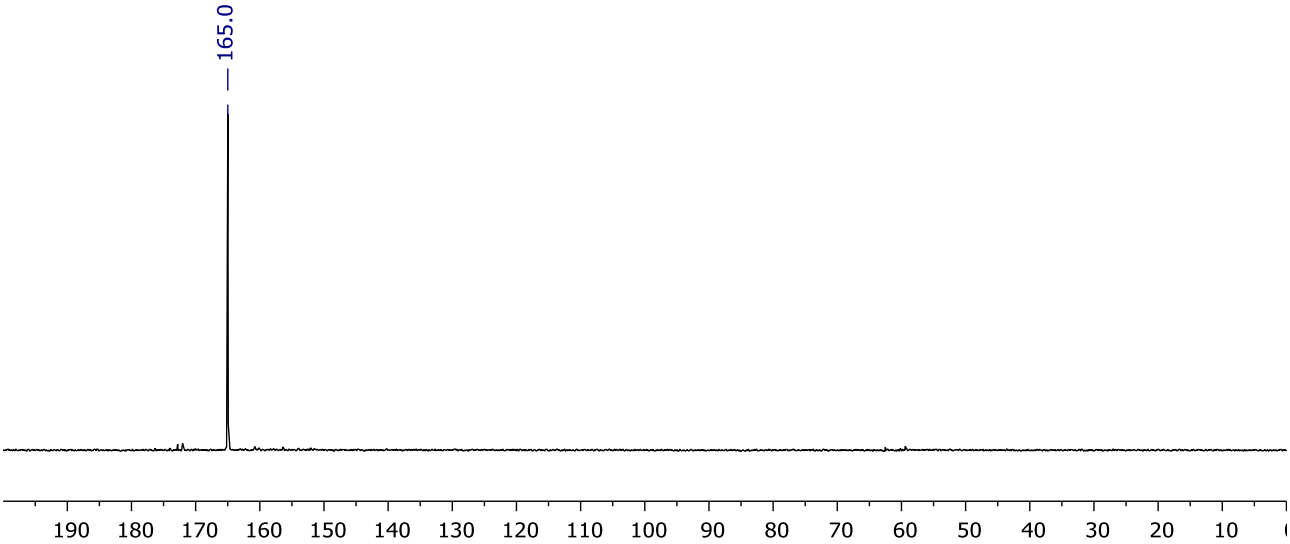


Figure S99. $^{31}P\{^{1}H\}$ NMR spectrum of **16b** (toluene-d_0, 162 MHz, H_2).

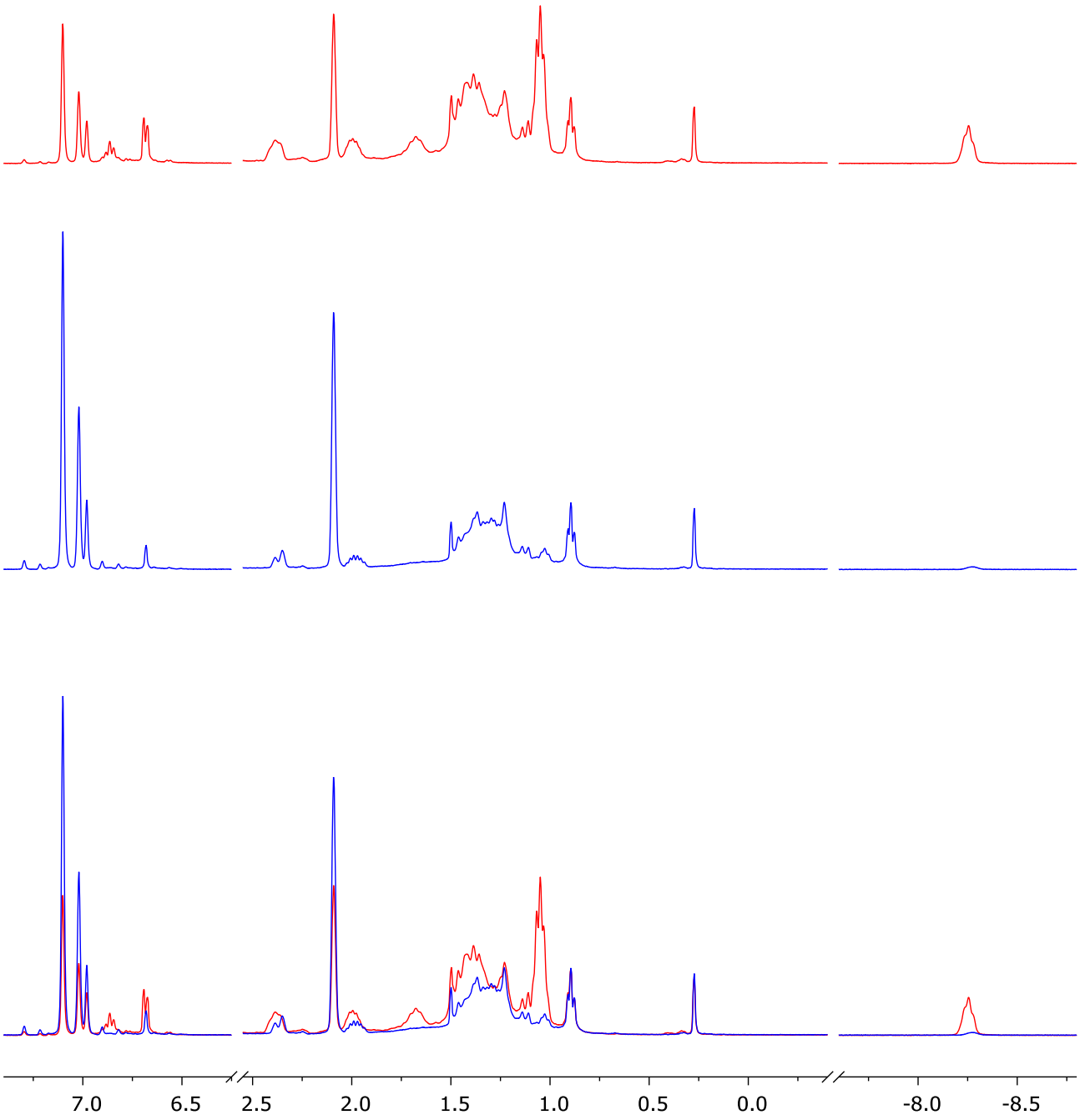


Figure S100. ^{1}H NMR spectra of **16b** dissolved in toluene-d_8 under H_2 (1 atm) after 5 min (top) and 17 h (middle) at RT: with overlap (bottom, toluene-d_8, 400 MHz, H_2).

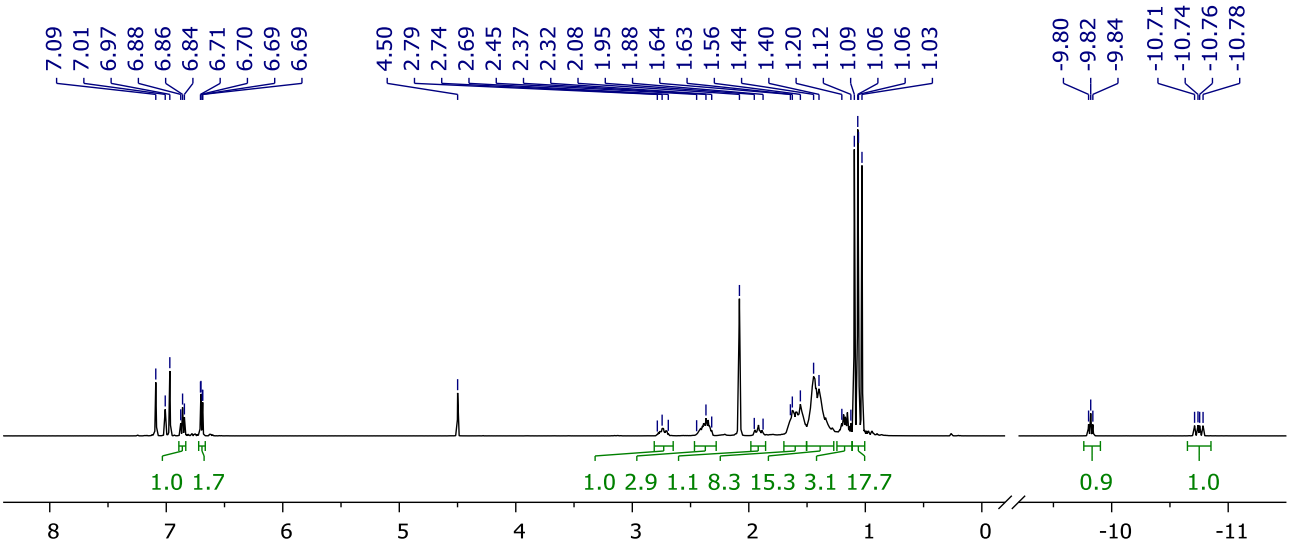


Figure S101. ^{1}H NMR spectrum of *cis*-**17b** (toluene-d_8, 500 MHz).

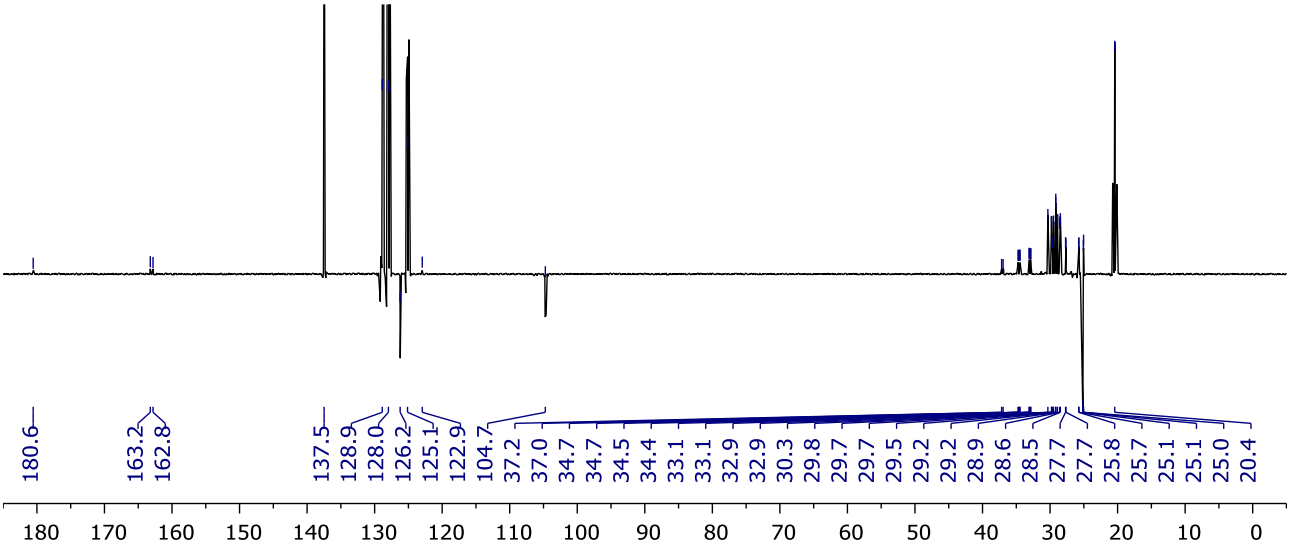


Figure S102. ^{13}C{^{1}H} APT NMR spectrum of *cis*-**17b** (toluene-d_8, 126 MHz).

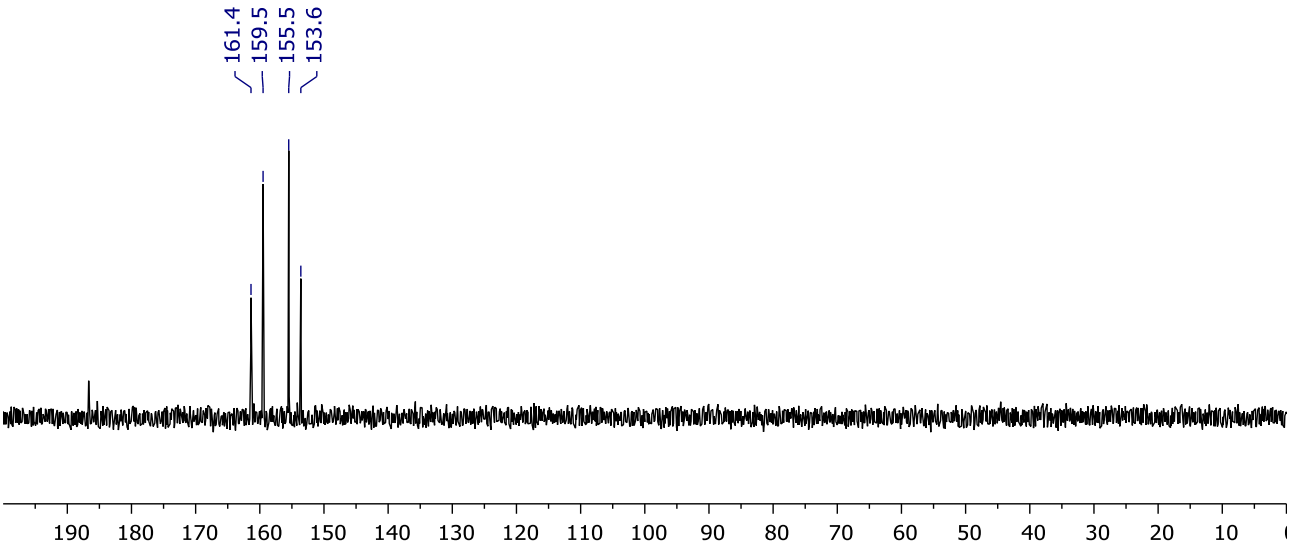


Figure S103. ^{31}P{^{1}H} NMR spectrum of *cis*-**17b** (toluene-d_8, 162 MHz).

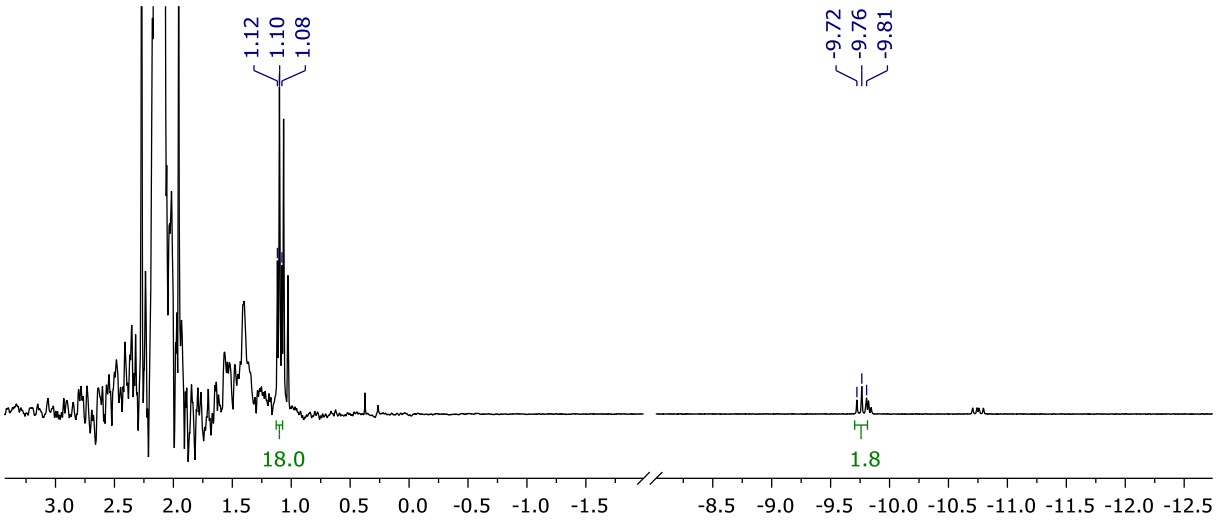


Figure S104. ^{1}H NMR spectrum of *trans*-**17b** (toluene-d_0, 400 MHz, CO).

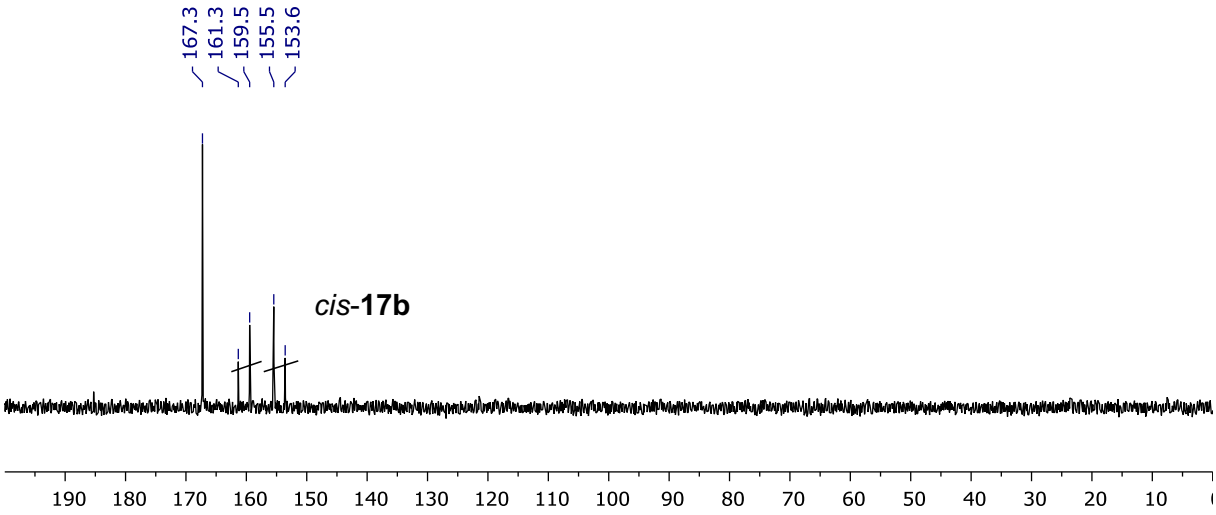


Figure S105. ^{31}P{^{1}H} NMR spectrum of *trans*-**17b** (toluene-d_0, 162 MHz, CO).

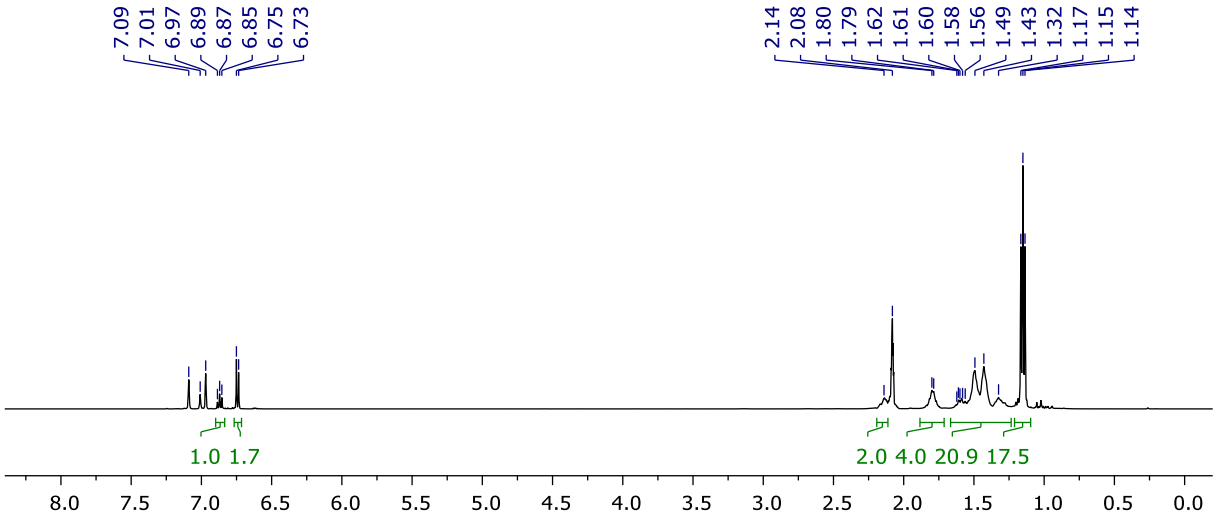


Figure S106. ^{1}H NMR spectrum of **18b** (toluene-d_8, 500 MHz).

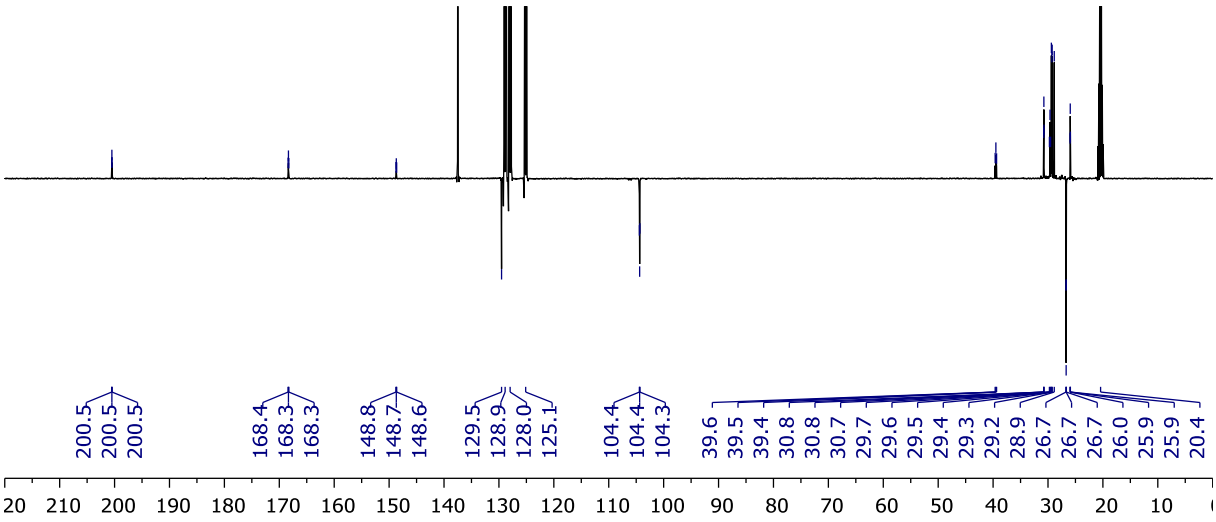


Figure S107. $^{13}C\{^{1}H\}$ APT NMR spectrum of **18b** (toluene-d_8, 126 MHz).

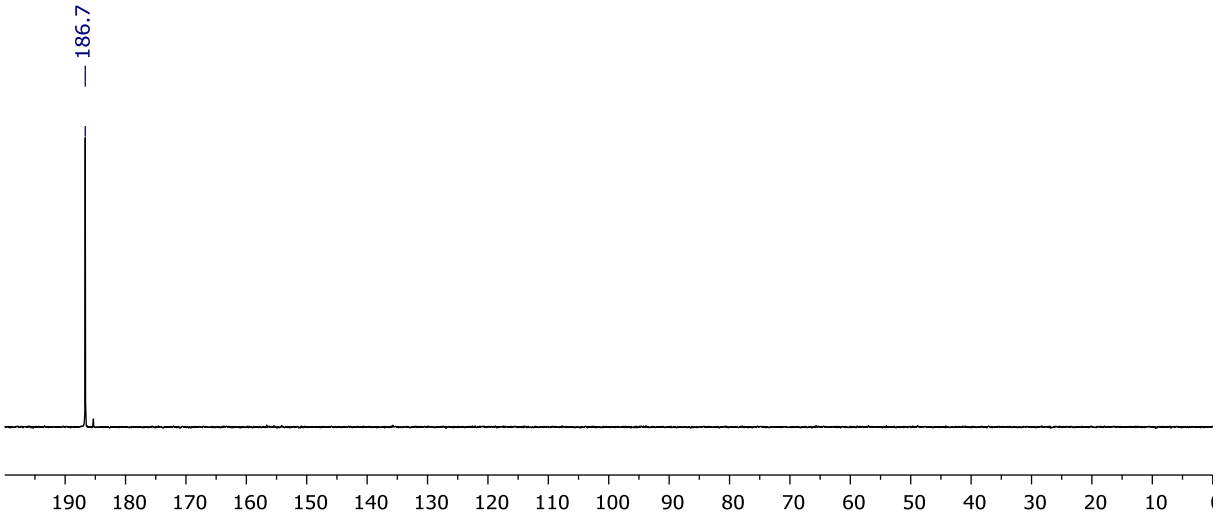


Figure S108. $^{31}P\{^{1}H\}$ NMR spectrum of **18b** (toluene-d_8, 162 MHz).

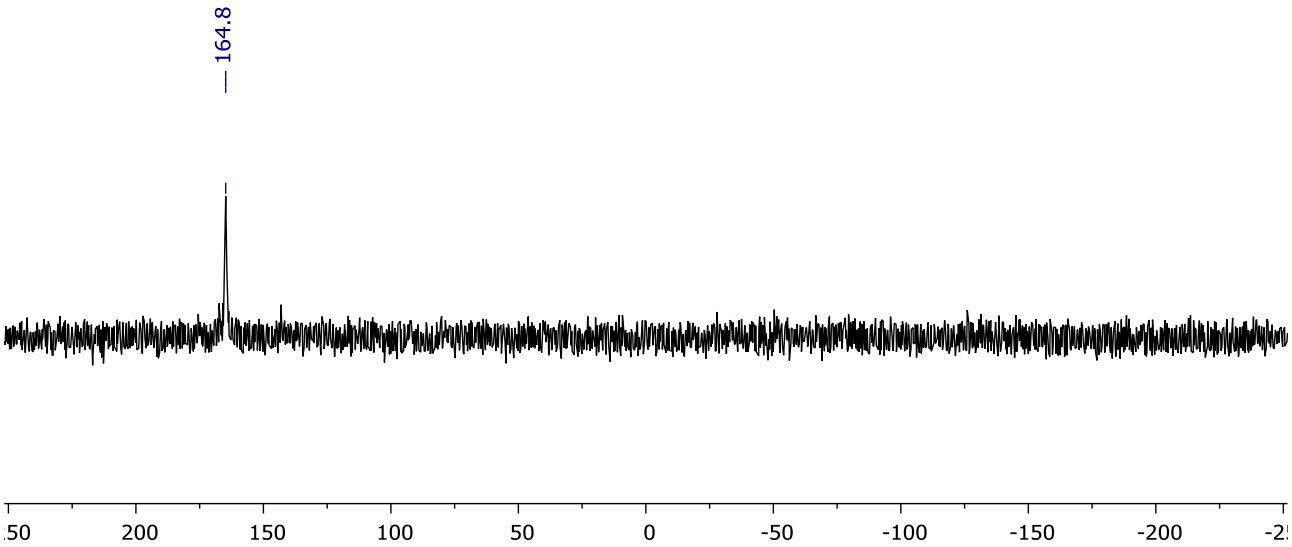


Figure S109. $^{31}P\{^{1}H\}$ NMR spectrum of [Ir(POCOP-14)$(CO)_2$] (toluene-d_8, 162 MHz, CO).

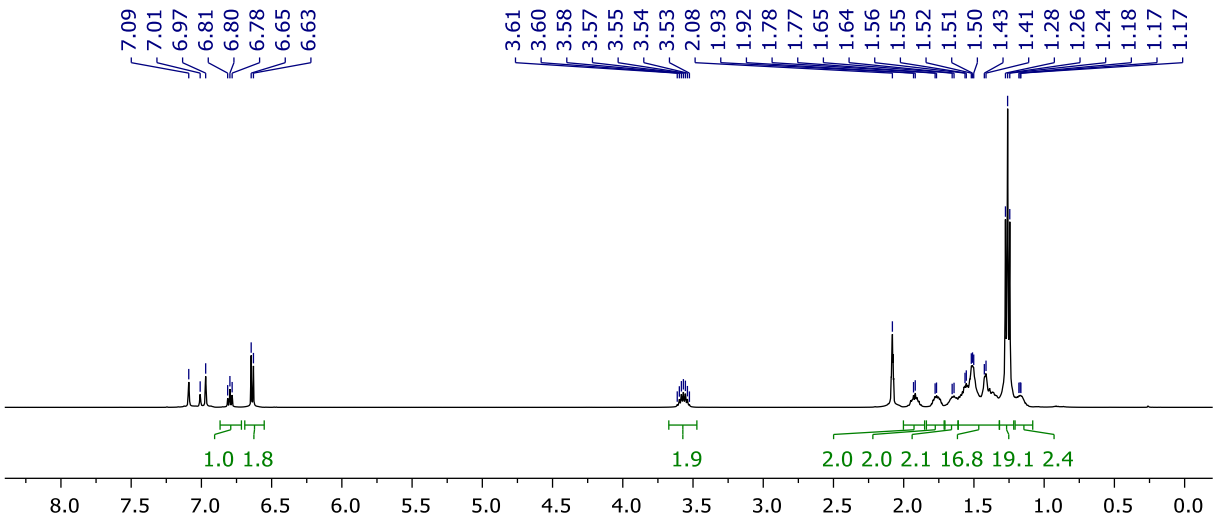


Figure S110. ^{1}H NMR spectrum of **19b** (toluene-d_8, 500 MHz).

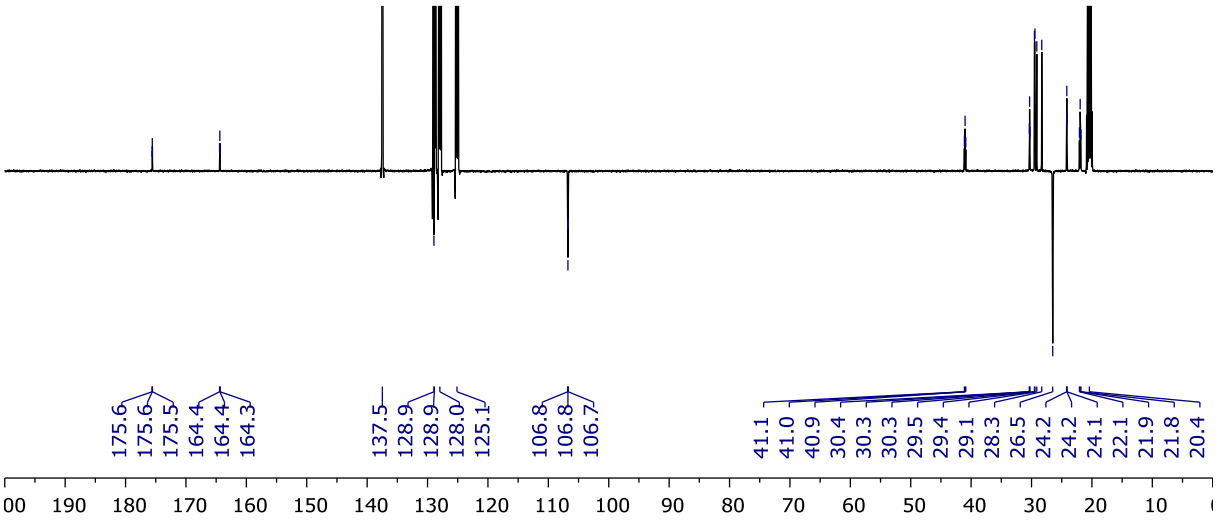


Figure S111. ^{13}C{^{1}H} APT NMR spectrum of **19b** (toluene-d_8, 126 MHz).

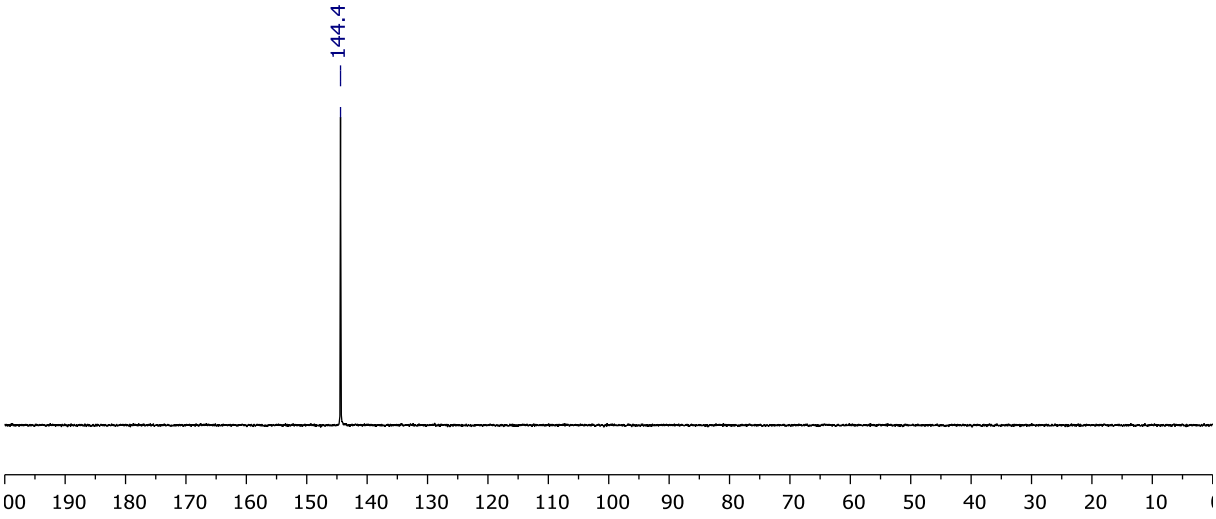


Figure S112. ^{31}P{^{1}H} NMR spectrum of **19b** (toluene-d_8, 121 MHz).

3. IR spectra of carbonyl complexes

3.1. Experimental method

All IR spectra were recorded using a Bruker Alpha Platinum ATR FT-IR spectrometer at RT. All measurements in the solid state were recorded in air. The high valent carbonyl complexes [M(pincer)Cl_2(CO)] (M = Rh, Ir; pincer = PCP-14, POCOP-14) are sufficiently stable in solution to be analysed in air; the low valent carbonyl complexes [M(pincer)(CO)] (M = Rh, Ir; pincer = PCP-14, POCOP-14, PCP-*t*Bu, POCOP-*t*Bu) are not and data were collected under an argon atmosphere using the experimental setup outlined in Figure S113; a right angle Rotaflo stopcock adapter was attached to the IR spectrometer over the ATR crystal using adhesive tack and connected to a Schlenk line. Solution-phase data were collected in toluene using the "drop method", whereby a drop of the desired solution (either prepared or generated by addition of a drop of solvent to the solid analyte on the ATR crystal) is placed directly onto the ATR crystal and the reflective anvil is not employed; reflection of the incident radiation from the inner surface of the droplet instead enables collection of high-quality data.

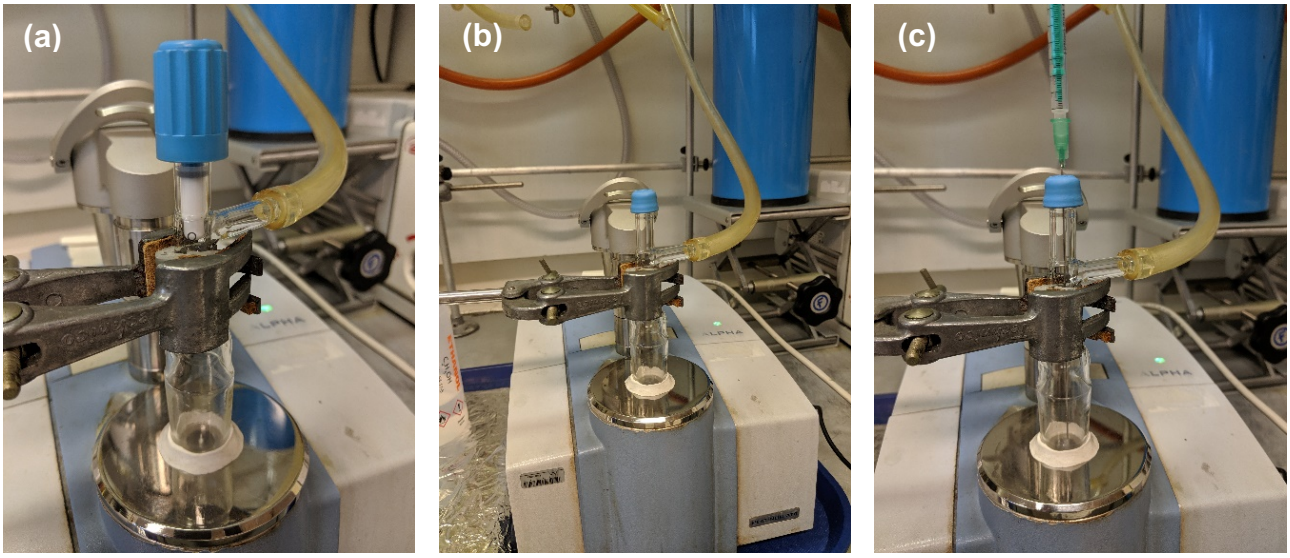


Figure S113. ATR-IR setup under argon atmosphere: (a) The atmosphere within can subjected to vacuum and cycled to the desired gas, but care was taken to adapt the overpressure in the Schlenk line to a minimum above atmospheric pressure so as to not put unnecessary strain on the seal; (b) The Rotaflo adapter can be fitted with a rubber septum and; (c) the background or sample solution to be measured can be transferred anaerobically onto the ATR crystal.

3.2. Macrocyclic pincers

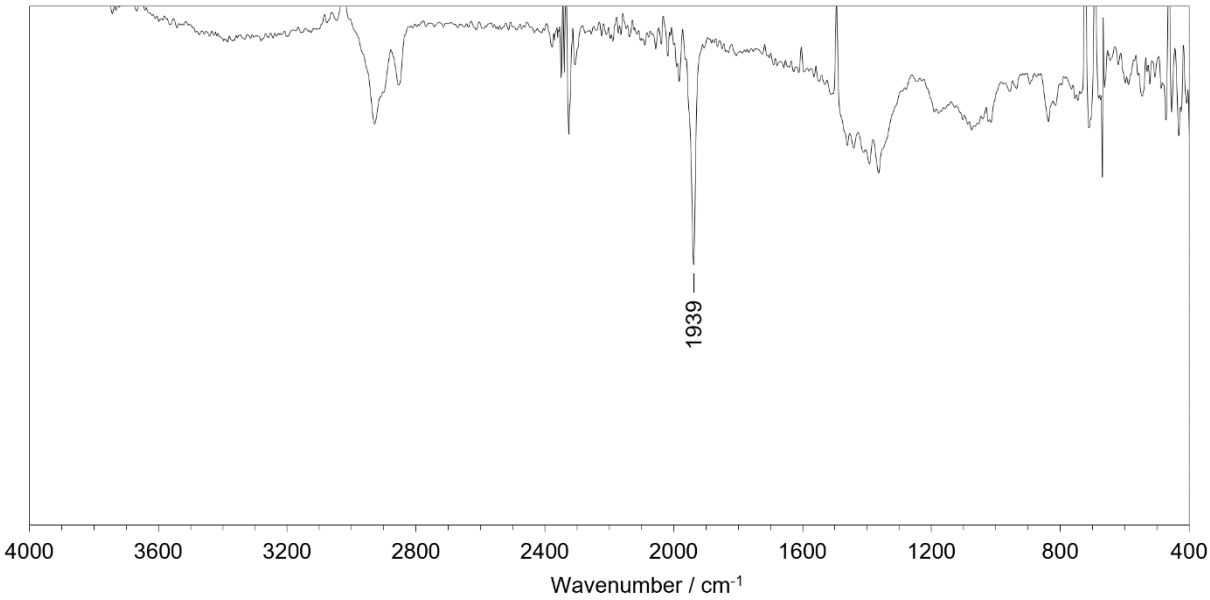


Figure S114. IR spectrum of **14a** (toluene).

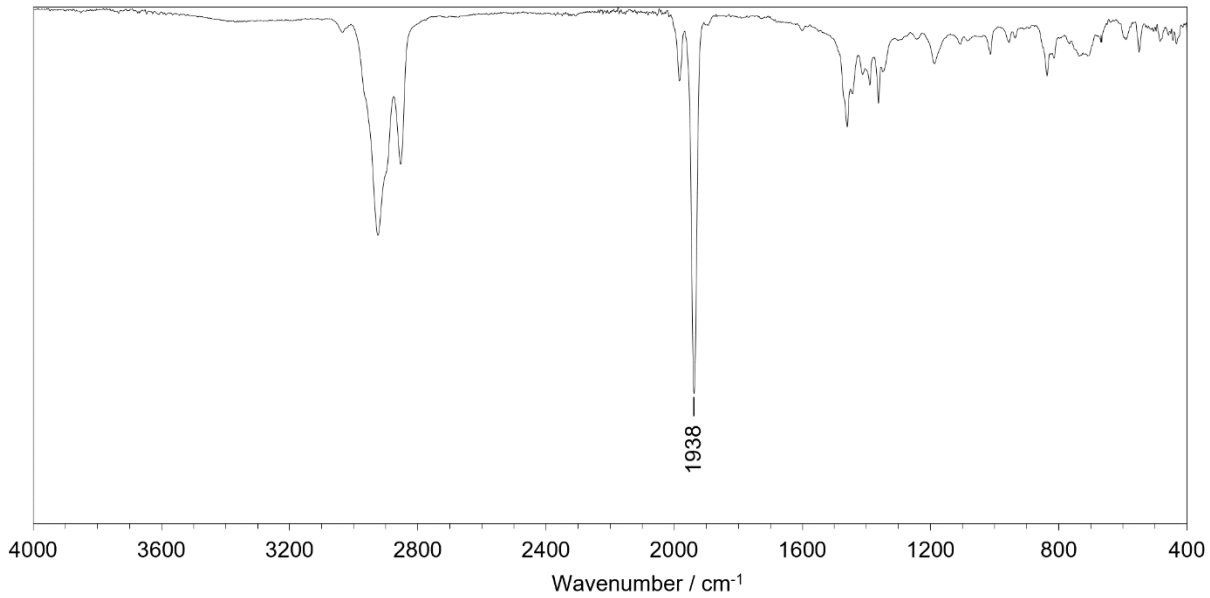


Figure S115. IR spectrum of **14a** (ATR).

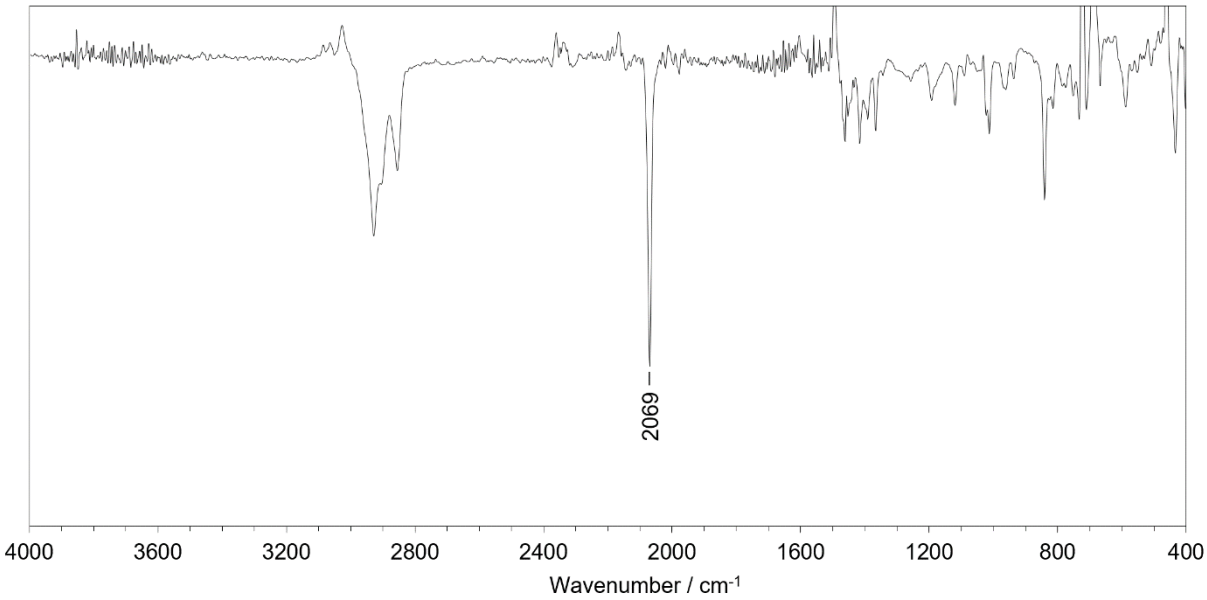


Figure S116. IR spectrum of **15a** (toluene).

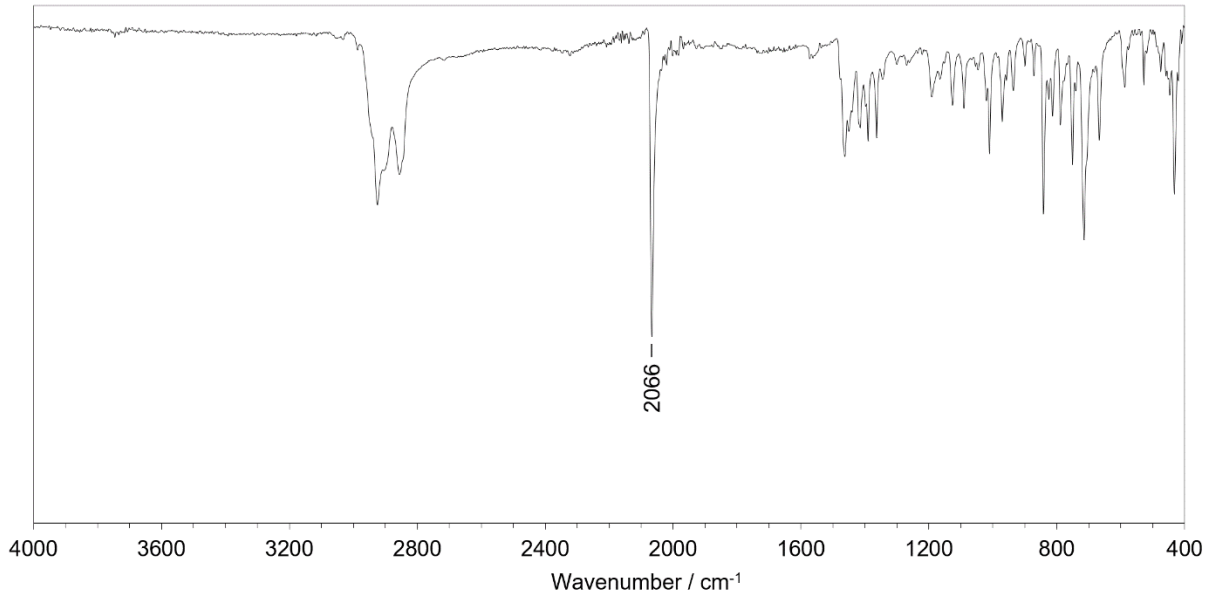


Figure S117. IR spectrum of **15a** (ATR).

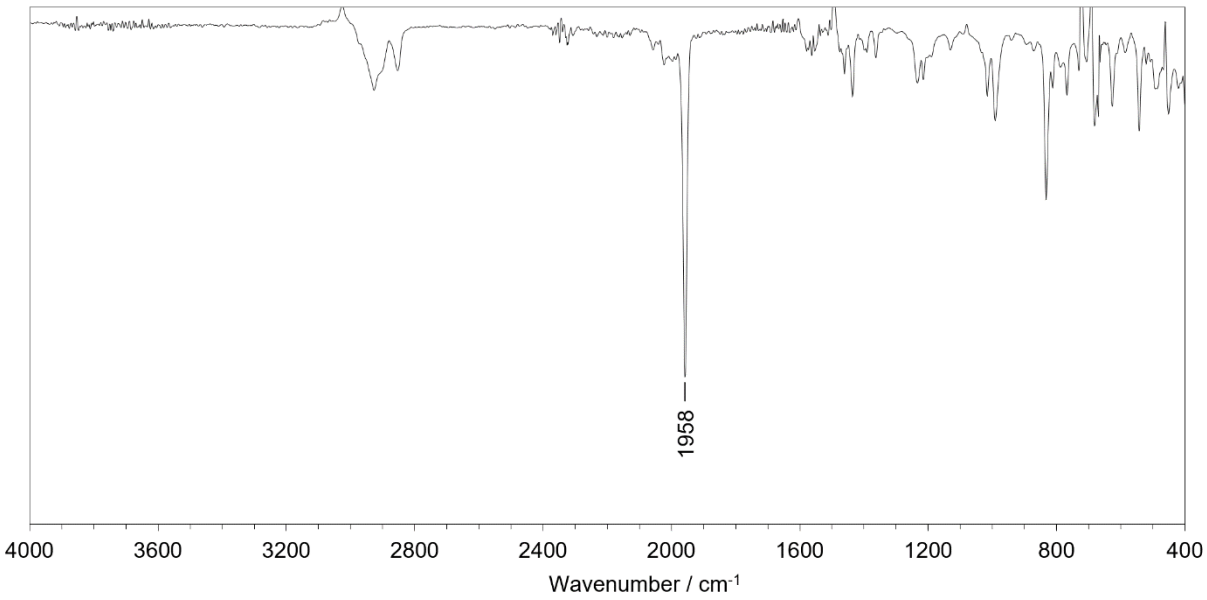


Figure S118. IR spectrum of **14b** (toluene).

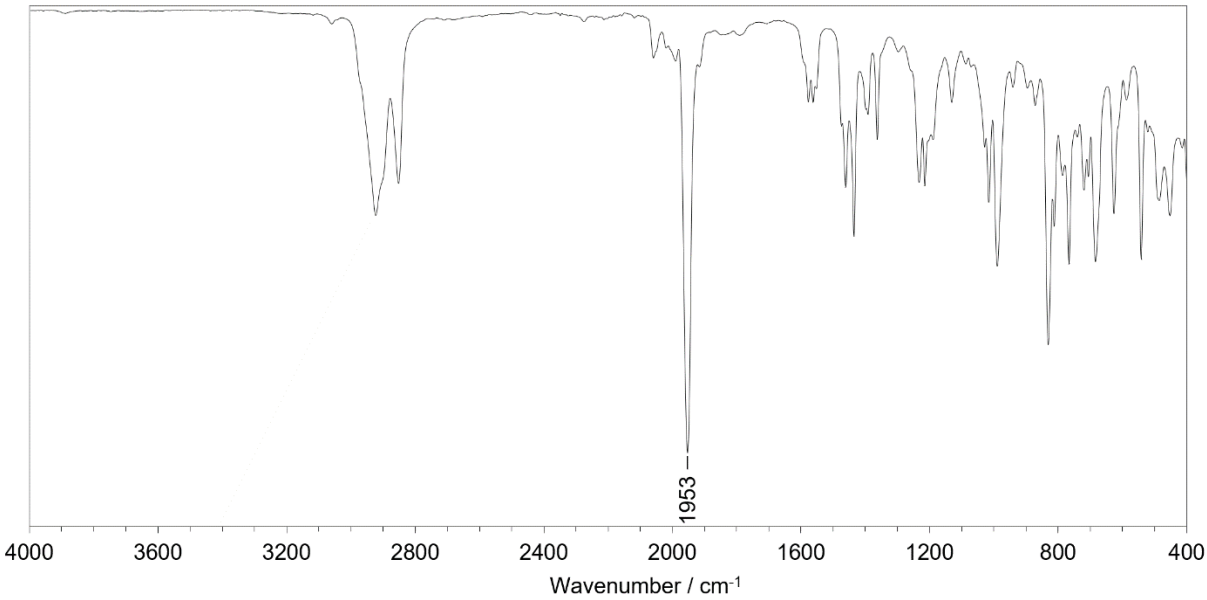


Figure S119. IR spectrum of **14b** (ATR).

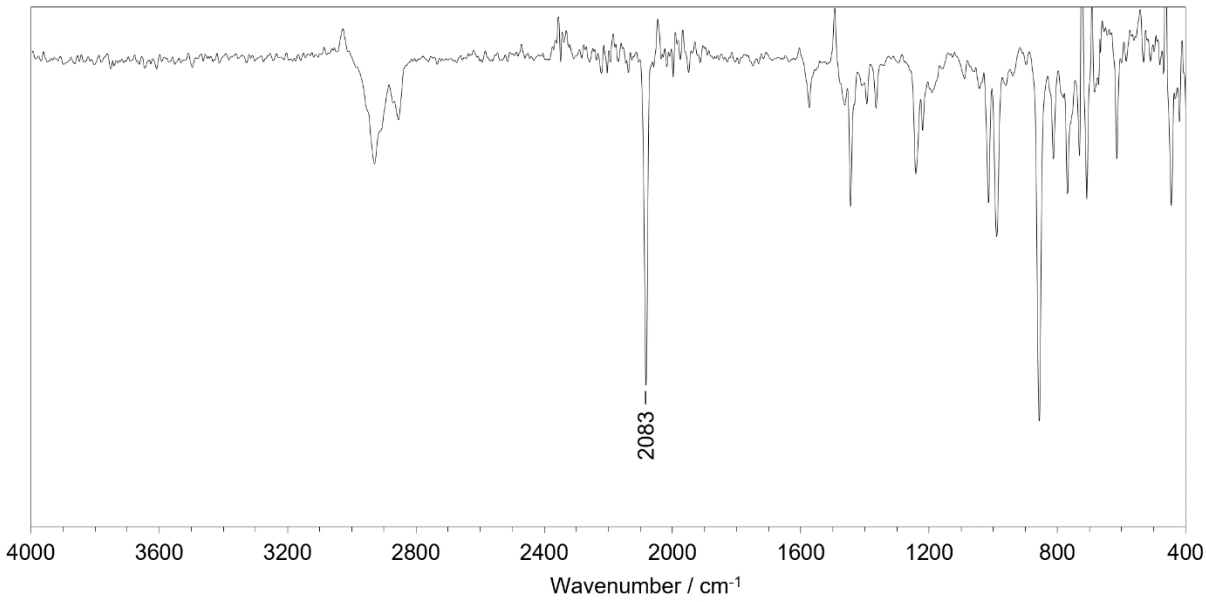


Figure S120. IR spectrum of **15b** (toluene).

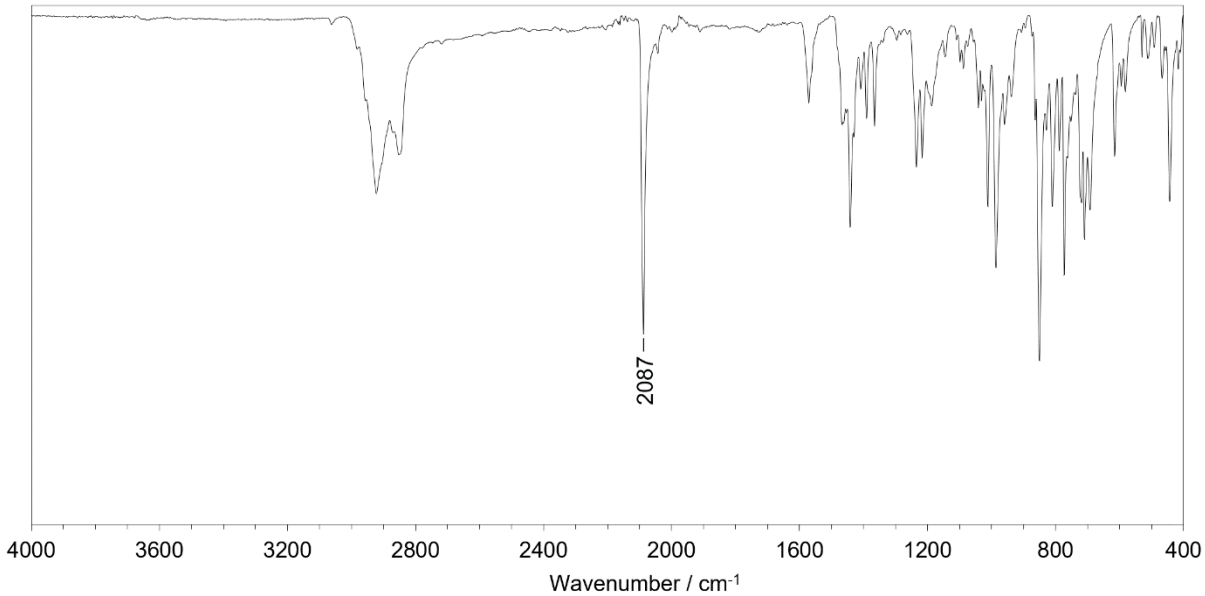


Figure S121. IR spectrum of **15b** (toluene).

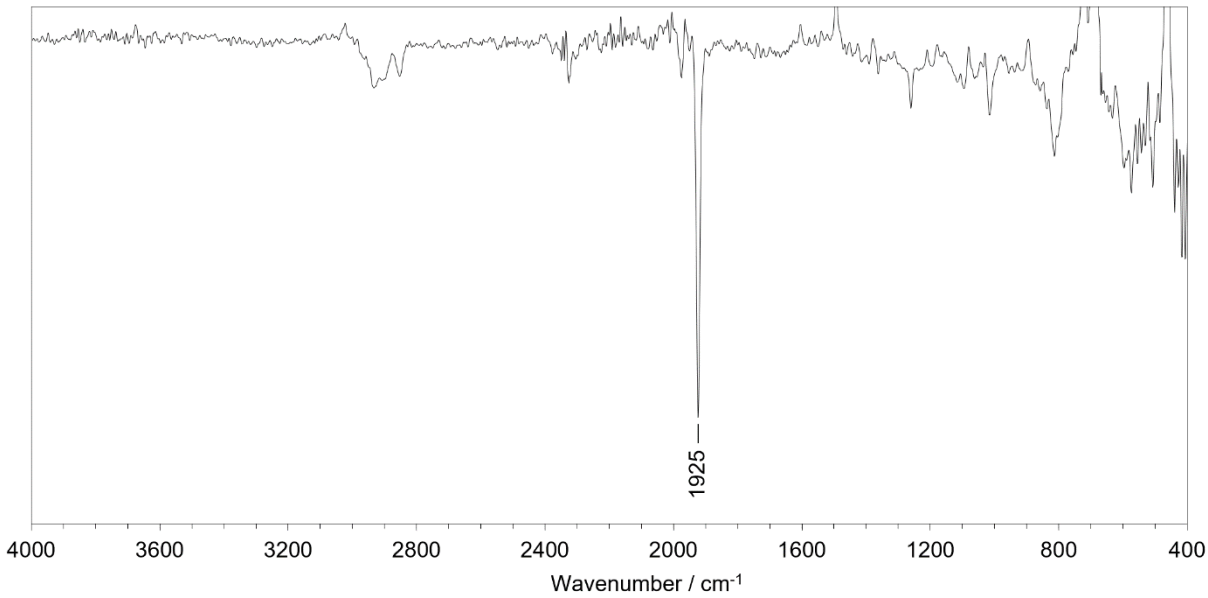


Figure S122. IR spectrum of **18a** (toluene).

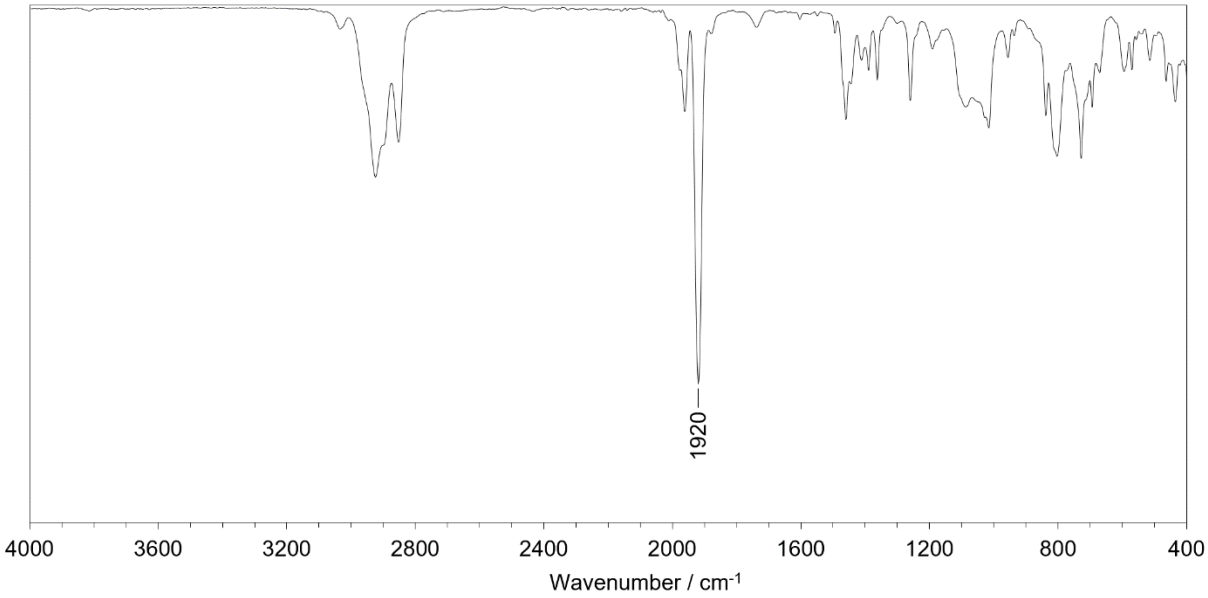


Figure S123. IR spectrum of **18a** (toluene).

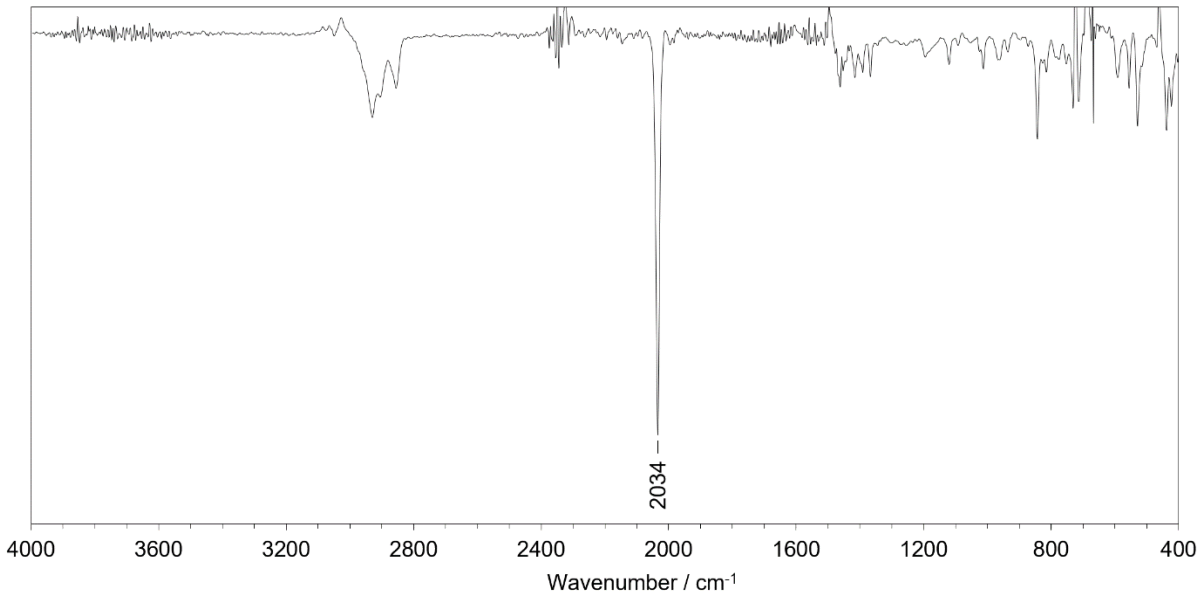


Figure S124. IR spectrum of **19a** (toluene).

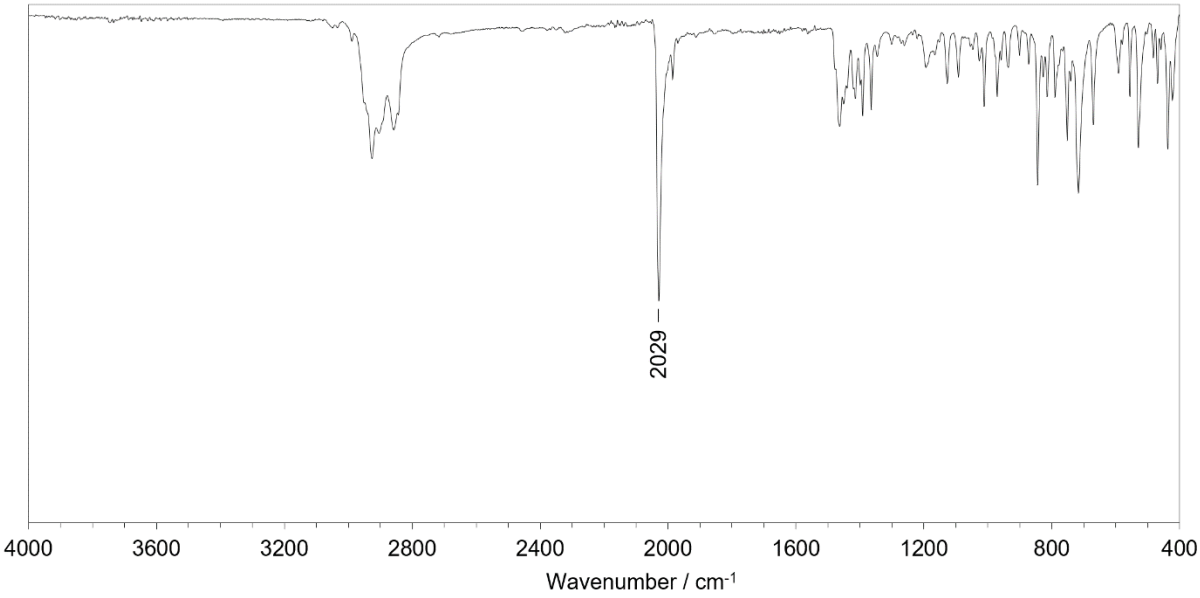


Figure S125. IR spectrum of **19a** (ATR).

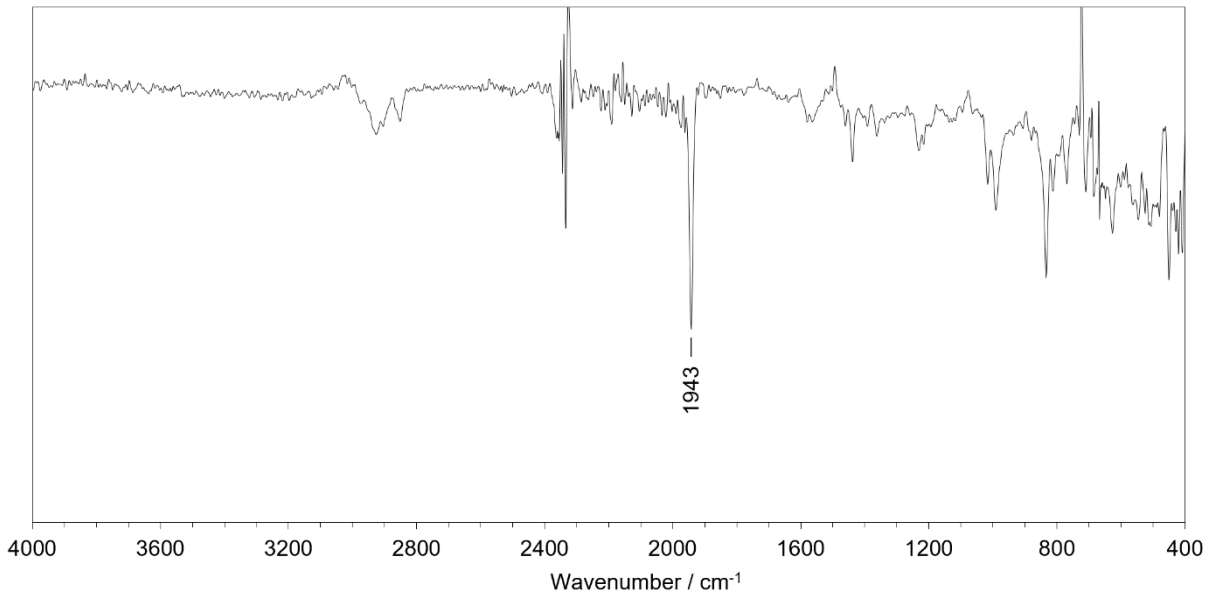


Figure S126. IR spectrum of **18b** (toluene).

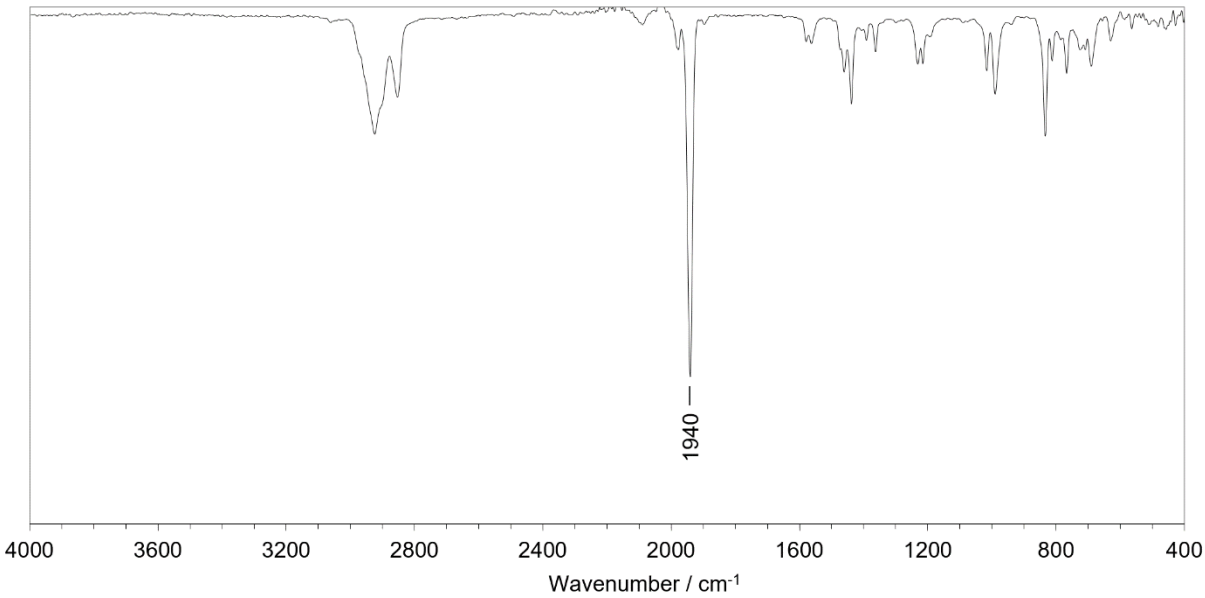


Figure S127. IR spectrum of **18b** (ATR).

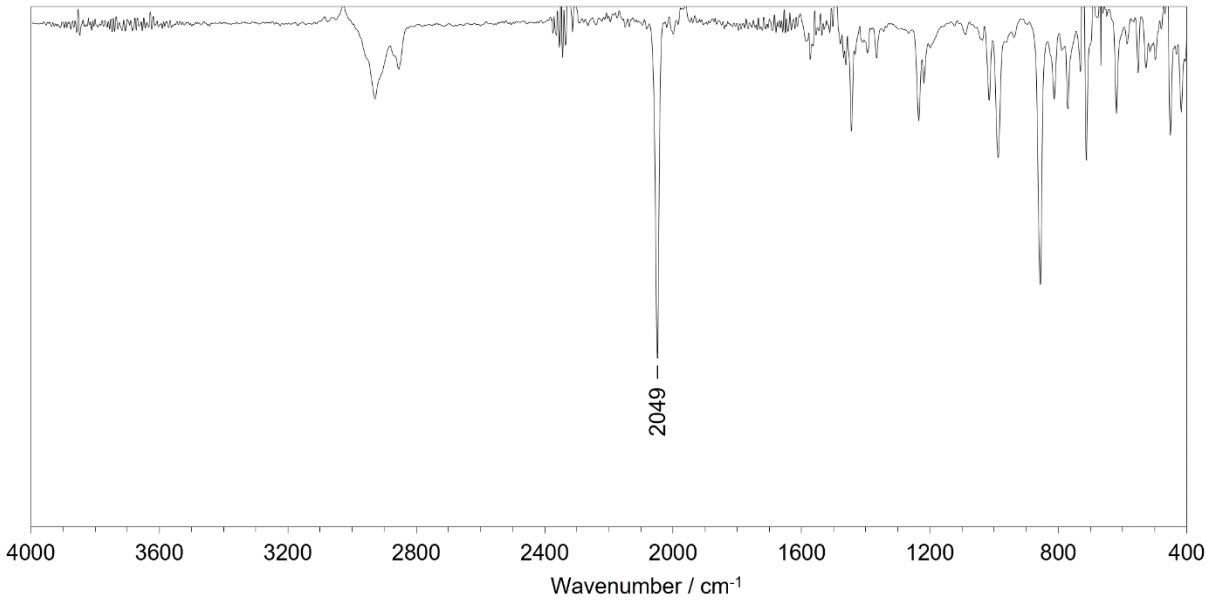


Figure S128. IR spectrum of **19b** (toluene).

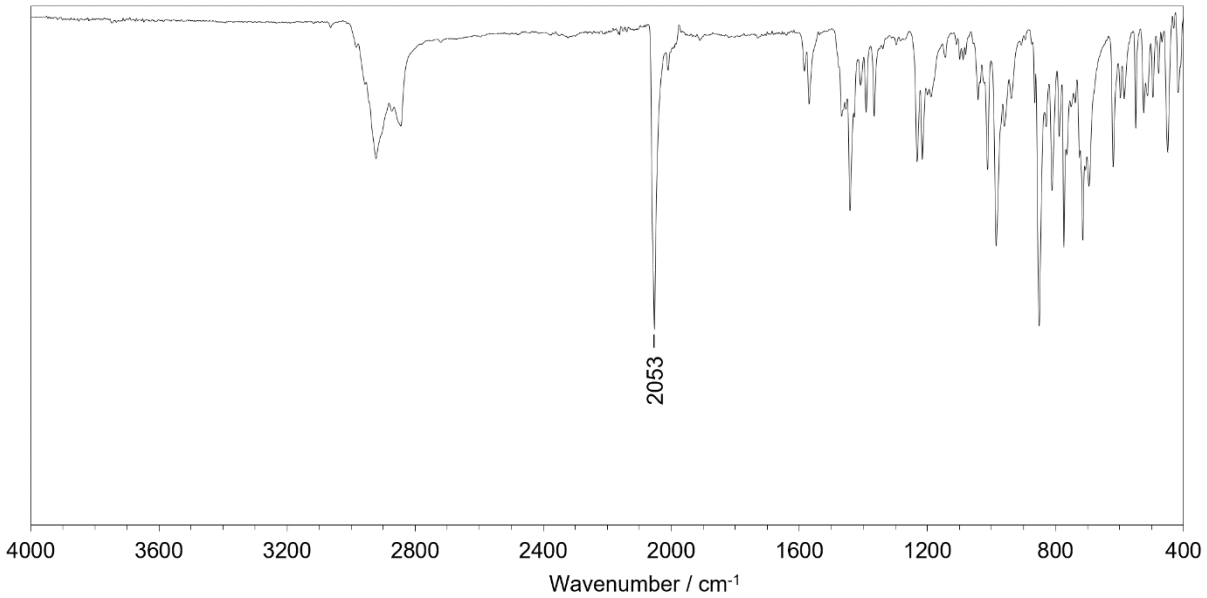


Figure S129. IR spectrum of **19b** (ATR).

3.3. Acyclic pincers

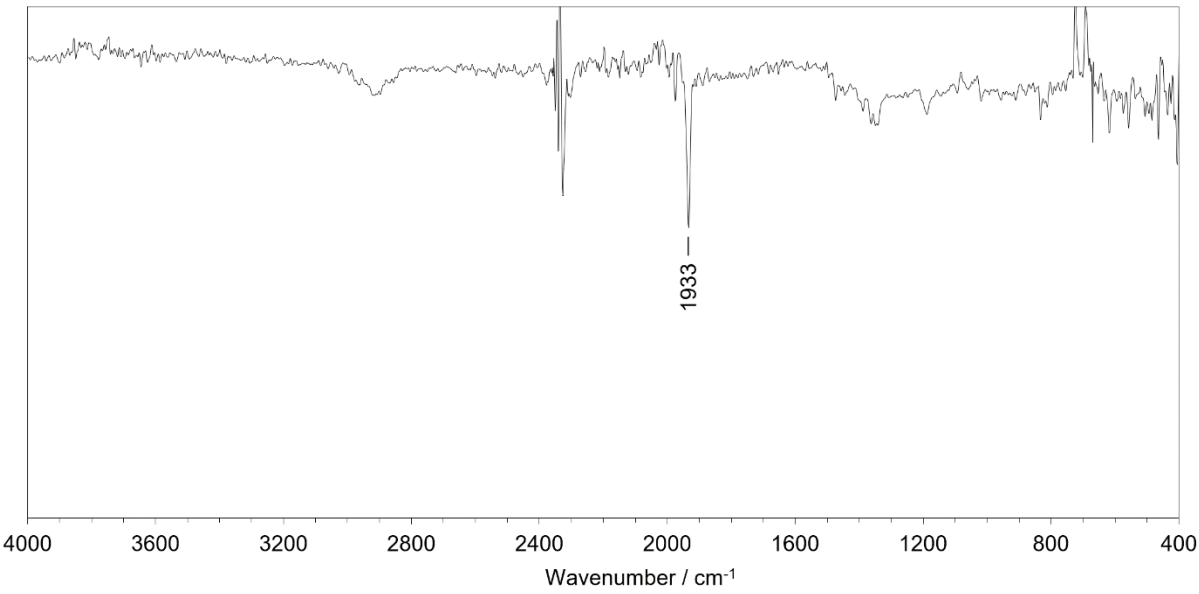


Figure S130. IR spectrum of [Rh(PCP-*t*Bu)(CO)] (toluene).

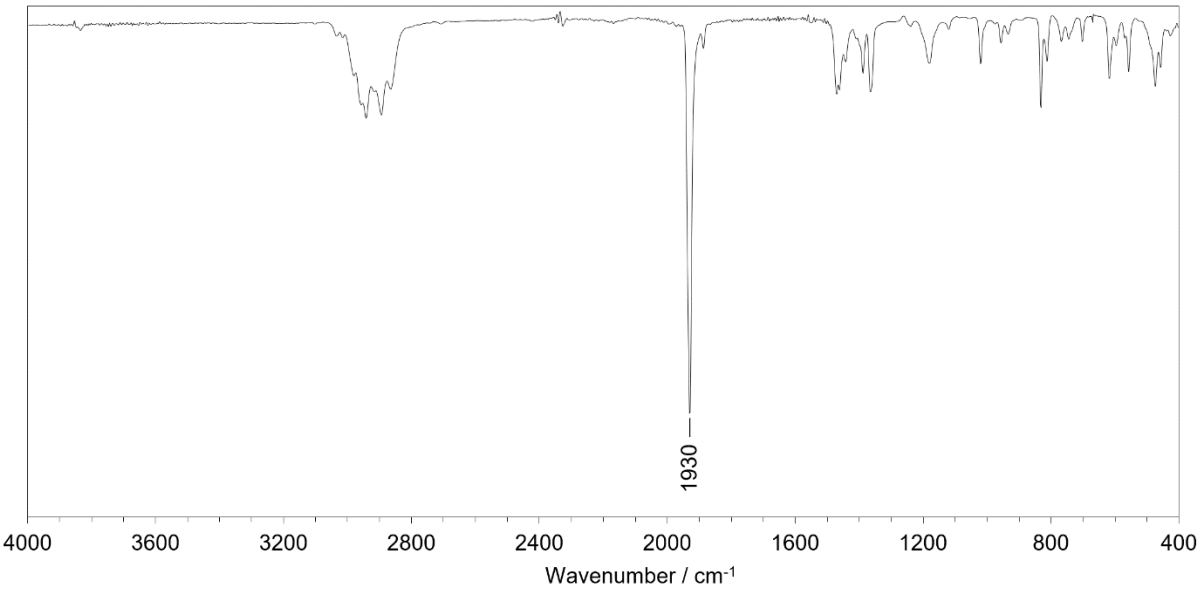


Figure S131. IR spectrum of [Rh(PCP-*t*Bu)(CO)] (ATR).

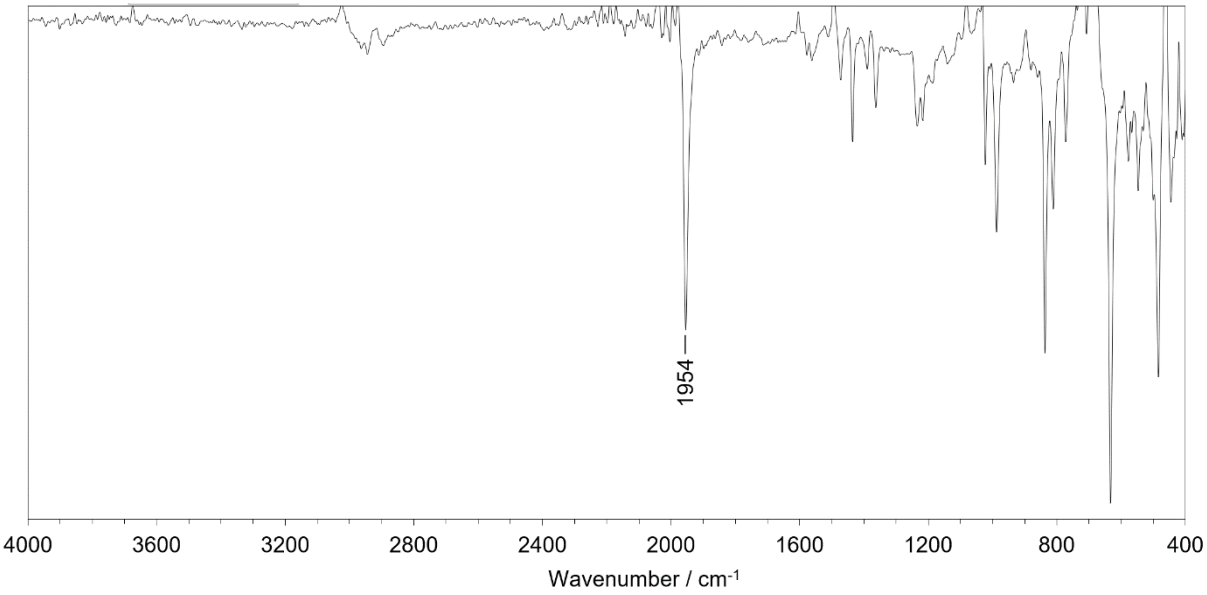


Figure S132. IR spectrum of [Rh(POCOP-*t*Bu)(CO)] (toluene).

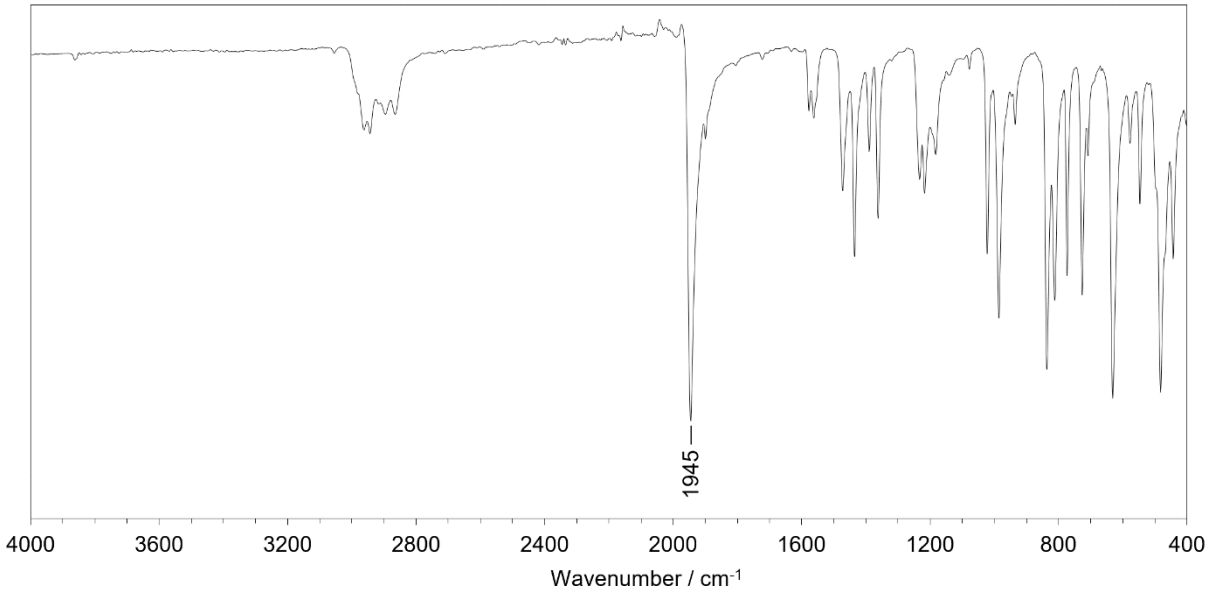


Figure S133. IR spectrum of [Rh(POCOP-*t*Bu)(CO)] (ATR).

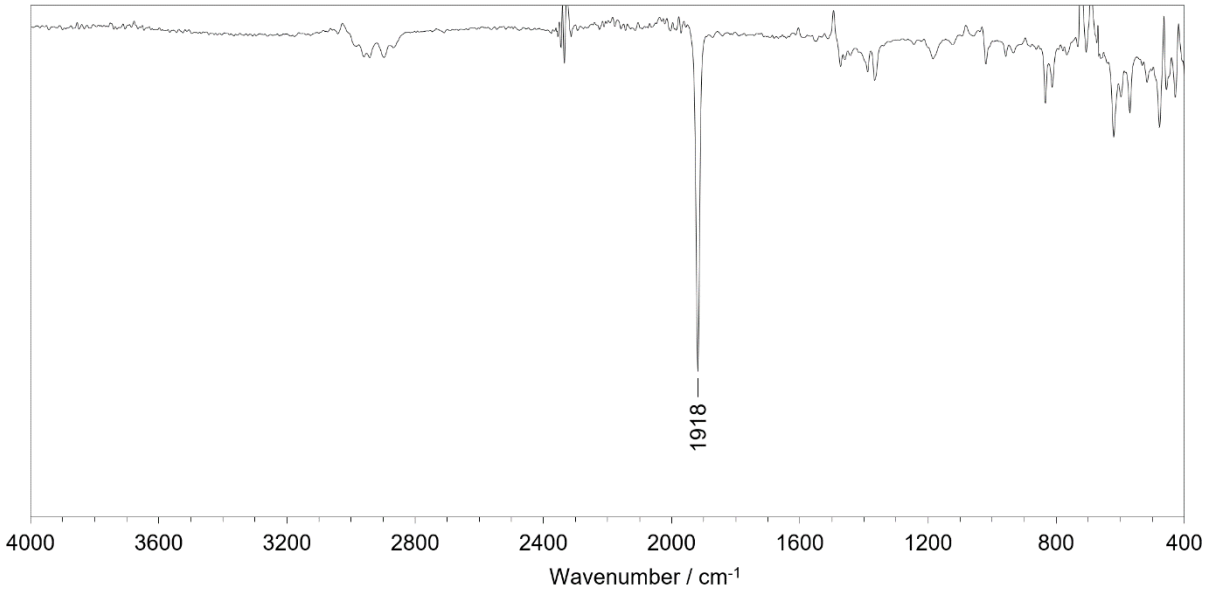


Figure S134. IR spectrum of [Ir(PCP-*t*Bu)(CO)] (toluene).

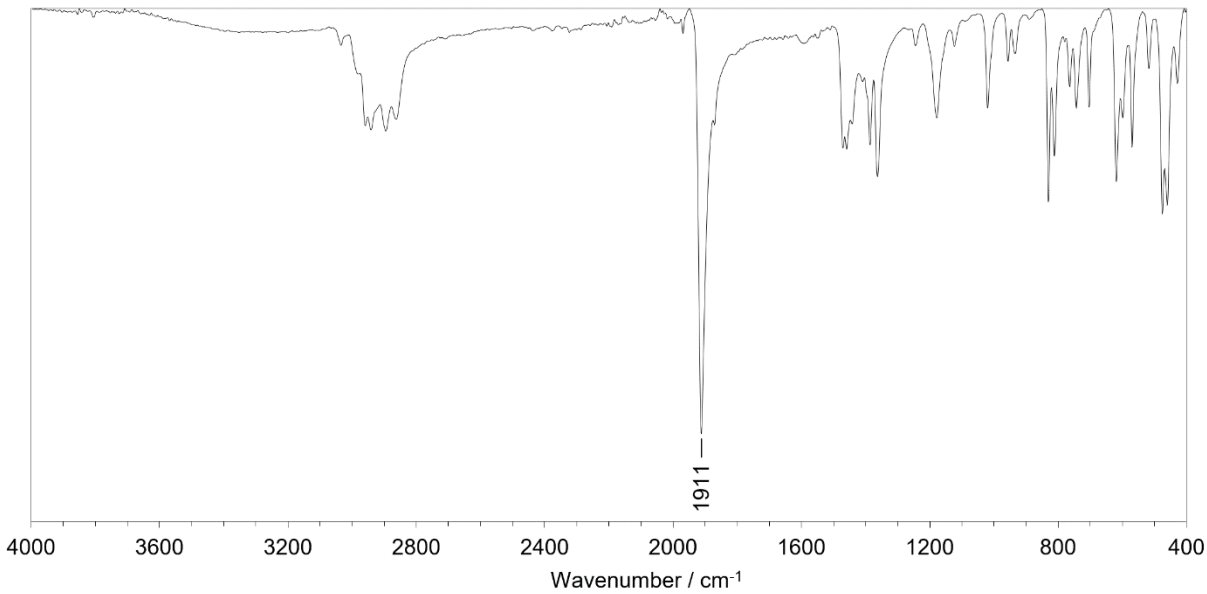


Figure S135. IR spectrum of [Ir(PCP-*t*Bu)(CO)] (ATR).

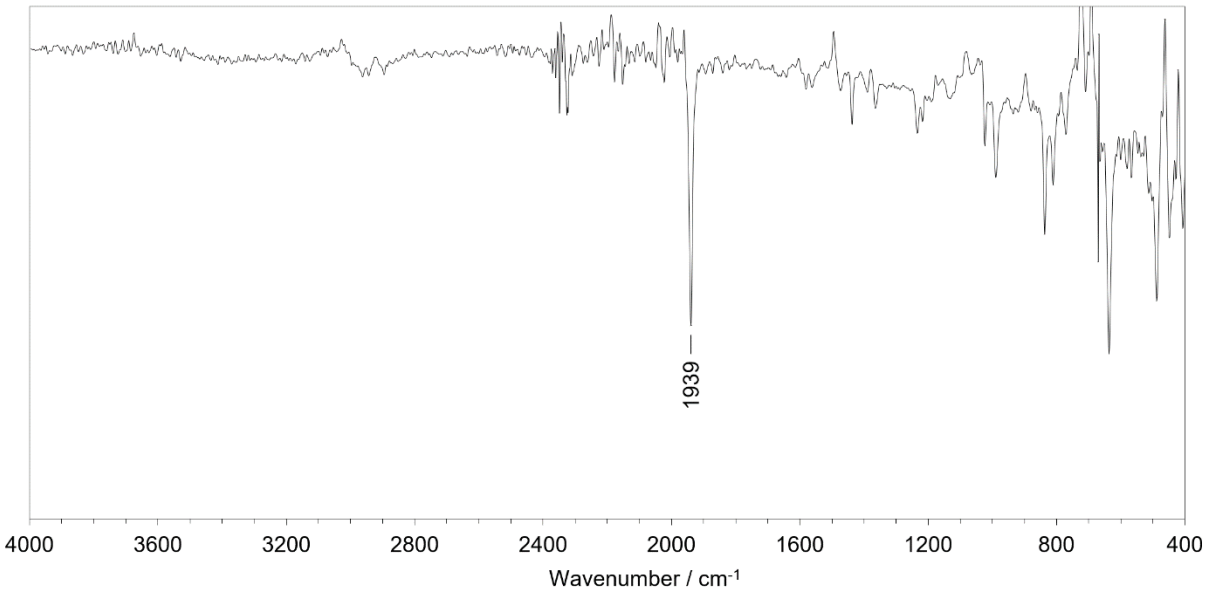


Figure S136. IR spectrum of [Ir(POCOP-*t*Bu)(CO)] (toluene).

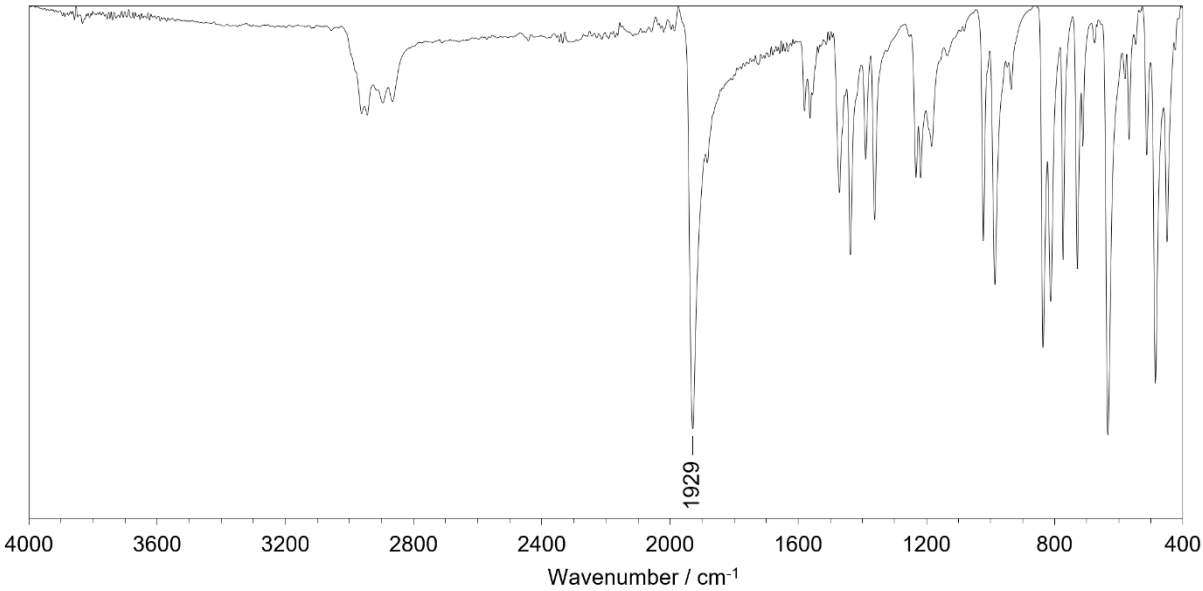


Figure S137. IR spectrum of [Ir(POCOP-*t*Bu)(CO)] (ATR).