

## Supporting Information

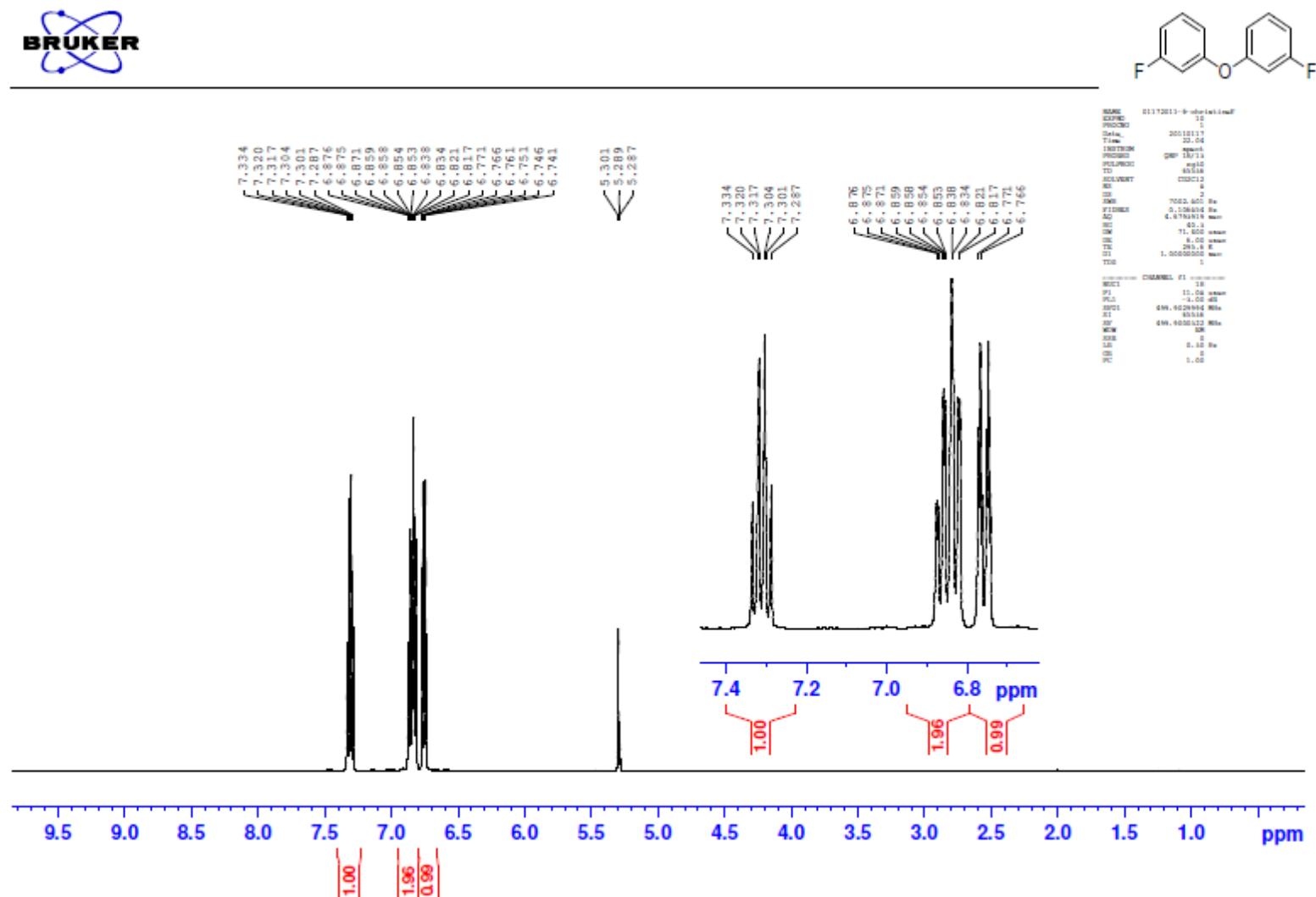
### Chiral Wide Bite Angle Diphosphine Ligands: Synthesis, Coordination Chemistry and Application in Pd-catalyzed Allylic Alkylation

Christine F. Czauderna,<sup>a,†</sup> Amanda G. Jarvis,<sup>a</sup> Frank J. L. Heutz,<sup>a</sup> David B. Cordes,<sup>a</sup> Alexandra M. Z. Slawin,<sup>a</sup> Jarl Ivar van der Vlugt,<sup>b</sup> Paul C. J. Kamer<sup>a\*</sup>

[a] EaSTCHEM, School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, United Kingdom E-mail: [pcjk@st-andrews.ac.uk](mailto:pcjk@st-andrews.ac.uk)

[b] van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands

## 1- Compound 11F



**Figure S1**  $^1\text{H}$  NMR spectrum of compound 11F (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



CC5077

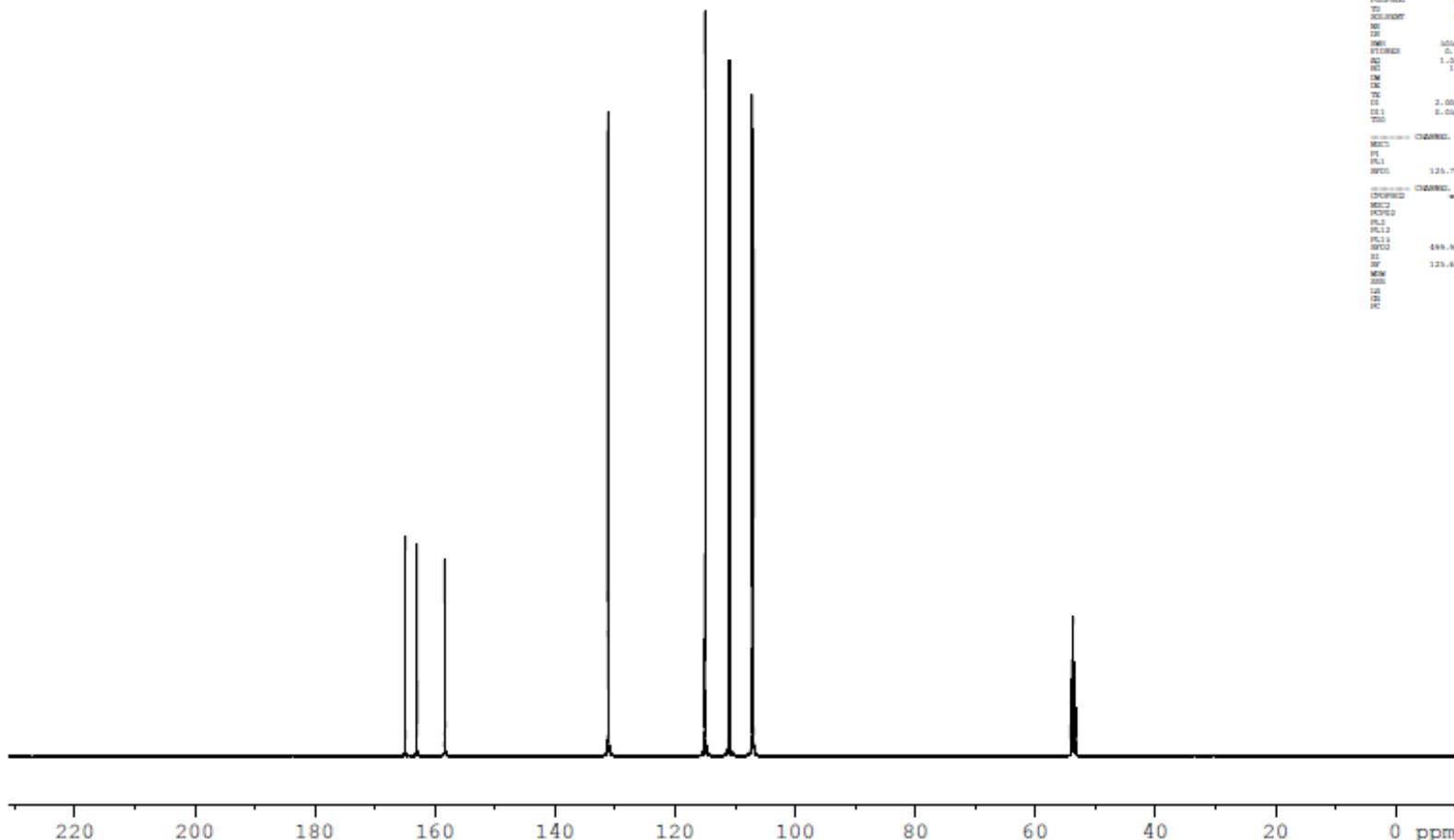
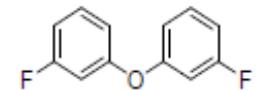


Figure S2 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound 11F (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)



CC5077

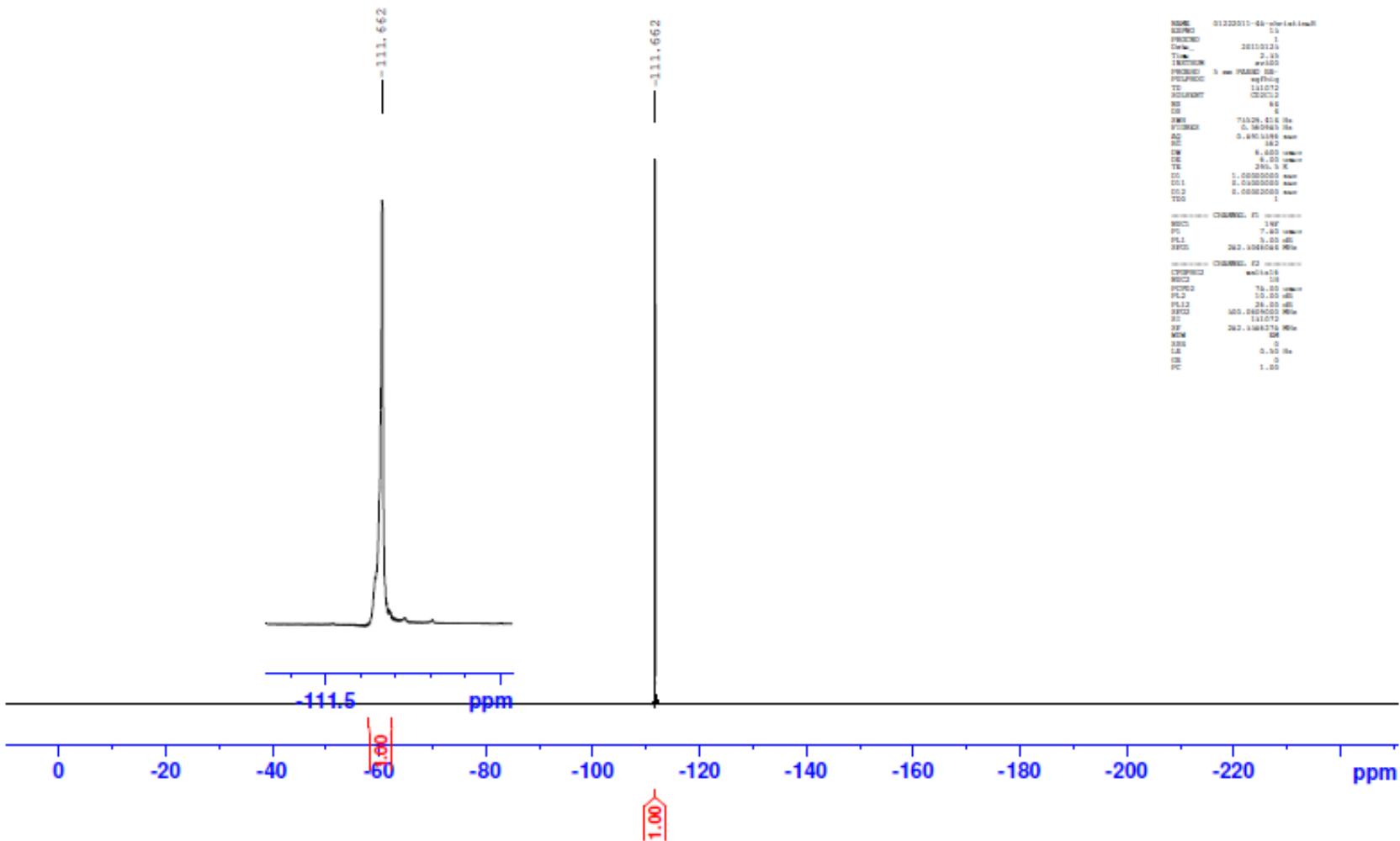
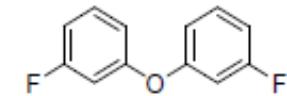
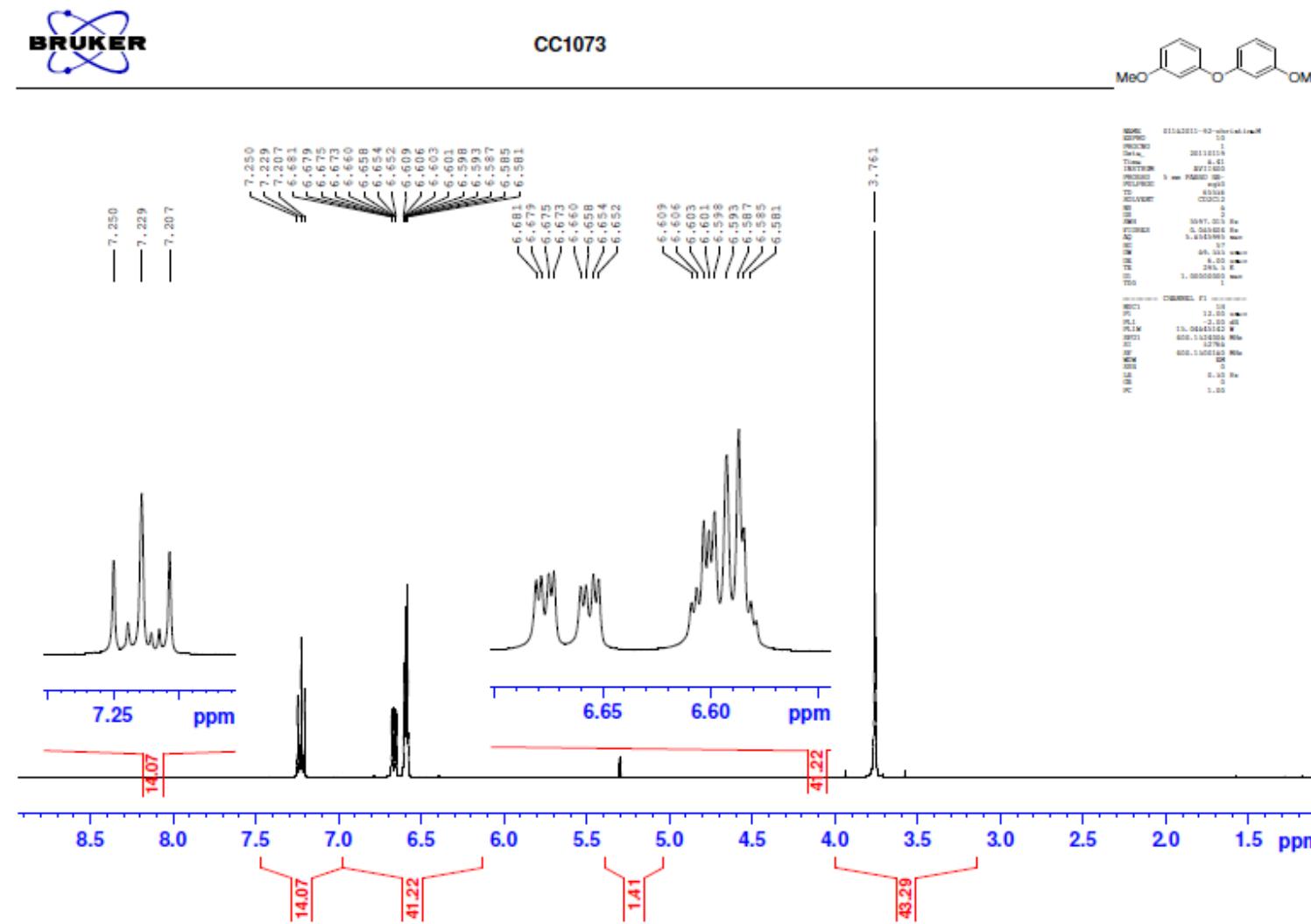


Figure S3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of compound 11F (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)

## 2- Compound 11OMe



**Figure S4**  $^1\text{H}$  NMR spectrum of compound 11OMe (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)



CC1073

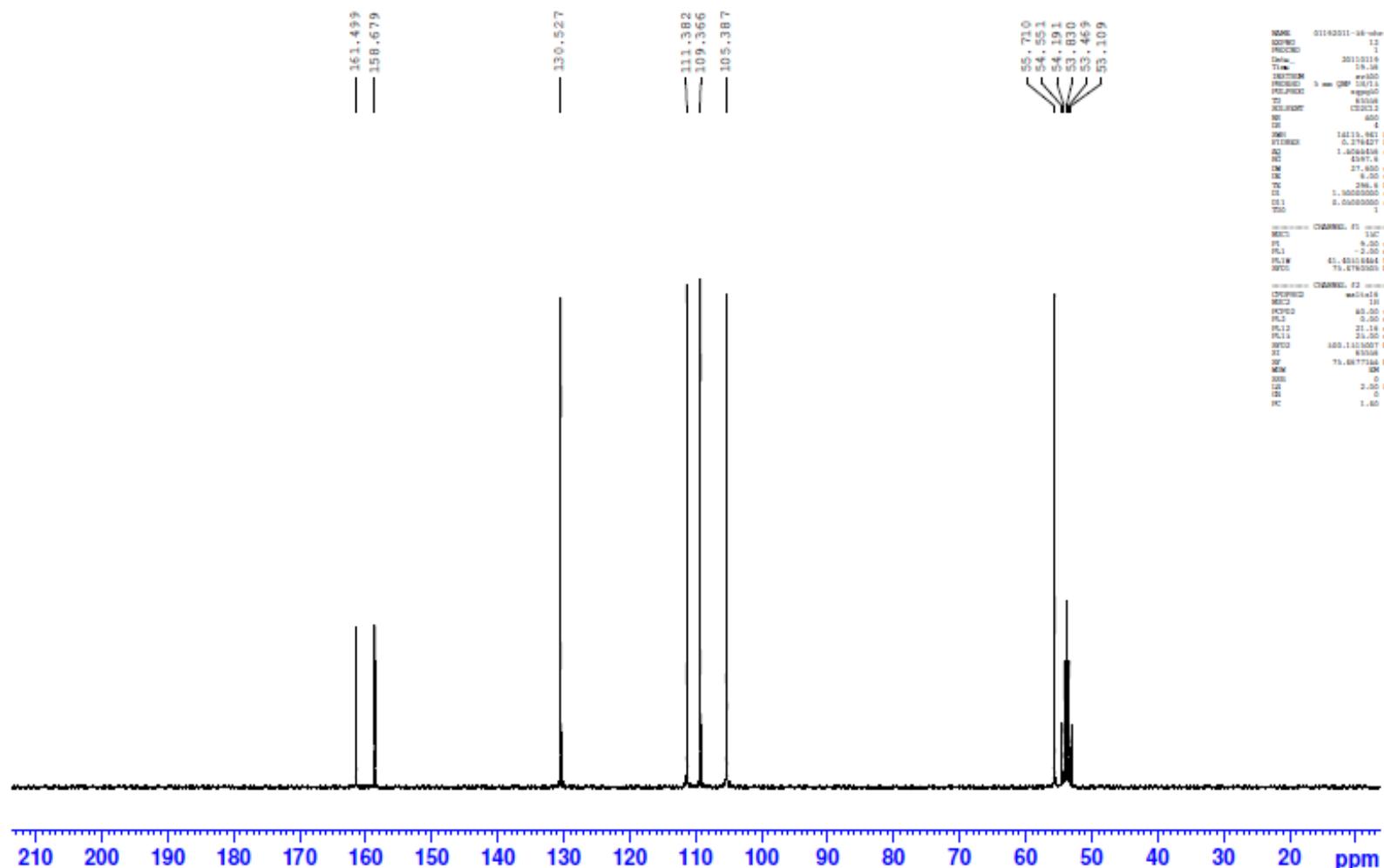
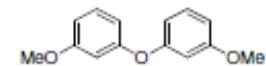


Figure S5  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 11OMe (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)



CC1073

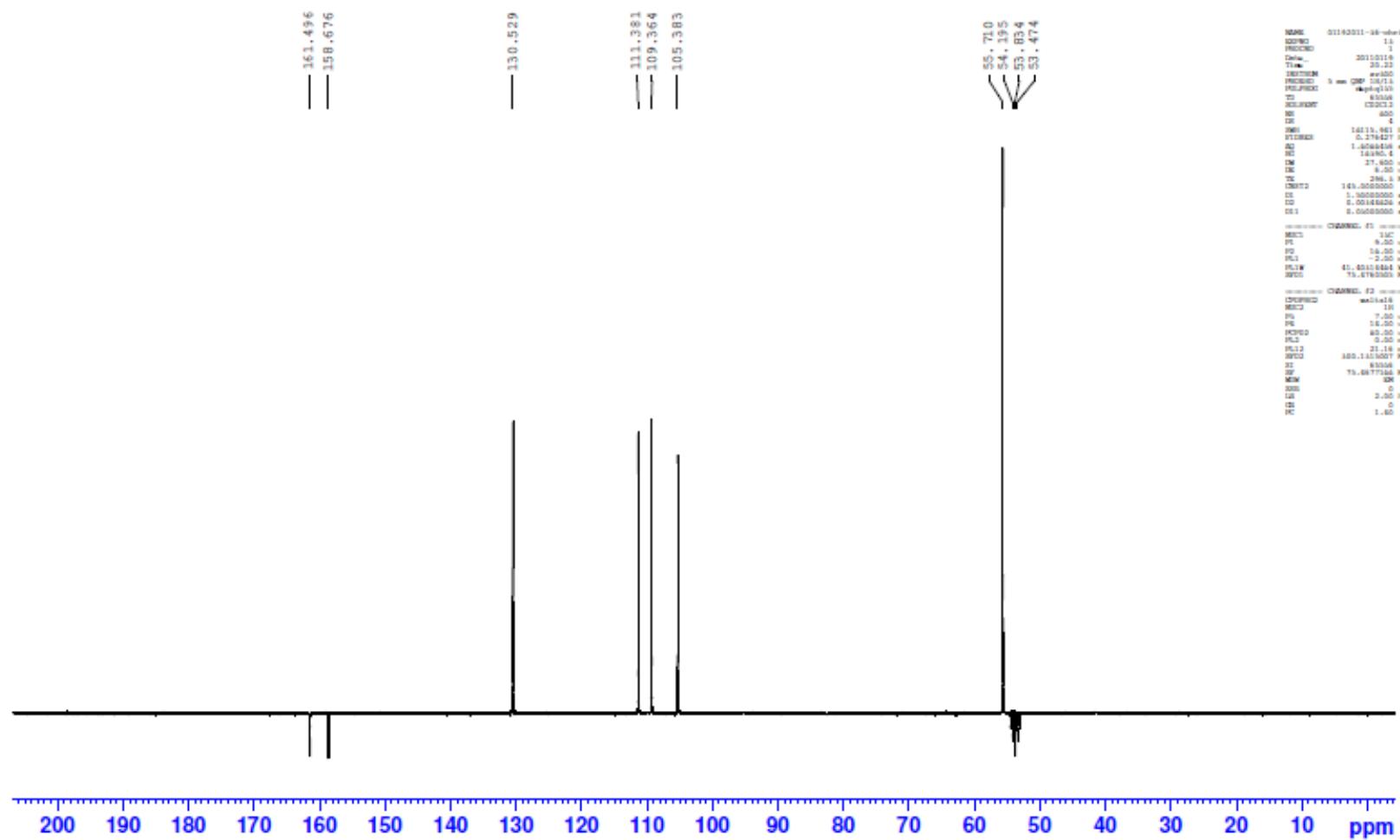
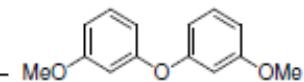


Figure S6 <sup>13</sup>C APT NMR spectrum of compound 11OMe (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)

3- Compound 12

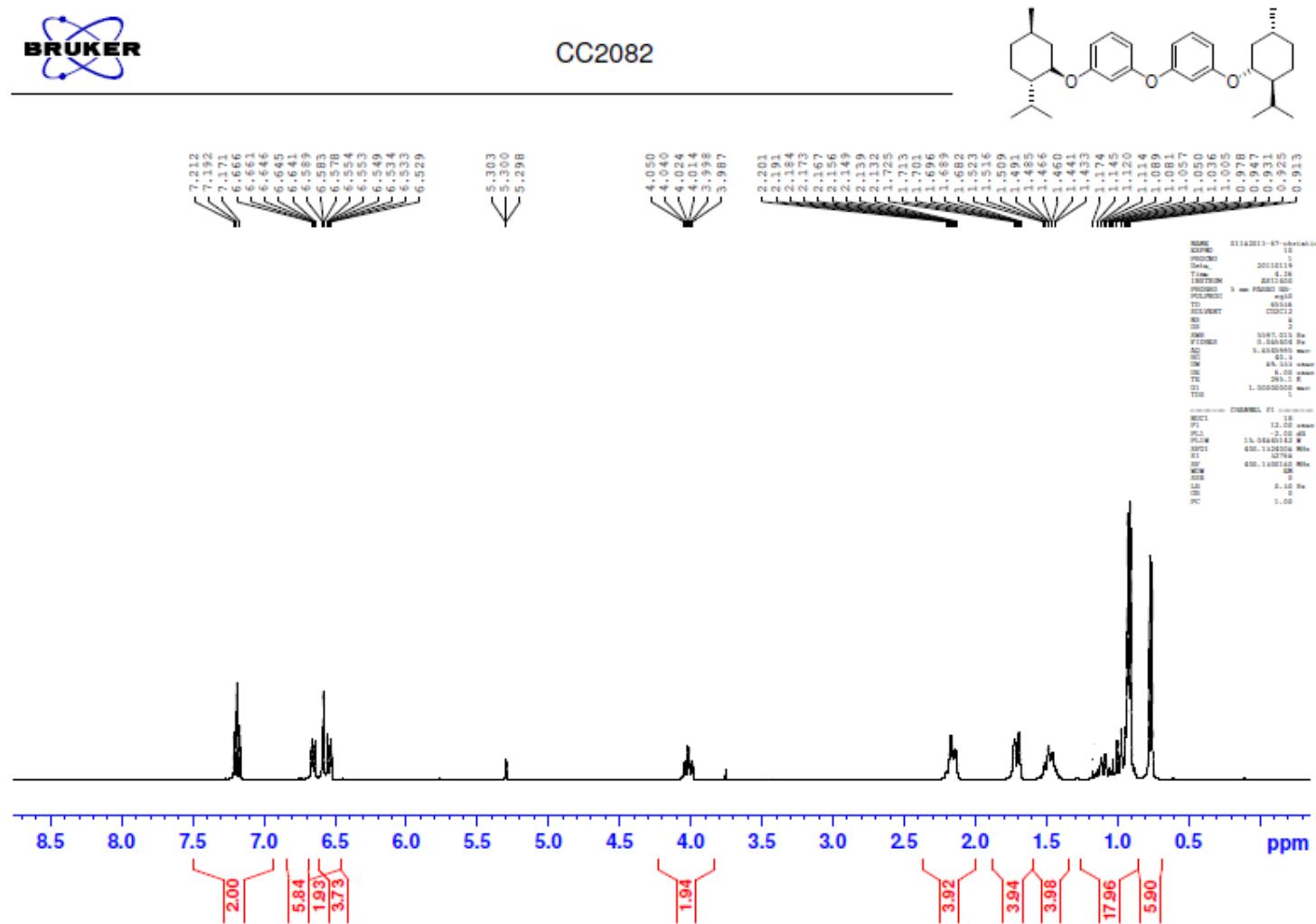
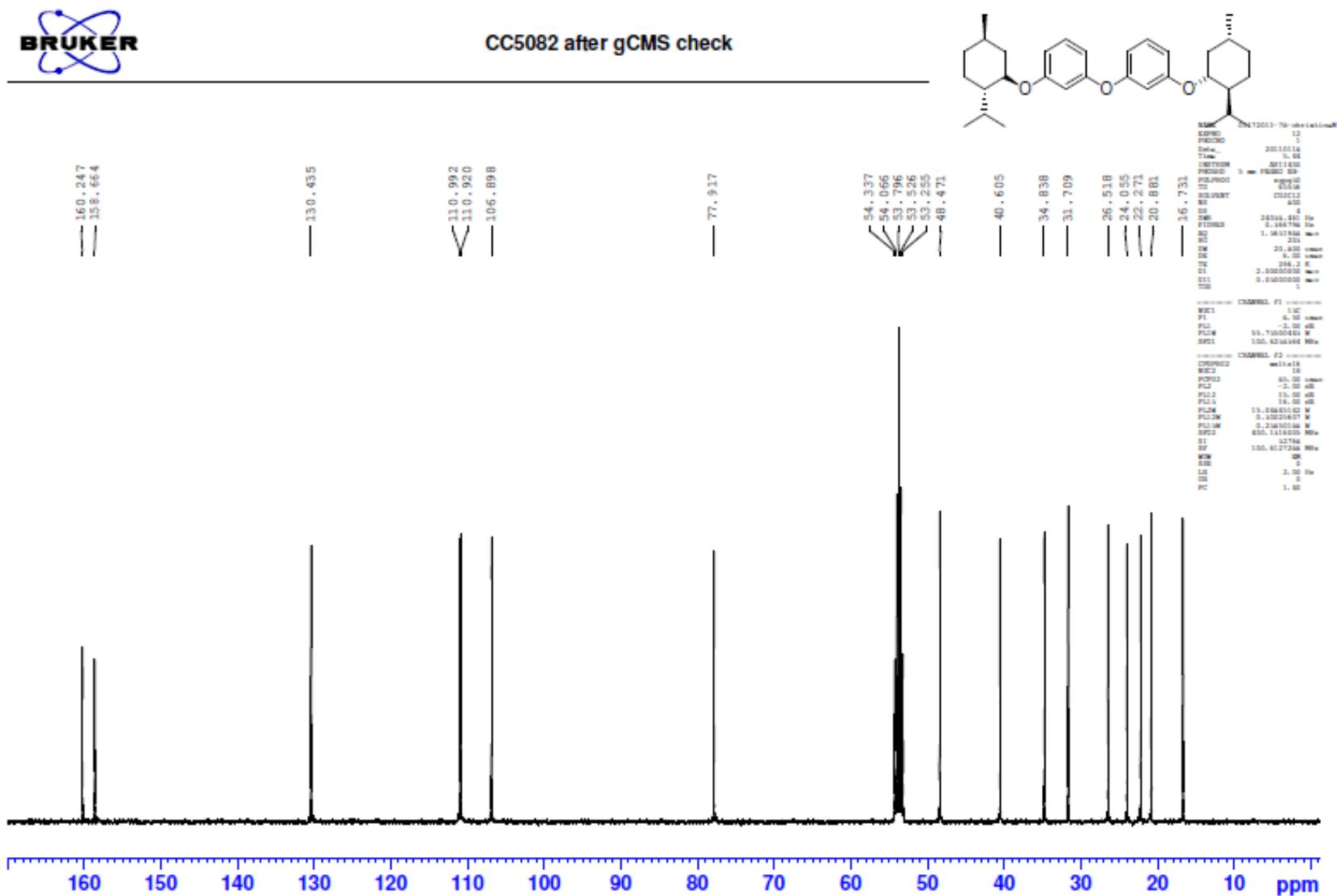
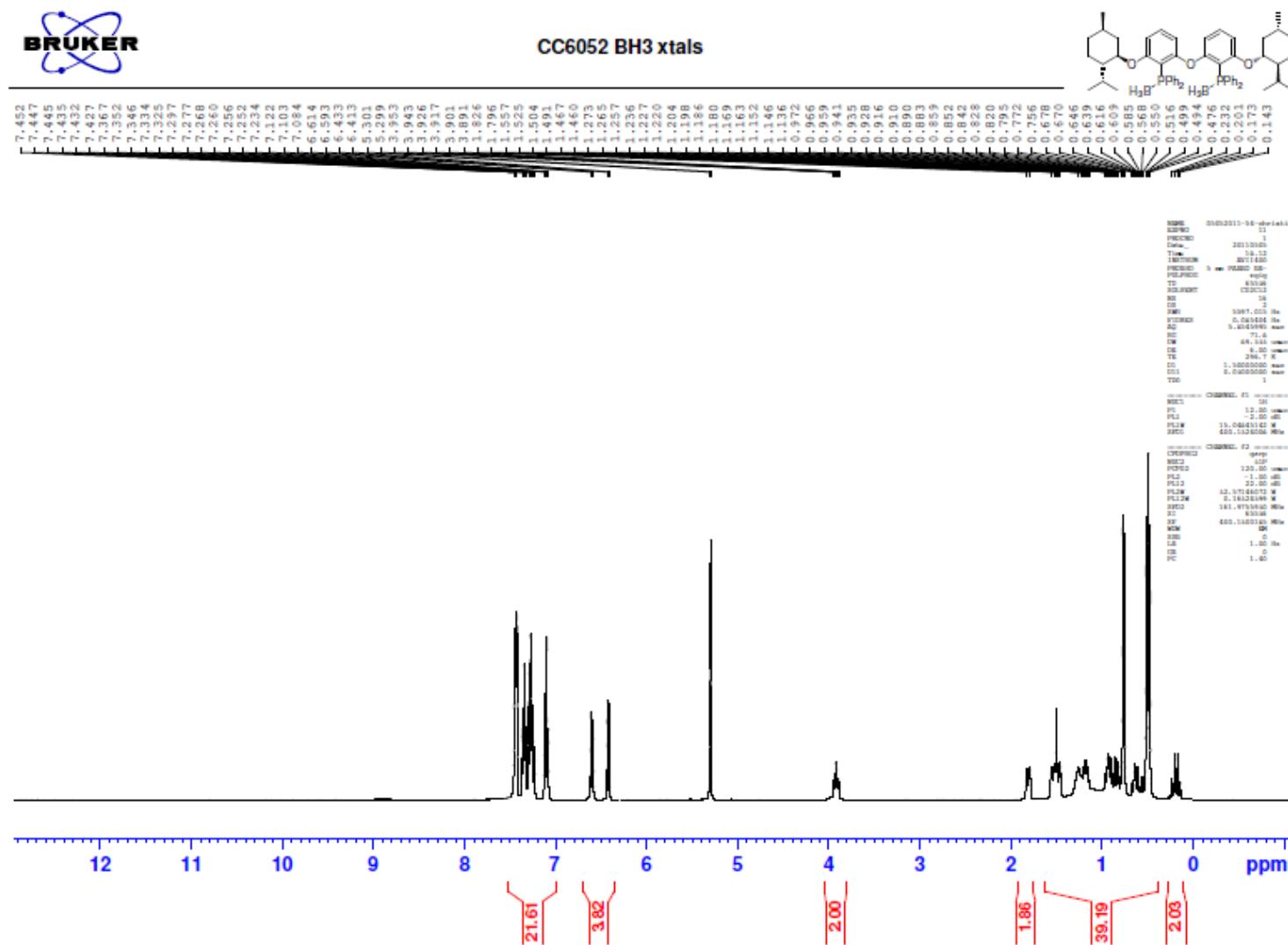


Figure S7 <sup>1</sup>H NMR spectrum of compound 12 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)



**Figure S8**  $^{13}\text{C}\{\text{H}\}$  NMR spectrum of compound **12** (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)

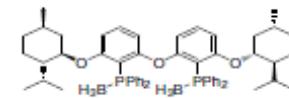
## 4- Compound 13



**Figure S9**  $^1\text{H}$  NMR spectrum of compound **13** (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



## CC6052 BH3 xtals

CC6052-13-*obtained*.cdx

NAME: CC6052-13-*obtained*  
EXPTIME: 10  
PROBODIA: 1  
DATE: 20210810  
TIME: 13:42:55  
INSTRUM: ASX100  
PROGNAME: 3  
PULPROG: 3  
TD: 65536  
SW: 10000  
SF: 24300.187 Hz  
FIDRES: 2.0000000 Hz  
AQ: 1.0000000 s  
RG: 20.400  
DW: 1.00 us  
TE: 29.400 ms  
TM: 1.00 ms  
C1NUC1: 141.000000000 Hz  
C1NUC2: 131.000000000 Hz  
C1NUC3: 121.000000000 Hz  
C1NUC4: 111.000000000 Hz  
C1NUC5: 101.000000000 Hz  
C1NUC6: 91.000000000 Hz  
C1NUC7: 81.000000000 Hz  
C1NUC8: 71.000000000 Hz  
C1NUC9: 61.000000000 Hz  
C1NUC10: 51.000000000 Hz  
C1NUC11: 41.000000000 Hz  
C1NUC12: 31.000000000 Hz  
C1NUC13: 21.000000000 Hz  
C1NUC14: 11.000000000 Hz  
C1NUC15: 1.0000000 Hz

TSP: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

DPPM: 1.0000000 s

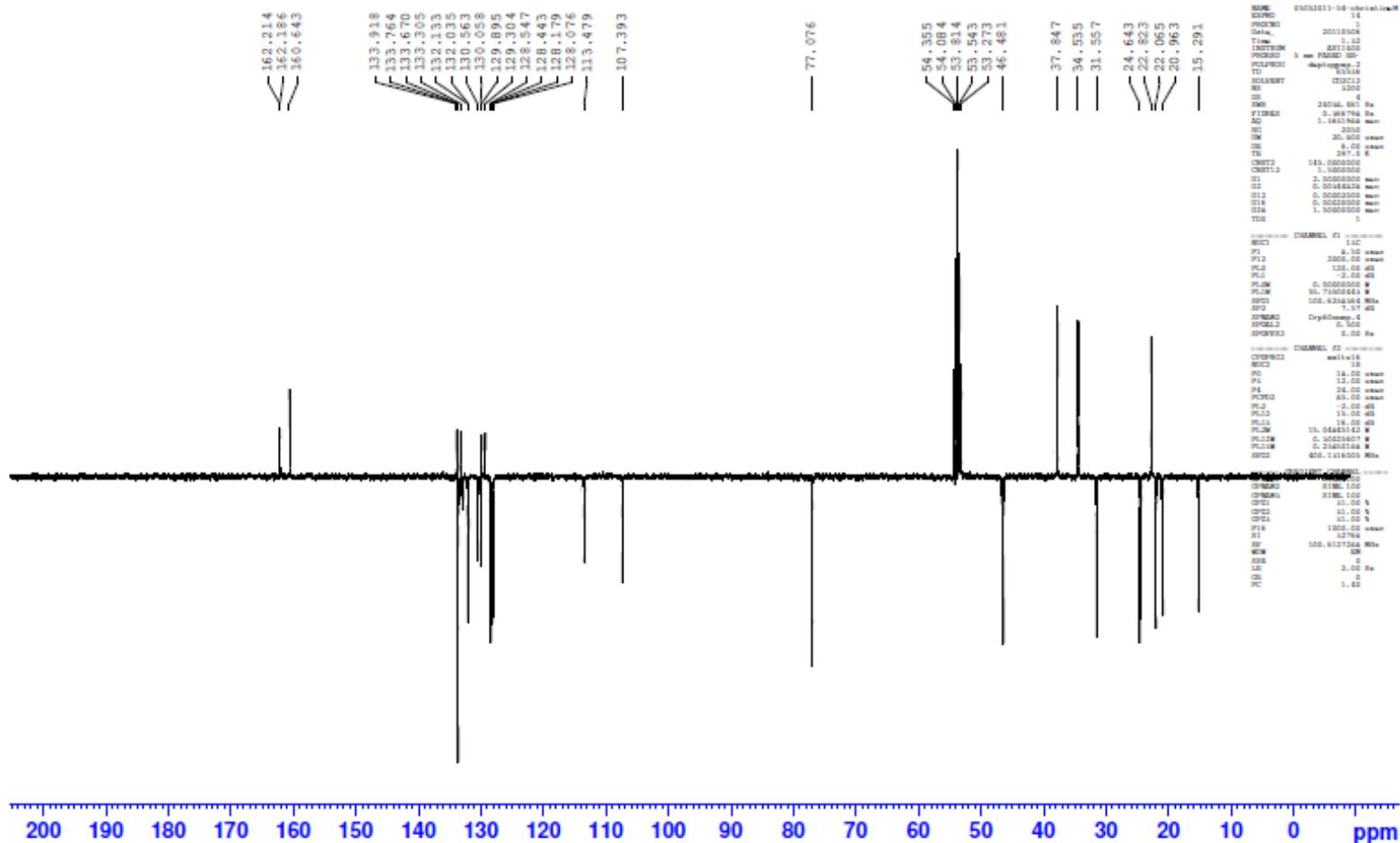
DPPH: 1.0000000 s

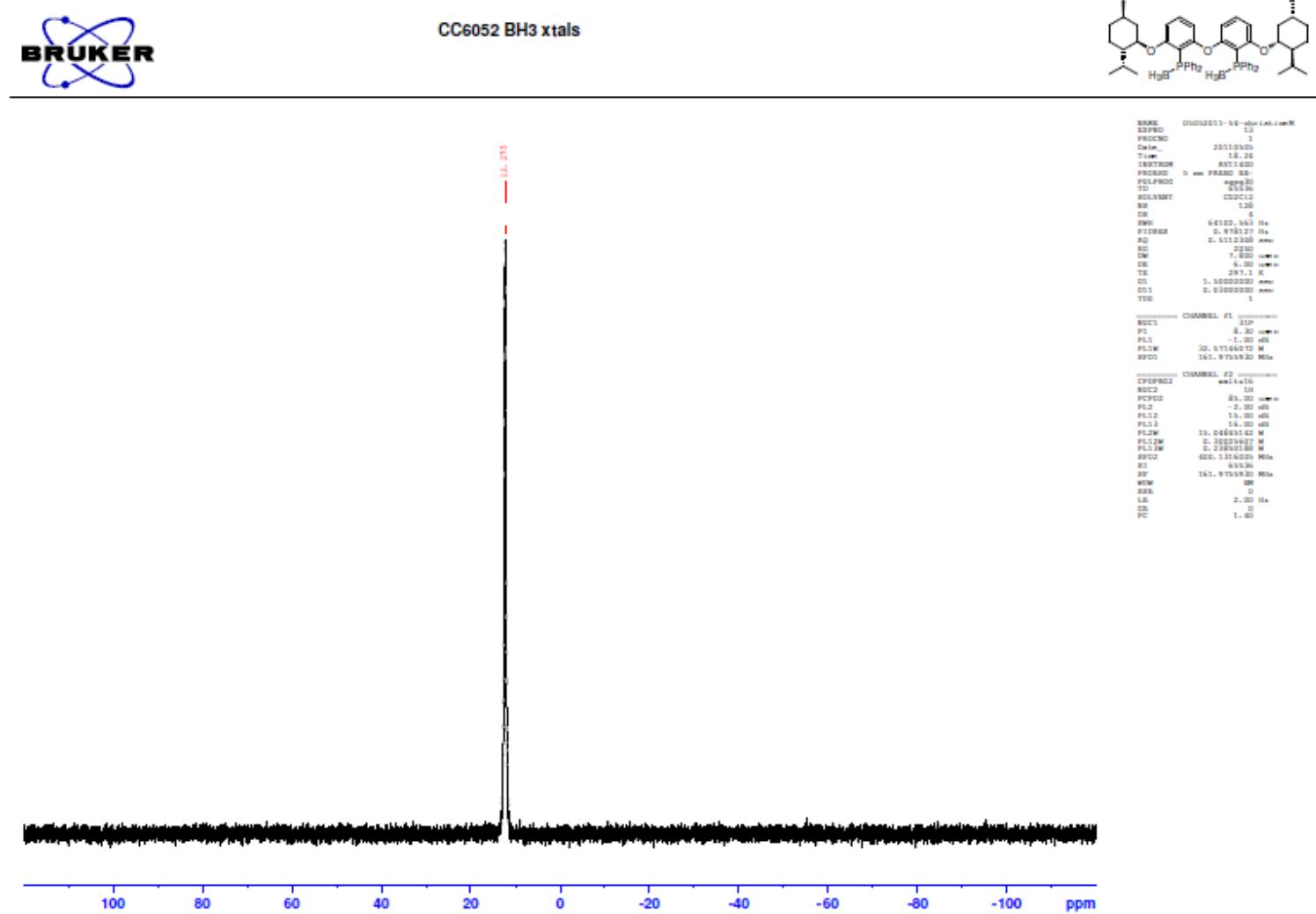
DPPG: 1.0000000 s

DPPM: 1.0000000 s

DPPH: 1.0000000 s

DPPG: 1.0000000 s

Figure S10    <sup>13</sup>C APT NMR spectrum of compound 13 (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)



**Figure S11**  $^{31}\text{P}^{\{1\}\text{H}}$  NMR spectrum of compound **13** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)

5- Compound 14

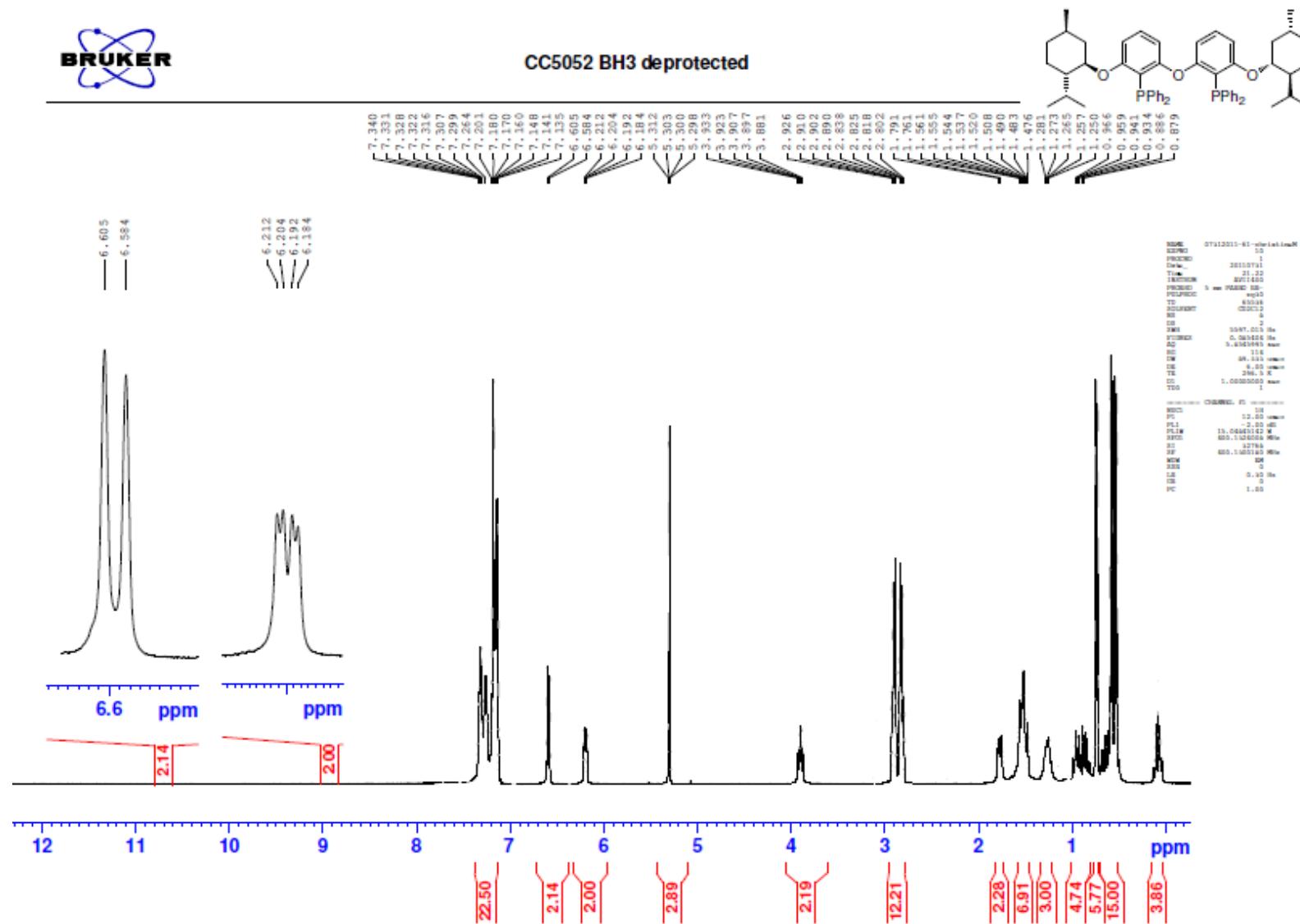
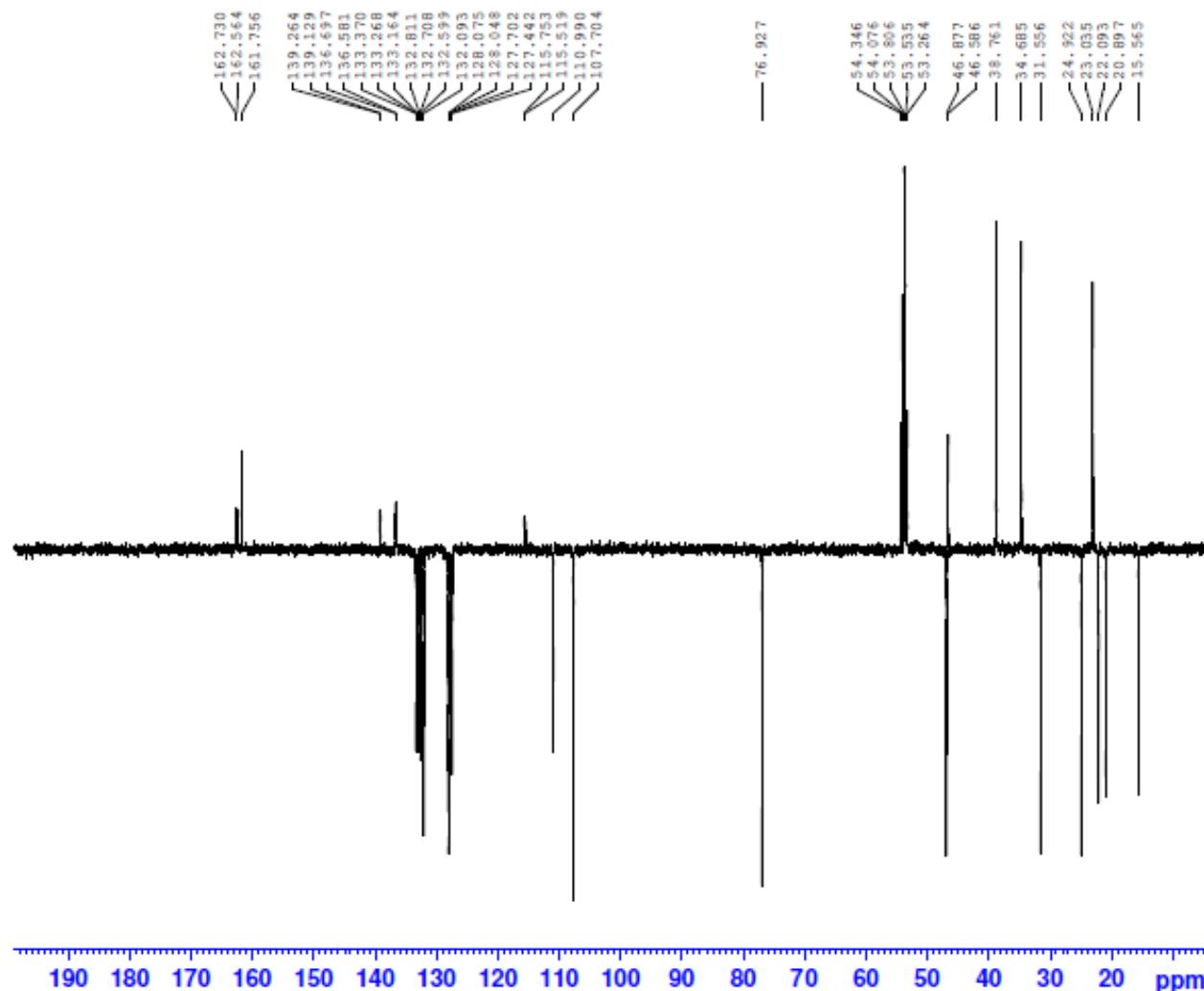
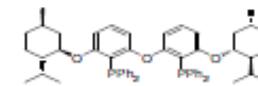


Figure S12  $^1\text{H}$  NMR spectrum of compound 14 (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



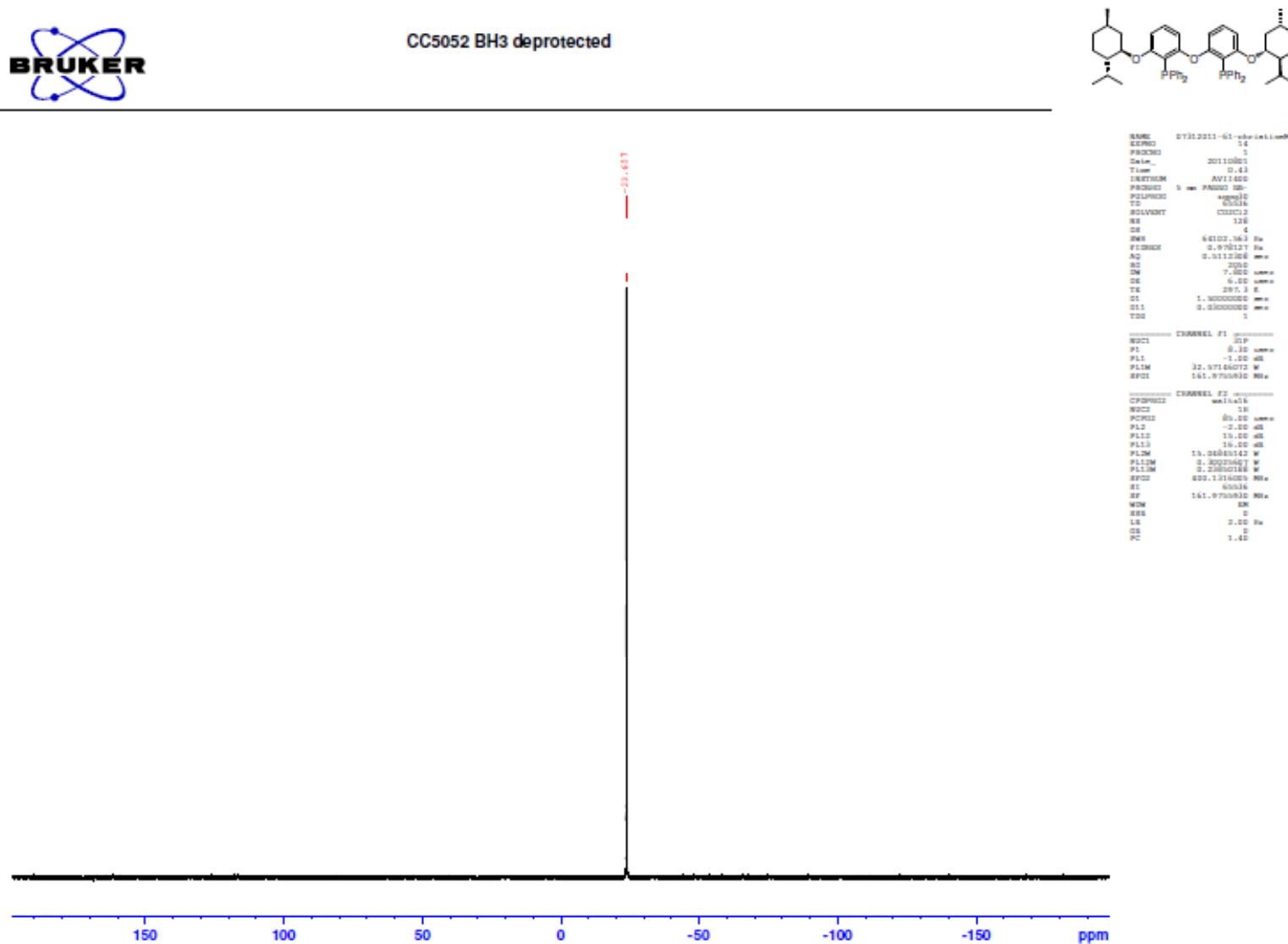
## CC5052 BH3 deprotected



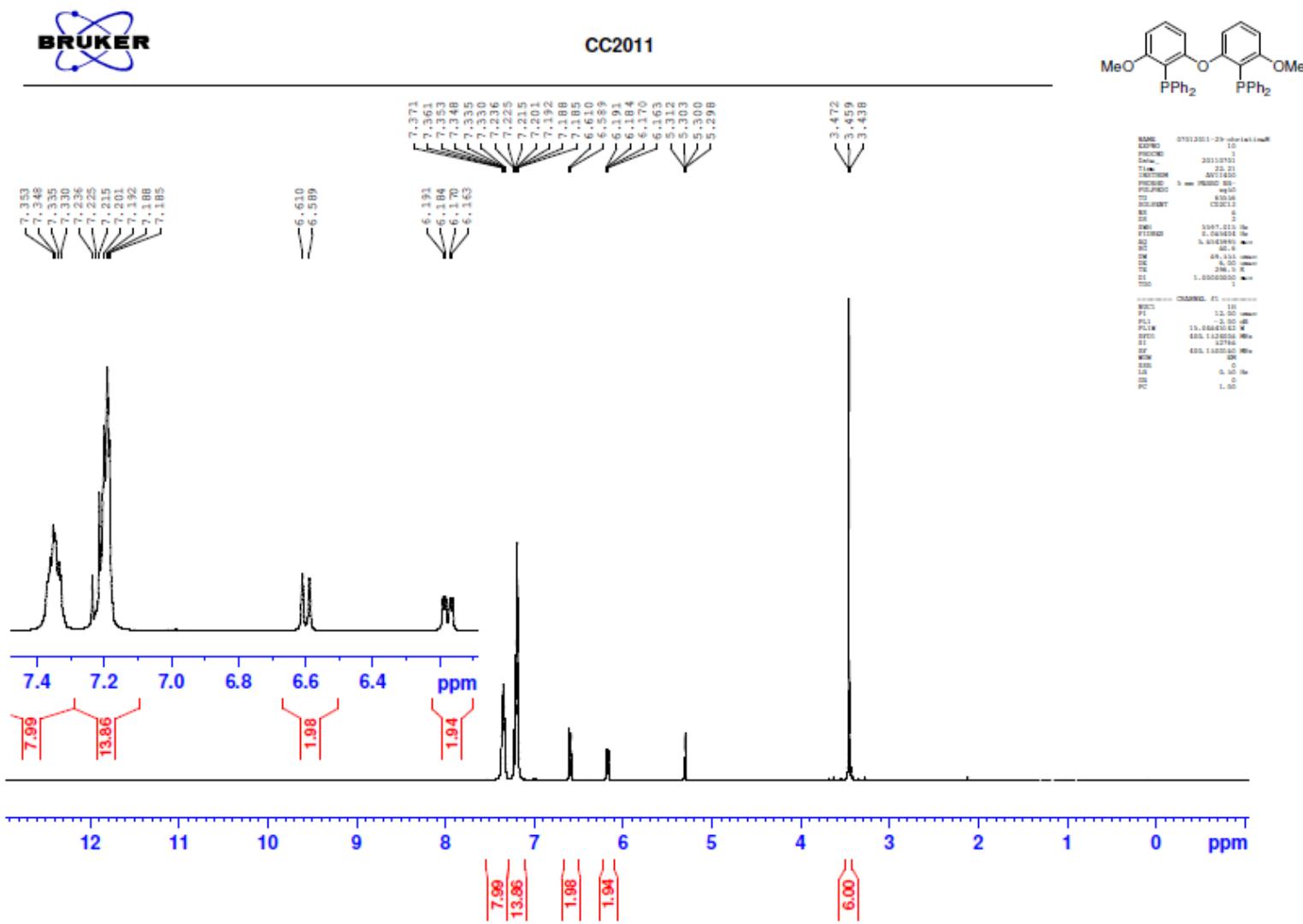
NAME: 27132013-62-chemical-14  
KIDNO: 12  
PROBOD: 1  
Date: 20130401  
Time: 0.10  
INSTRUM: ASX1400  
PULPROG: 3 <sup>13</sup>C DEPT135  
POLPROG: DEPHSFGPP,3  
TD: 65536  
SWEVENT: 65536  
NS: 1200  
DS: 20000, 100, Re  
P1: 8.00, 7.00, Re  
AQ: 1.161764, 0.000000  
SW1: 20,400, 0.000000  
DW: 6.00, 0.000000  
TE: 24.00, 0.000000  
CR1T2: 143, 0.000000  
CR1T2: 1, 0.000000  
SI1: 2, 0.000000  
SI2: 0.00044324, 0.000000  
SI3: 0.00052000, 0.000000  
SI4: 0.00020000, 0.000000  
SI5: 1, 0.00020000, 0.000000  
TDS: CHANNEL F1: 13C  
SI1: 8.00, 0.000000  
P1: 2000, 0.000000  
PL1: 130, 0.00, 0.00  
PL2: -1.00, 0.00, 0.00  
PL3W: 0, 0.000000, W  
PL4W: 30, 74350.644, W  
SP1C1: 100, 0.000000, W  
SP1C2: 100, 0.000000, W  
SP2C1: 0.000000, 0.000000  
SP2C2: 0.000000, 0.000000  
SP3C1: 0.000000, 0.000000  
SP3C2: 0.000000, 0.000000  
CHANNEL F2: 1H  
SI1: 18, 0.00, 0.00  
P1: 14.00, 0.000000  
PL1: 12, 0.00, 0.00  
PL2: 20, 0.00, 0.00  
PL3: 45, 0.00, 0.00  
PL4: -2, 0.00, 0.00  
PL5: 15, 0.00, 0.00  
PL6: 14, 0.00, 0.00  
PL7: 18, 0.000000, W  
PL8: 18, 0.000000, W  
PL9: 18, 0.000000, W  
PL10: 18, 0.000000, W  
PL11: 18, 0.000000, W  
PL12: 18, 0.000000, W  
PL13: 18, 0.000000, W  
PL14: 18, 0.000000, W  
PL15: 18, 0.000000, W  
PL16: 18, 0.000000, W  
PL17: 18, 0.000000, W  
PL18: 18, 0.000000, W  
PL19: 18, 0.000000, W  
PL20: 18, 0.000000, W  
PL21: 18, 0.000000, W  
PL22: 18, 0.000000, W  
PL23: 18, 0.000000, W  
PL24: 18, 0.000000, W  
PL25: 18, 0.000000, W  
PL26: 18, 0.000000, W  
PL27: 18, 0.000000, W  
PL28: 18, 0.000000, W  
PL29: 18, 0.000000, W  
PL30: 18, 0.000000, W  
PL31: 18, 0.000000, W  
PL32: 18, 0.000000, W  
PL33: 18, 0.000000, W  
PL34: 18, 0.000000, W  
PL35: 18, 0.000000, W  
PL36: 18, 0.000000, W  
PL37: 18, 0.000000, W  
PL38: 18, 0.000000, W  
PL39: 18, 0.000000, W  
PL40: 18, 0.000000, W  
PL41: 18, 0.000000, W  
PL42: 18, 0.000000, W  
PL43: 18, 0.000000, W  
PL44: 18, 0.000000, W  
PL45: 18, 0.000000, W  
PL46: 18, 0.000000, W  
PL47: 18, 0.000000, W  
PL48: 18, 0.000000, W  
PL49: 18, 0.000000, W  
PL50: 18, 0.000000, W  
PL51: 18, 0.000000, W  
PL52: 18, 0.000000, W  
PL53: 18, 0.000000, W  
PL54: 18, 0.000000, W  
PL55: 18, 0.000000, W  
PL56: 18, 0.000000, W  
PL57: 18, 0.000000, W  
PL58: 18, 0.000000, W  
PL59: 18, 0.000000, W  
PL60: 18, 0.000000, W  
PL61: 18, 0.000000, W  
PL62: 18, 0.000000, W  
PL63: 18, 0.000000, W  
PL64: 18, 0.000000, W  
PL65: 18, 0.000000, W  
PL66: 18, 0.000000, W  
PL67: 18, 0.000000, W  
PL68: 18, 0.000000, W  
PL69: 18, 0.000000, W  
PL70: 18, 0.000000, W  
PL71: 18, 0.000000, W  
PL72: 18, 0.000000, W  
PL73: 18, 0.000000, W  
PL74: 18, 0.000000, W  
PL75: 18, 0.000000, W  
PL76: 18, 0.000000, W  
PL77: 18, 0.000000, W  
PL78: 18, 0.000000, W  
PL79: 18, 0.000000, W  
PL80: 18, 0.000000, W  
PL81: 18, 0.000000, W  
PL82: 18, 0.000000, W  
PL83: 18, 0.000000, W  
PL84: 18, 0.000000, W  
PL85: 18, 0.000000, W  
PL86: 18, 0.000000, W  
PL87: 18, 0.000000, W  
PL88: 18, 0.000000, W  
PL89: 18, 0.000000, W  
PL90: 18, 0.000000, W  
PL91: 18, 0.000000, W  
PL92: 18, 0.000000, W  
PL93: 18, 0.000000, W  
PL94: 18, 0.000000, W  
PL95: 18, 0.000000, W  
PL96: 18, 0.000000, W  
PL97: 18, 0.000000, W  
PL98: 18, 0.000000, W  
PL99: 18, 0.000000, W  
PL100: 18, 0.000000, W  
PL101: 18, 0.000000, W  
PL102: 18, 0.000000, W  
PL103: 18, 0.000000, W  
PL104: 18, 0.000000, W  
PL105: 18, 0.000000, W  
PL106: 18, 0.000000, W  
PL107: 18, 0.000000, W  
PL108: 18, 0.000000, W  
PL109: 18, 0.000000, W  
PL110: 18, 0.000000, W  
PL111: 18, 0.000000, W  
PL112: 18, 0.000000, W  
PL113: 18, 0.000000, W  
PL114: 18, 0.000000, W  
PL115: 18, 0.000000, W  
PL116: 18, 0.000000, W  
PL117: 18, 0.000000, W  
PL118: 18, 0.000000, W  
PL119: 18, 0.000000, W  
PL120: 18, 0.000000, W  
PL121: 18, 0.000000, W  
PL122: 18, 0.000000, W  
PL123: 18, 0.000000, W  
PL124: 18, 0.000000, W  
PL125: 18, 0.000000, W  
PL126: 18, 0.000000, W  
PL127: 18, 0.000000, W  
PL128: 18, 0.000000, W  
PL129: 18, 0.000000, W  
PL130: 18, 0.000000, W  
PL131: 18, 0.000000, W  
PL132: 18, 0.000000, W  
PL133: 18, 0.000000, W  
PL134: 18, 0.000000, W  
PL135: 18, 0.000000, W  
PL136: 18, 0.000000, W  
PL137: 18, 0.000000, W  
PL138: 18, 0.000000, W  
PL139: 18, 0.000000, W  
PL140: 18, 0.000000, W  
PL141: 18, 0.000000, W  
PL142: 18, 0.000000, W  
PL143: 18, 0.000000, W  
PL144: 18, 0.000000, W  
PL145: 18, 0.000000, W  
PL146: 18, 0.000000, W  
PL147: 18, 0.000000, W  
PL148: 18, 0.000000, W  
PL149: 18, 0.000000, W  
PL150: 18, 0.000000, W  
PL151: 18, 0.000000, W  
PL152: 18, 0.000000, W  
PL153: 18, 0.000000, W  
PL154: 18, 0.000000, W  
PL155: 18, 0.000000, W  
PL156: 18, 0.000000, W  
PL157: 18, 0.000000, W  
PL158: 18, 0.000000, W  
PL159: 18, 0.000000, W  
PL160: 18, 0.000000, W  
PL161: 18, 0.000000, W  
PL162: 18, 0.000000, W  
PL163: 18, 0.000000, W  
PL164: 18, 0.000000, W  
PL165: 18, 0.000000, W  
PL166: 18, 0.000000, W  
PL167: 18, 0.000000, W  
PL168: 18, 0.000000, W  
PL169: 18, 0.000000, W  
PL170: 18, 0.000000, W  
PL171: 18, 0.000000, W  
PL172: 18, 0.000000, W  
PL173: 18, 0.000000, W  
PL174: 18, 0.000000, W  
PL175: 18, 0.000000, W  
PL176: 18, 0.000000, W  
PL177: 18, 0.000000, W  
PL178: 18, 0.000000, W  
PL179: 18, 0.000000, W  
PL180: 18, 0.000000, W  
PL181: 18, 0.000000, W  
PL182: 18, 0.000000, W  
PL183: 18, 0.000000, W  
PL184: 18, 0.000000, W  
PL185: 18, 0.000000, W  
PL186: 18, 0.000000, W  
PL187: 18, 0.000000, W  
PL188: 18, 0.000000, W  
PL189: 18, 0.000000, W  
PL190: 18, 0.000000, W  
PL191: 18, 0.000000, W  
PL192: 18, 0.000000, W  
PL193: 18, 0.000000, W  
PL194: 18, 0.000000, W  
PL195: 18, 0.000000, W  
PL196: 18, 0.000000, W  
PL197: 18, 0.000000, W  
PL198: 18, 0.000000, W  
PL199: 18, 0.000000, W  
PL200: 18, 0.000000, W  
PL201: 18, 0.000000, W  
PL202: 18, 0.000000, W  
PL203: 18, 0.000000, W  
PL204: 18, 0.000000, W  
PL205: 18, 0.000000, W  
PL206: 18, 0.000000, W  
PL207: 18, 0.000000, W  
PL208: 18, 0.000000, W  
PL209: 18, 0.000000, W  
PL210: 18, 0.000000, W  
PL211: 18, 0.000000, W  
PL212: 18, 0.000000, W  
PL213: 18, 0.000000, W  
PL214: 18, 0.000000, W  
PL215: 18, 0.000000, W  
PL216: 18, 0.000000, W  
PL217: 18, 0.000000, W  
PL218: 18, 0.000000, W  
PL219: 18, 0.000000, W  
PL220: 18, 0.000000, W  
PL221: 18, 0.000000, W  
PL222: 18, 0.000000, W  
PL223: 18, 0.000000, W  
PL224: 18, 0.000000, W  
PL225: 18, 0.000000, W  
PL226: 18, 0.000000, W  
PL227: 18, 0.000000, W  
PL228: 18, 0.000000, W  
PL229: 18, 0.000000, W  
PL230: 18, 0.000000, W  
PL231: 18, 0.000000, W  
PL232: 18, 0.000000, W  
PL233: 18, 0.000000, W  
PL234: 18, 0.000000, W  
PL235: 18, 0.000000, W  
PL236: 18, 0.000000, W  
PL237: 18, 0.000000, W  
PL238: 18, 0.000000, W  
PL239: 18, 0.000000, W  
PL240: 18, 0.000000, W  
PL241: 18, 0.000000, W  
PL242: 18, 0.000000, W  
PL243: 18, 0.000000, W  
PL244: 18, 0.000000, W  
PL245: 18, 0.000000, W  
PL246: 18, 0.000000, W  
PL247: 18, 0.000000, W  
PL248: 18, 0.000000, W  
PL249: 18, 0.000000, W  
PL250: 18, 0.000000, W  
PL251: 18, 0.000000, W  
PL252: 18, 0.000000, W  
PL253: 18, 0.000000, W  
PL254: 18, 0.000000, W  
PL255: 18, 0.000000, W  
PL256: 18, 0.000000, W  
PL257: 18, 0.000000, W  
PL258: 18, 0.000000, W  
PL259: 18, 0.000000, W  
PL260: 18, 0.000000, W  
PL261: 18, 0.000000, W  
PL262: 18, 0.000000, W  
PL263: 18, 0.000000, W  
PL264: 18, 0.000000, W  
PL265: 18, 0.000000, W  
PL266: 18, 0.000000, W  
PL267: 18, 0.000000, W  
PL268: 18, 0.000000, W  
PL269: 18, 0.000000, W  
PL270: 18, 0.000000, W  
PL271: 18, 0.000000, W  
PL272: 18, 0.000000, W  
PL273: 18, 0.000000, W  
PL274: 18, 0.000000, W  
PL275: 18, 0.000000, W  
PL276: 18, 0.000000, W  
PL277: 18, 0.000000, W  
PL278: 18, 0.000000, W  
PL279: 18, 0.000000, W  
PL280: 18, 0.000000, W  
PL281: 18, 0.000000, W  
PL282: 18, 0.000000, W  
PL283: 18, 0.000000, W  
PL284: 18, 0.000000, W  
PL285: 18, 0.000000, W  
PL286: 18, 0.000000, W  
PL287: 18, 0.000000, W  
PL288: 18, 0.000000, W  
PL289: 18, 0.000000, W  
PL290: 18, 0.000000, W  
PL291: 18, 0.000000, W  
PL292: 18, 0.000000, W  
PL293: 18, 0.000000, W  
PL294: 18, 0.000000, W  
PL295: 18, 0.000000, W  
PL296: 18, 0.000000, W  
PL297: 18, 0.000000, W  
PL298: 18, 0.000000, W  
PL299: 18, 0.000000, W  
PL300: 18, 0.000000, W  
PL301: 18, 0.000000, W  
PL302: 18, 0.000000, W  
PL303: 18, 0.000000, W  
PL304: 18, 0.000000, W  
PL305: 18, 0.000000, W  
PL306: 18, 0.000000, W  
PL307: 18, 0.000000, W  
PL308: 18, 0.000000, W  
PL309: 18, 0.000000, W  
PL310: 18, 0.000000, W  
PL311: 18, 0.000000, W  
PL312: 18, 0.000000, W  
PL313: 18, 0.000000, W  
PL314: 18, 0.000000, W  
PL315: 18, 0.000000, W  
PL316: 18, 0.000000, W  
PL317: 18, 0.000000, W  
PL318: 18, 0.000000, W  
PL319: 18, 0.000000, W  
PL320: 18, 0.000000, W  
PL321: 18, 0.000000, W  
PL322: 18, 0.000000, W  
PL323: 18, 0.000000, W  
PL324: 18, 0.000000, W  
PL325: 18, 0.000000, W  
PL326: 18, 0.000000, W  
PL327: 18, 0.000000, W  
PL328: 18, 0.000000, W  
PL329: 18, 0.000000, W  
PL330: 18, 0.000000, W  
PL331: 18, 0.000000, W  
PL332: 18, 0.000000, W  
PL333: 18, 0.000000, W  
PL334: 18, 0.000000, W  
PL335: 18, 0.000000, W  
PL336: 18, 0.000000, W  
PL337: 18, 0.000000, W  
PL338: 18, 0.000000, W  
PL339: 18, 0.000000, W  
PL340: 18, 0.000000, W  
PL341: 18, 0.000000, W  
PL342: 18, 0.000000, W  
PL343: 18, 0.000000, W  
PL344: 18, 0.000000, W  
PL345: 18, 0.000000, W  
PL346: 18, 0.000000, W  
PL347: 18, 0.000000, W  
PL348: 18, 0.000000, W  
PL349: 18, 0.000000, W  
PL350: 18, 0.000000, W  
PL351: 18, 0.000000, W  
PL352: 18, 0.000000, W  
PL353: 18, 0.000000, W  
PL354: 18, 0.000000, W  
PL355: 18, 0.000000, W  
PL356: 18, 0.000000, W  
PL357: 18, 0.000000, W  
PL358: 18, 0.000000, W  
PL359: 18, 0.000000, W  
PL360: 18, 0.000000, W  
PL361: 18, 0.000000, W  
PL362: 18, 0.000000, W  
PL363: 18, 0.000000, W  
PL364: 18, 0.000000, W  
PL365: 18, 0.000000, W  
PL366: 18, 0.000000, W  
PL367: 18, 0.000000, W  
PL368: 18, 0.000000, W  
PL369: 18, 0.000000, W  
PL370: 18, 0.000000, W  
PL371: 18, 0.000000, W  
PL372: 18, 0.000000, W  
PL373: 18, 0.000000, W  
PL374: 18, 0.000000, W  
PL375: 18, 0.000000, W  
PL376: 18, 0.000000, W  
PL377: 18, 0.000000, W  
PL378: 18, 0.000000, W  
PL379: 18, 0.000000, W  
PL380: 18, 0.000000, W  
PL381: 18, 0.000000, W  
PL382: 18, 0.000000, W  
PL383: 18, 0.000000, W  
PL384: 18, 0.000000, W  
PL385: 18, 0.000000, W  
PL386: 18, 0.000000, W  
PL387: 18, 0.000000, W  
PL388: 18, 0.000000, W  
PL389: 18, 0.000000, W  
PL390: 18, 0.000000, W  
PL391: 18, 0.000000, W  
PL392: 18, 0.000000, W  
PL393: 18, 0.000000, W  
PL394: 18, 0.000000, W  
PL395: 18, 0.000000, W  
PL396: 18, 0.000000, W  
PL397: 18, 0.000000, W  
PL398: 18, 0.000000, W  
PL399: 18, 0.000000, W  
PL400: 18, 0.000000, W  
PL401: 18, 0.000000, W  
PL402: 18, 0.000000, W  
PL403: 18, 0.000000, W  
PL404: 18, 0.000000, W  
PL405: 18, 0.000000, W  
PL406: 18, 0.000000, W  
PL407: 18, 0.000000, W  
PL408: 18, 0.000000, W  
PL409: 18, 0.000000, W  
PL410: 18, 0.000000, W  
PL411: 18, 0.000000, W  
PL412: 18, 0.000000, W  
PL413: 18, 0.000000, W  
PL414: 18, 0.000000, W  
PL415: 18, 0.000000, W  
PL416: 18, 0.000000, W  
PL417: 18, 0.000000, W  
PL418: 18, 0.000000, W  
PL419: 18, 0.000000, W  
PL420: 18, 0.000000, W  
PL421: 18, 0.000000, W  
PL422: 18, 0.000000, W  
PL423: 18, 0.000000, W  
PL424: 18, 0.000000, W  
PL425: 18, 0.000000, W  
PL426: 18, 0.000000, W  
PL427: 18, 0.000000, W  
PL428: 18, 0.000000, W  
PL429: 18, 0.000000, W  
PL430: 18, 0.000000, W  
PL431: 18, 0.000000, W  
PL432: 18, 0.000000, W  
PL433: 18, 0.000000, W  
PL434: 18, 0.000000, W  
PL435: 18, 0.000000, W  
PL436: 18, 0.000000, W  
PL437: 18, 0.000000, W  
PL438: 18, 0.000000, W  
PL439: 18, 0.000000, W  
PL440: 18, 0.000000, W  
PL441: 18, 0.000000, W  
PL442: 18, 0.000000, W  
PL443: 18, 0.000000, W  
PL444: 18, 0.000000, W  
PL445: 18, 0.000000, W  
PL446: 18, 0.000000, W  
PL447: 18, 0.000000, W  
PL448: 18, 0.000000, W  
PL449: 18, 0.000000, W  
PL450: 18, 0.000000, W  
PL451: 18, 0.000000, W  
PL452: 18, 0.000000, W  
PL453: 18, 0.000000, W  
PL454: 18, 0.000000, W  
PL455: 18, 0.00



CC5052 BH3 deprotected

Figure S14  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 14 (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 296 K)

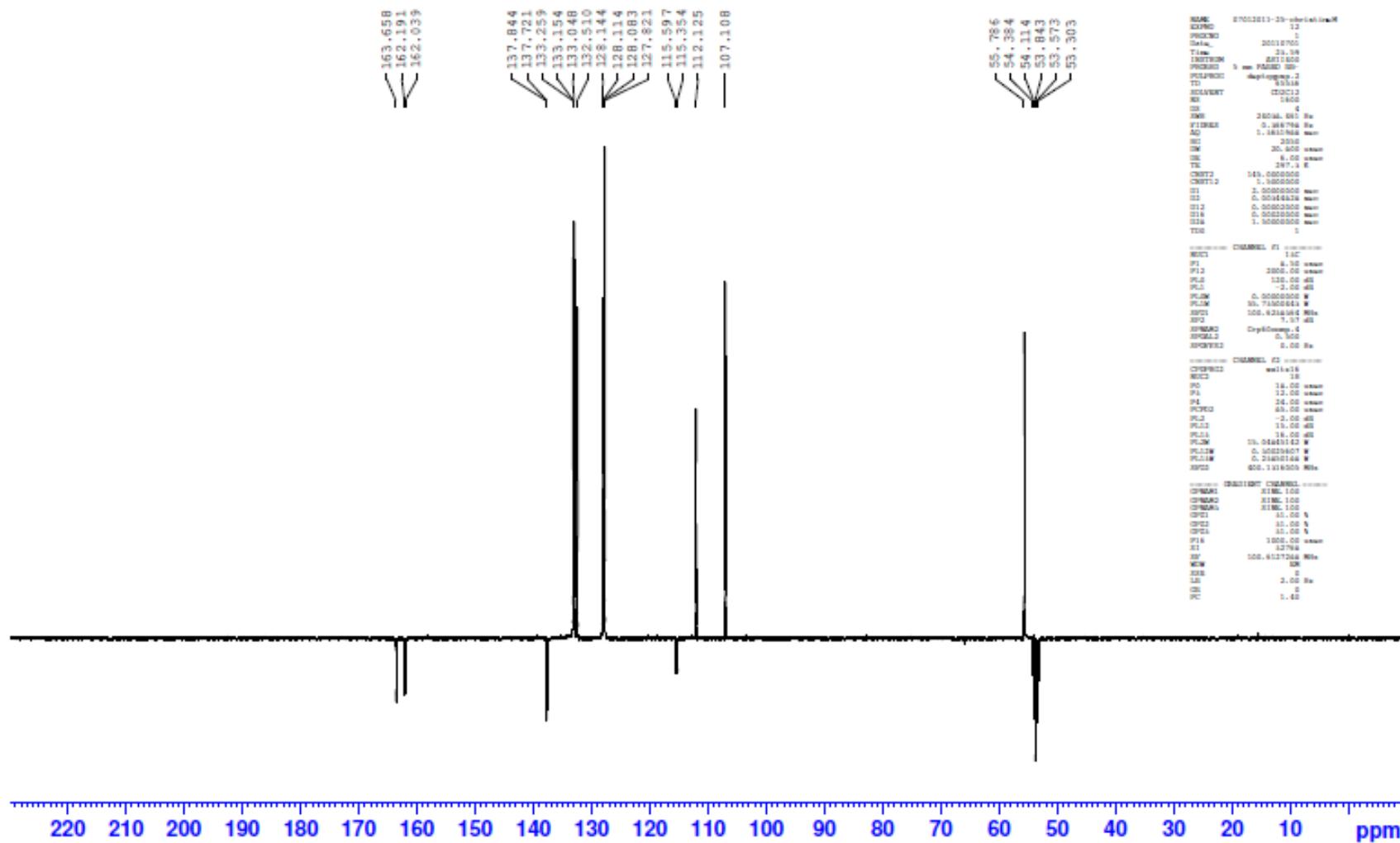
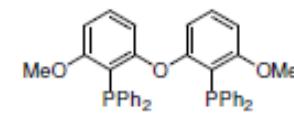
## 6- Compound 15



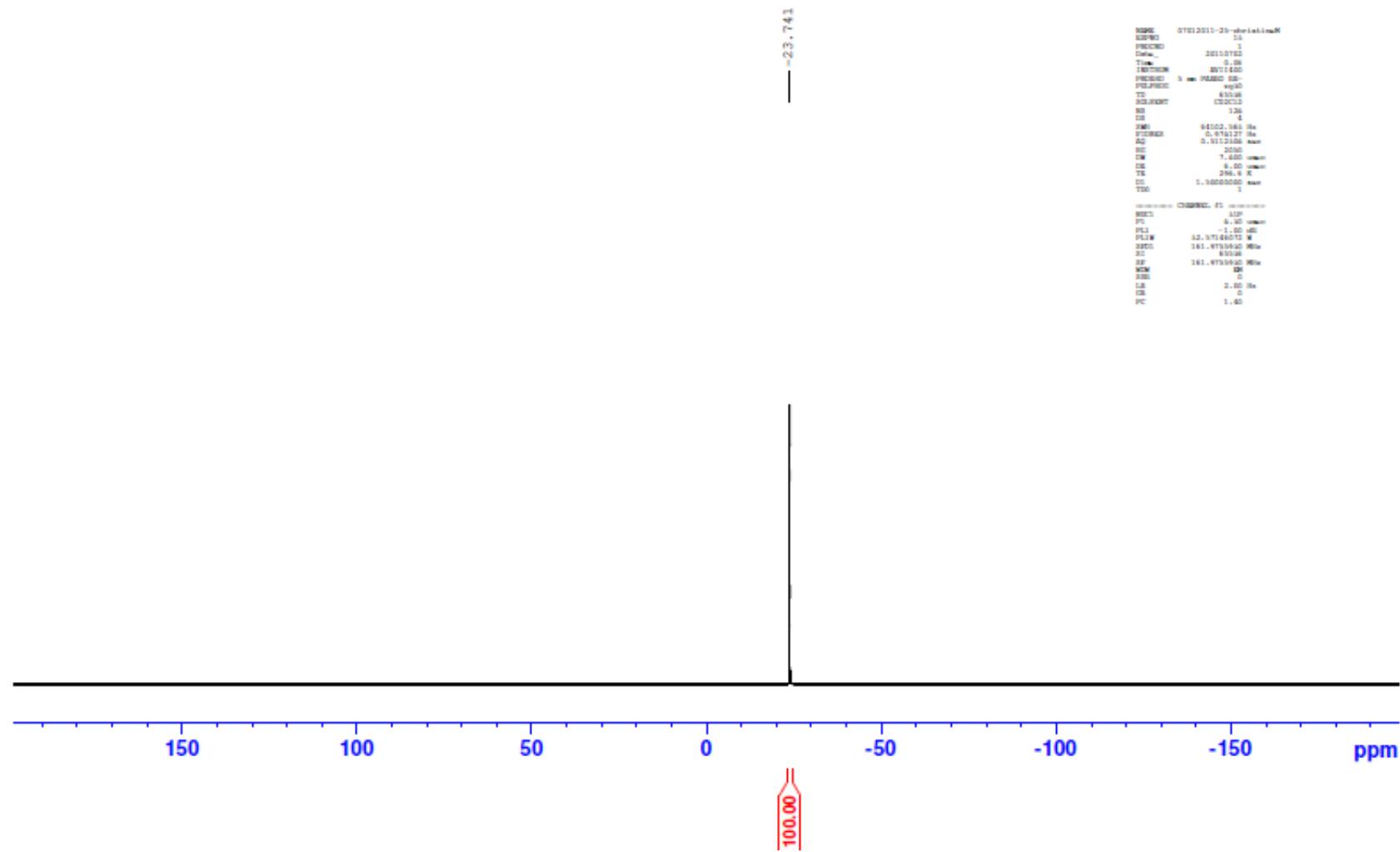
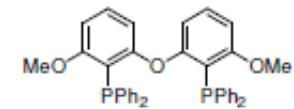
**Figure S15**  $^1\text{H}$  NMR spectrum of compound 15 (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



CC2011

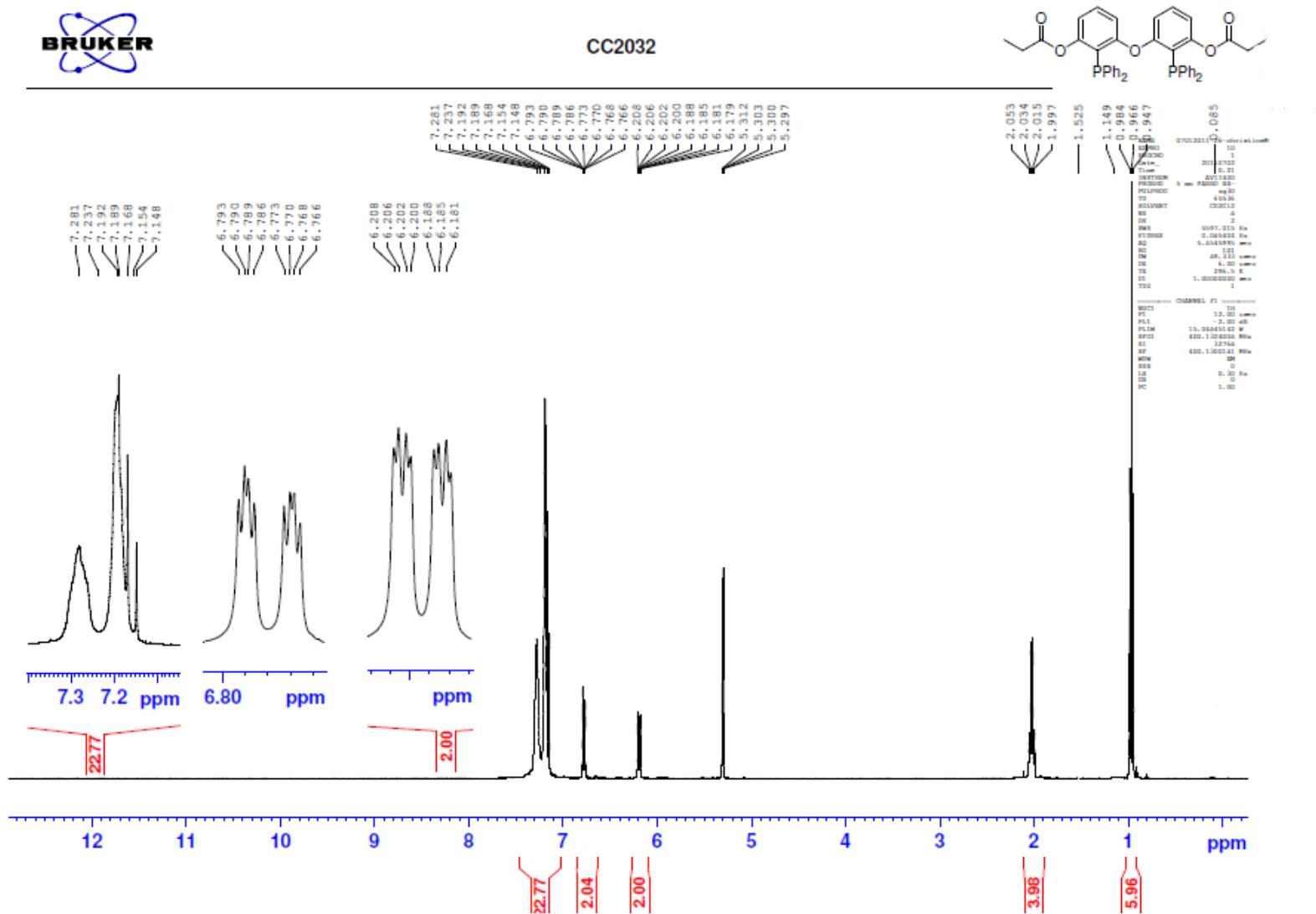


**Figure S16**  $^{13}\text{C}$  CPT NMR spectrum of compound 15 (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



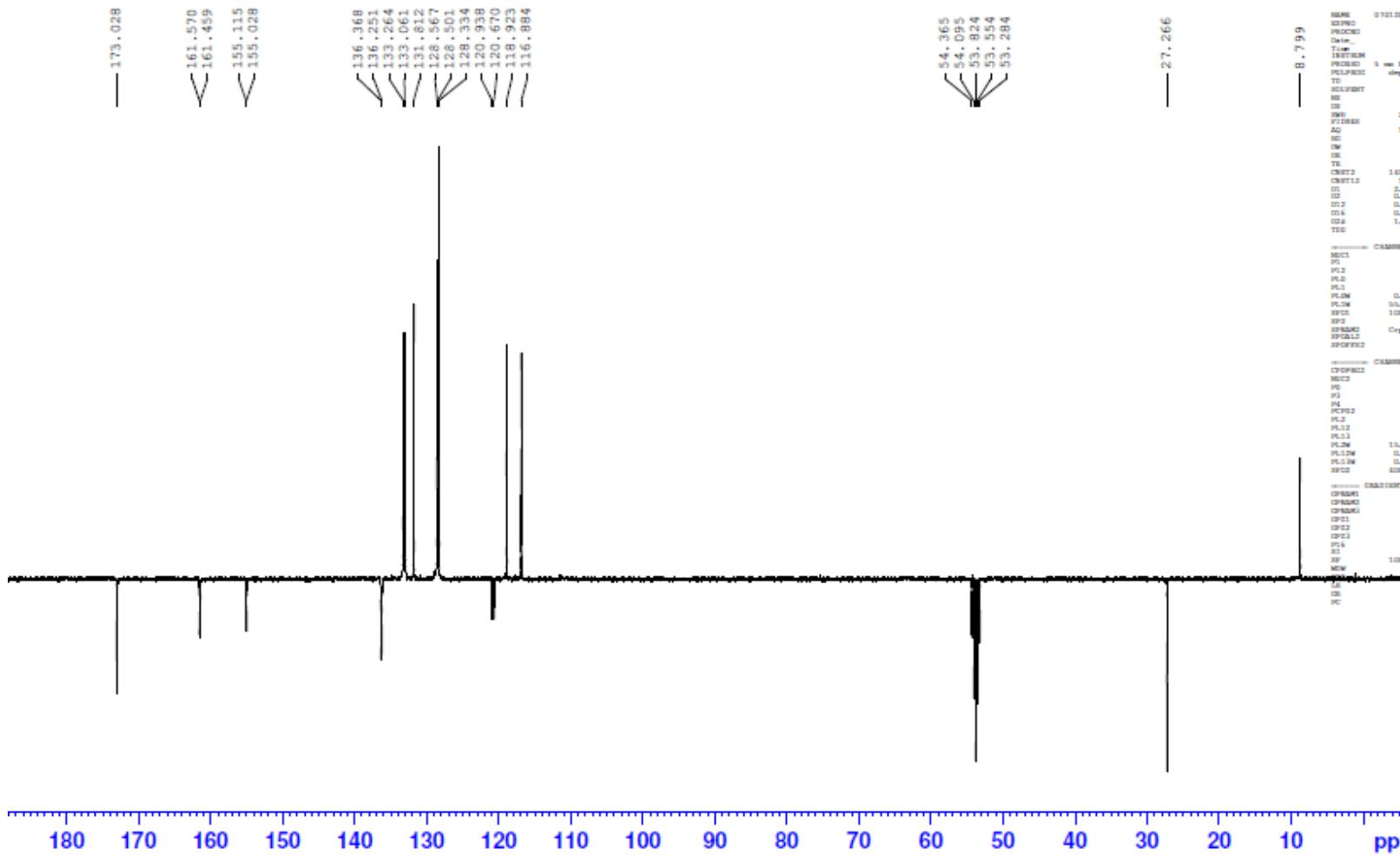
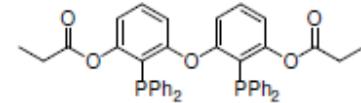
**Figure S17**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 15 (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)

7- Compound 17a





CC2032



**Figure S19**  $^{13}\text{C}$  APT NMR spectrum of compound **17a** (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CC2032

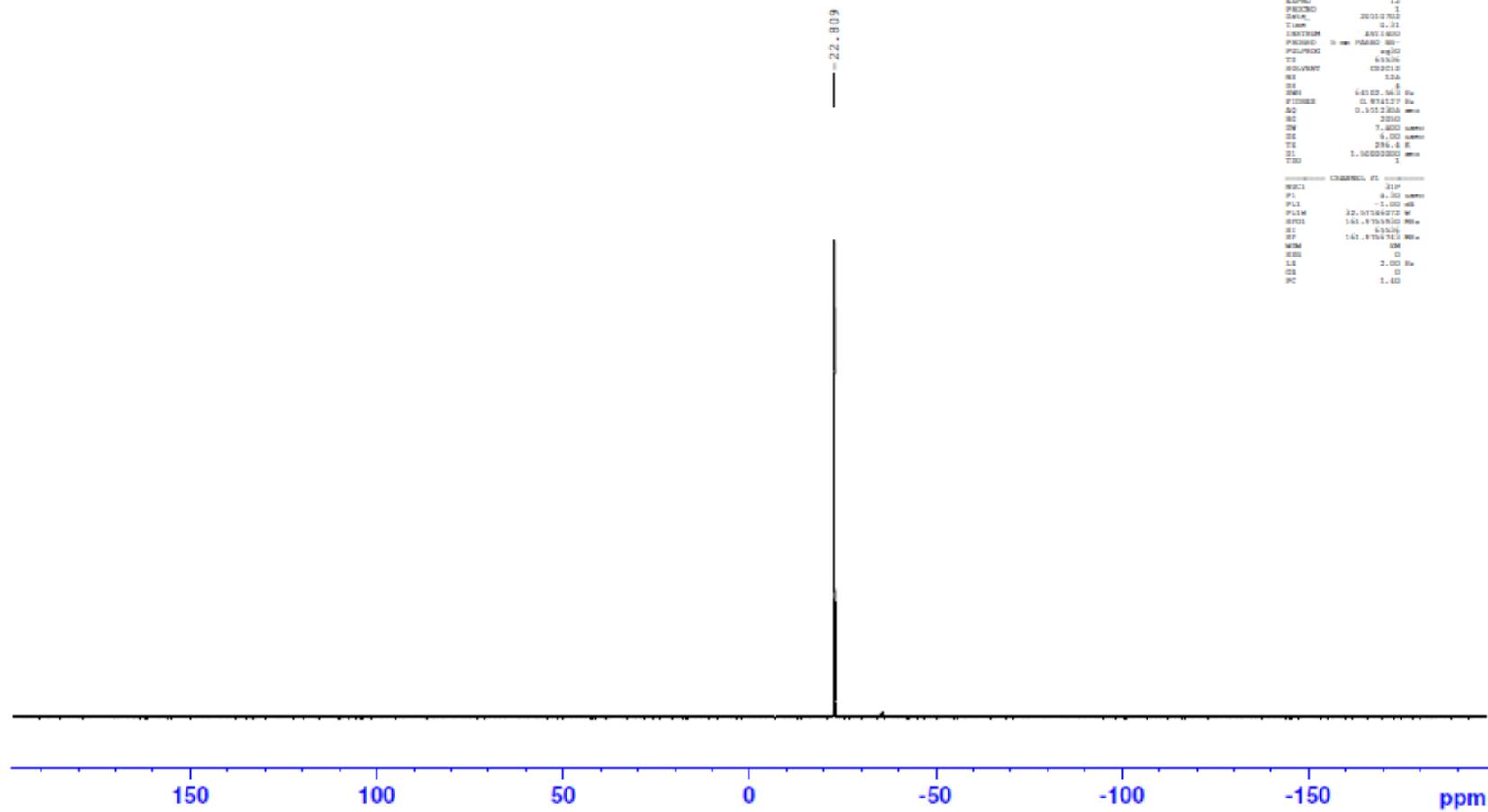
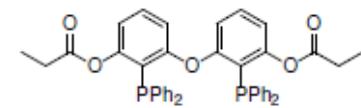


Figure S20  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 17a (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

8- Compound 17a

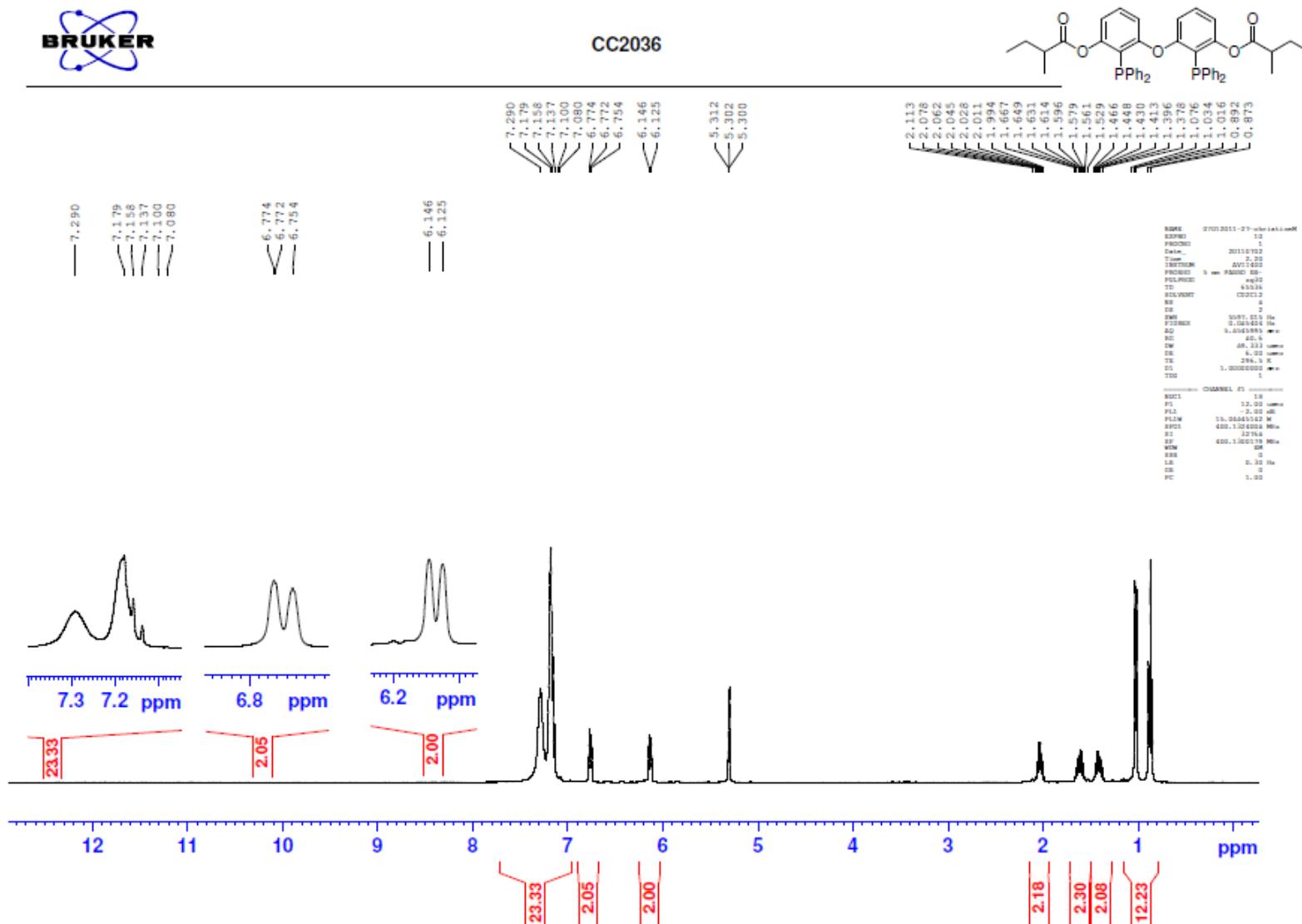


Figure S21      <sup>1</sup>H NMR spectrum of compound 17b (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



CC2036

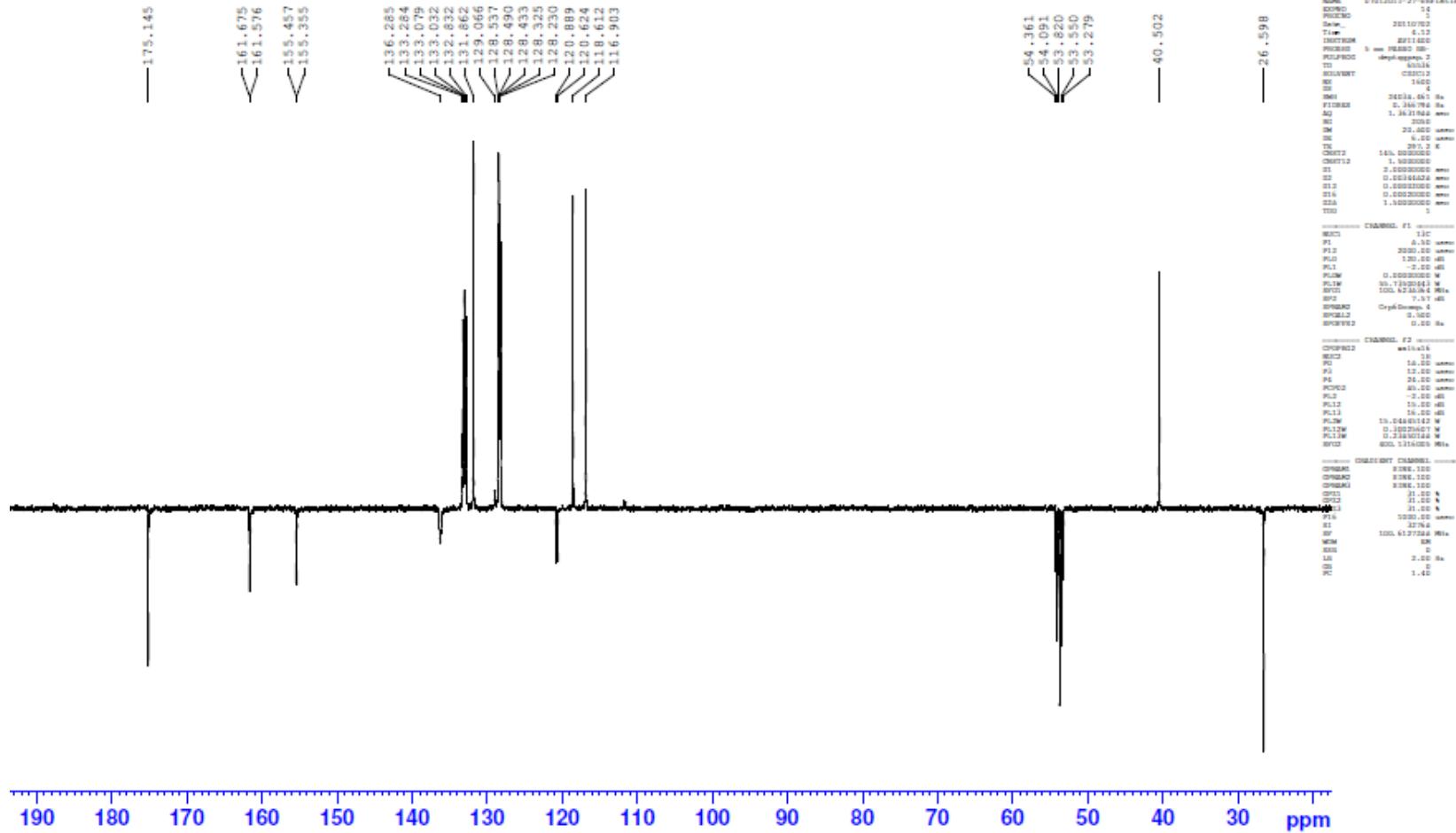


Figure S22  $^{13}\text{C}$  APT NMR spectrum of compound **17b** (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CC2036

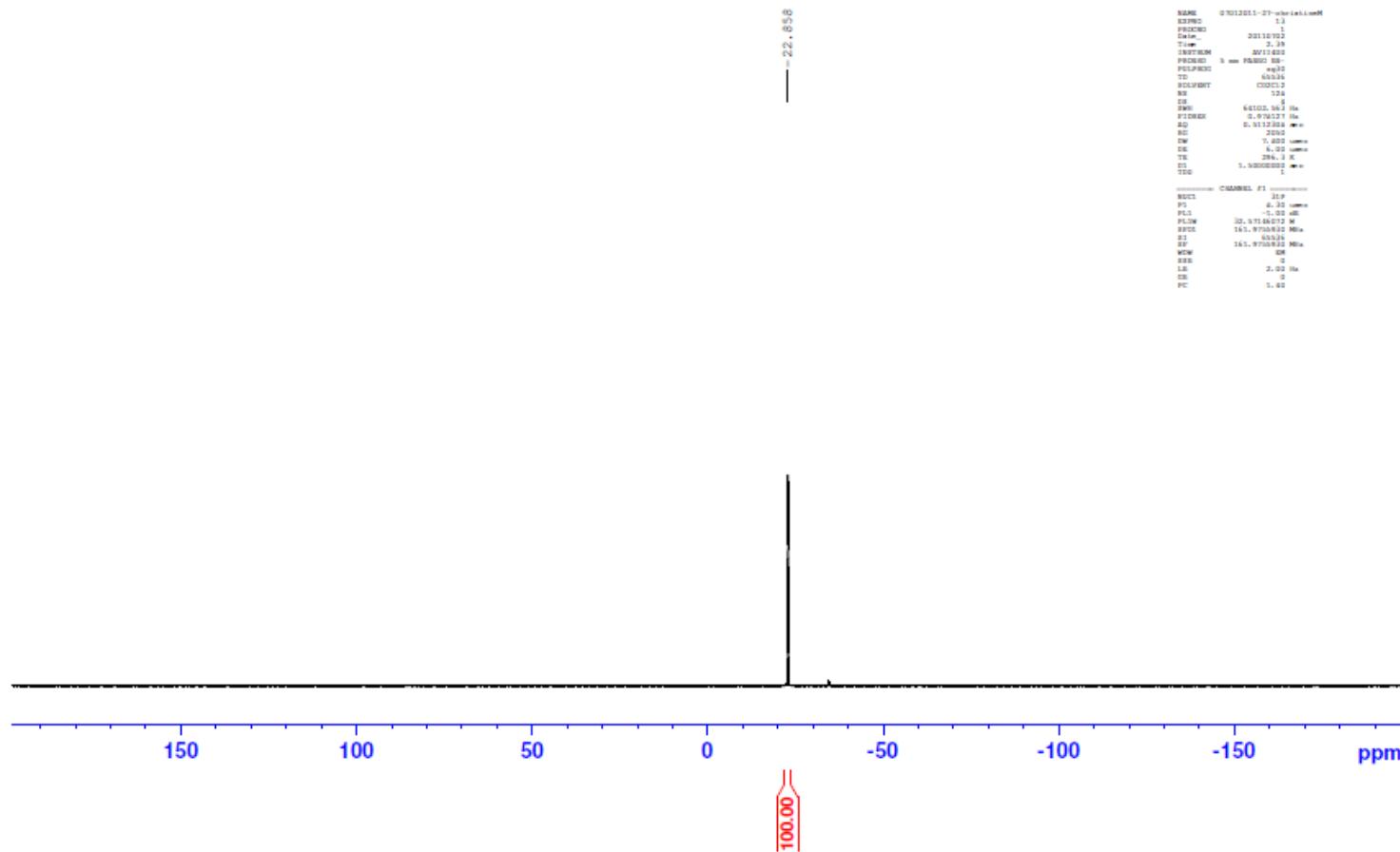
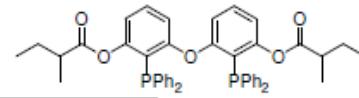


Figure S23  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 17b (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

9- Compound 17c

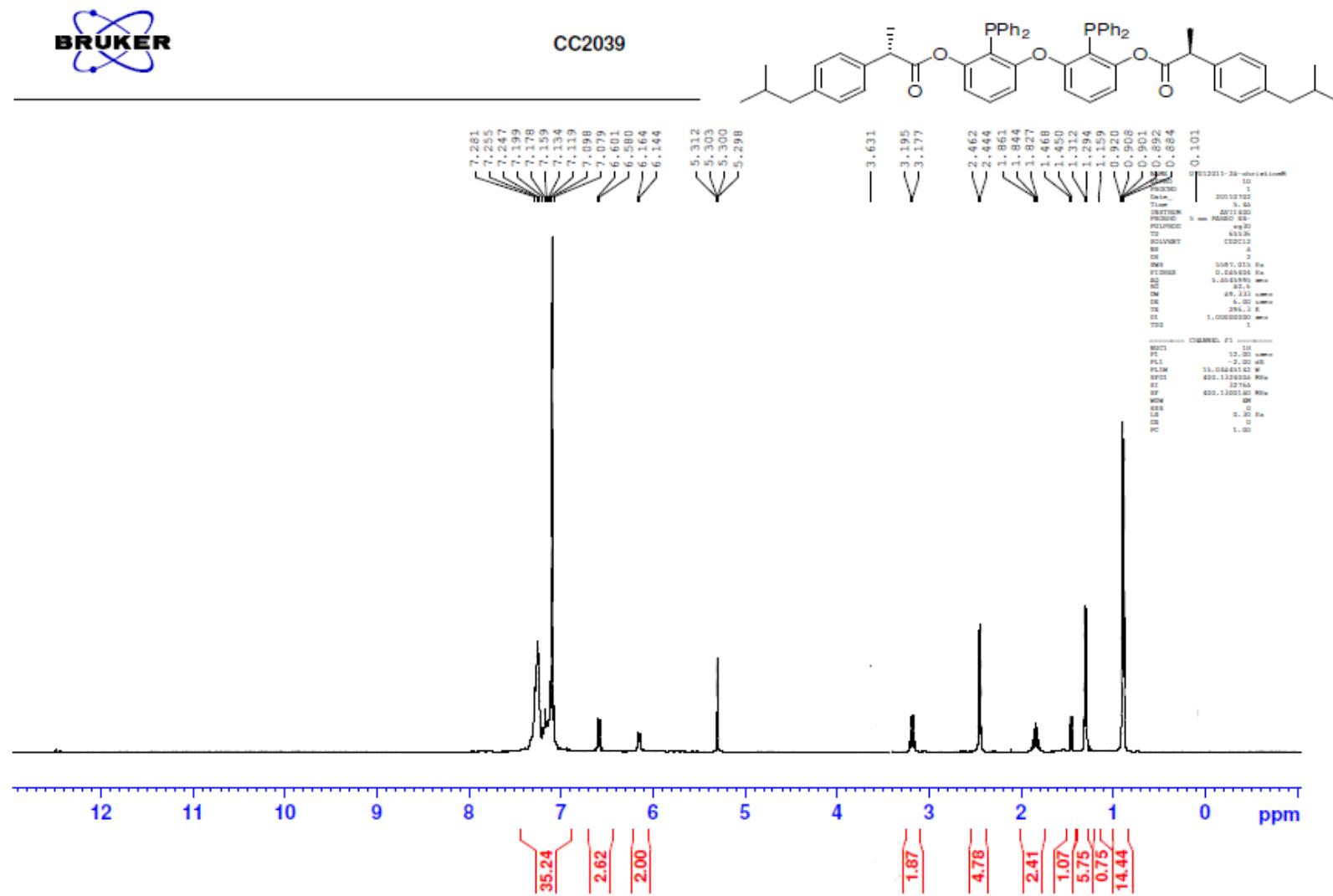


Figure S24  $^1\text{H}$  NMR spectrum of compound 17c (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CC2039

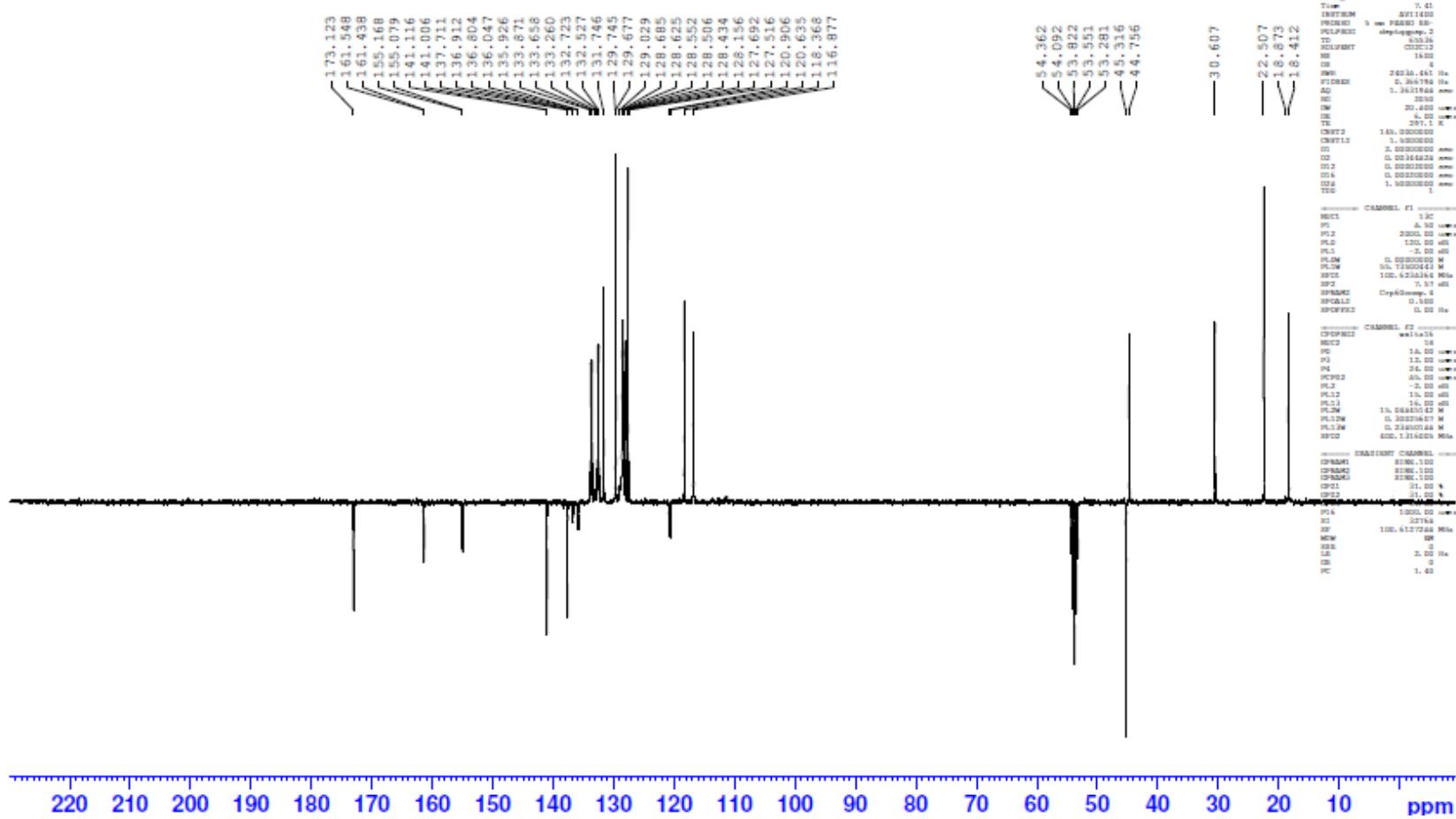
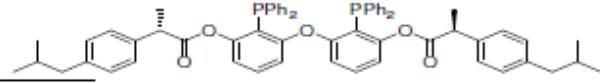
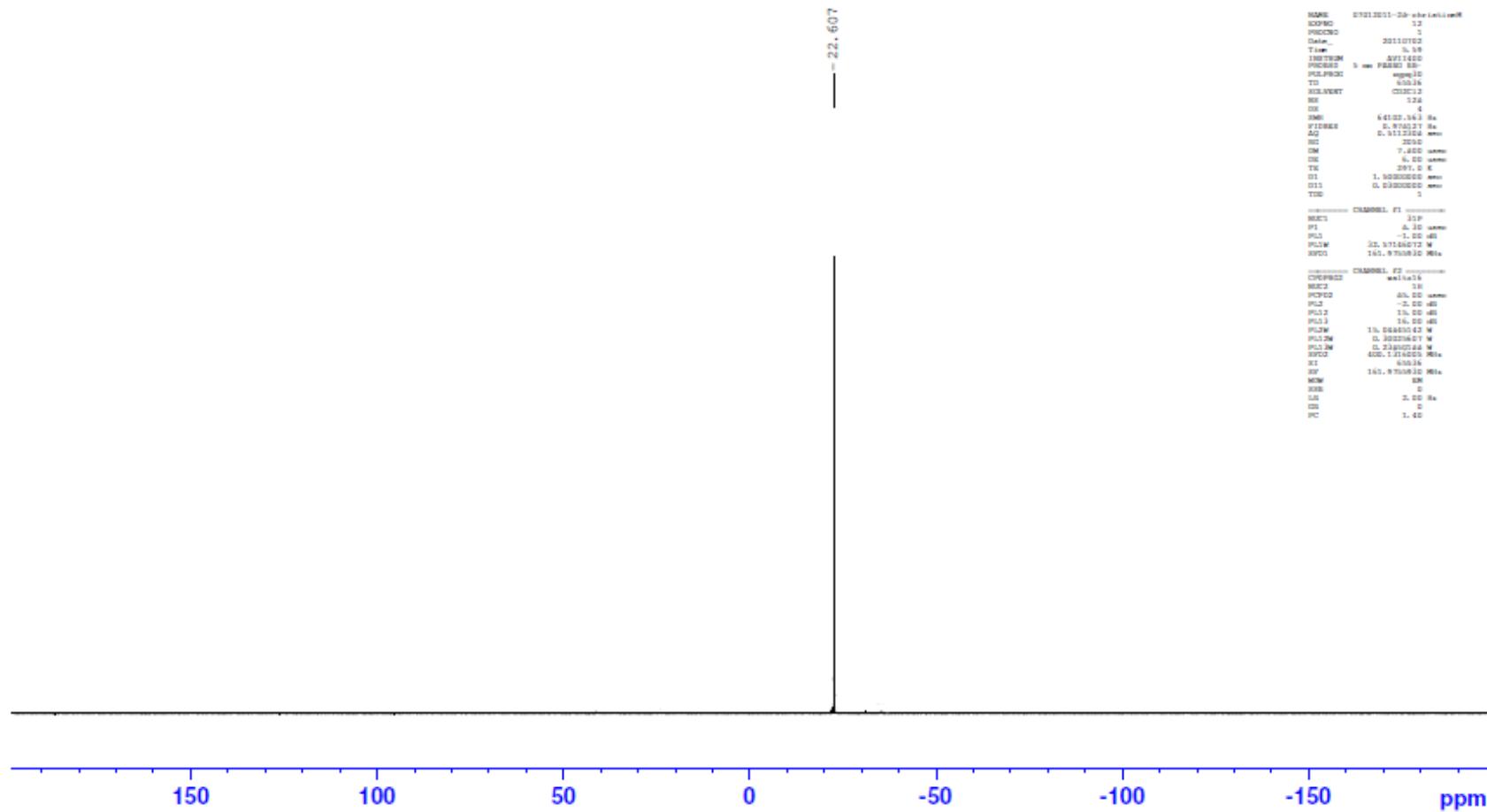
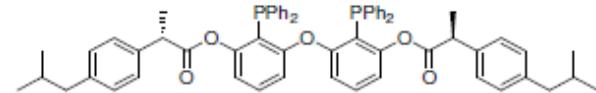


Figure S25 <sup>13</sup>C APT NMR spectrum of compound 17c (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



**Figure S26**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound **17c** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

10- Compound 17d

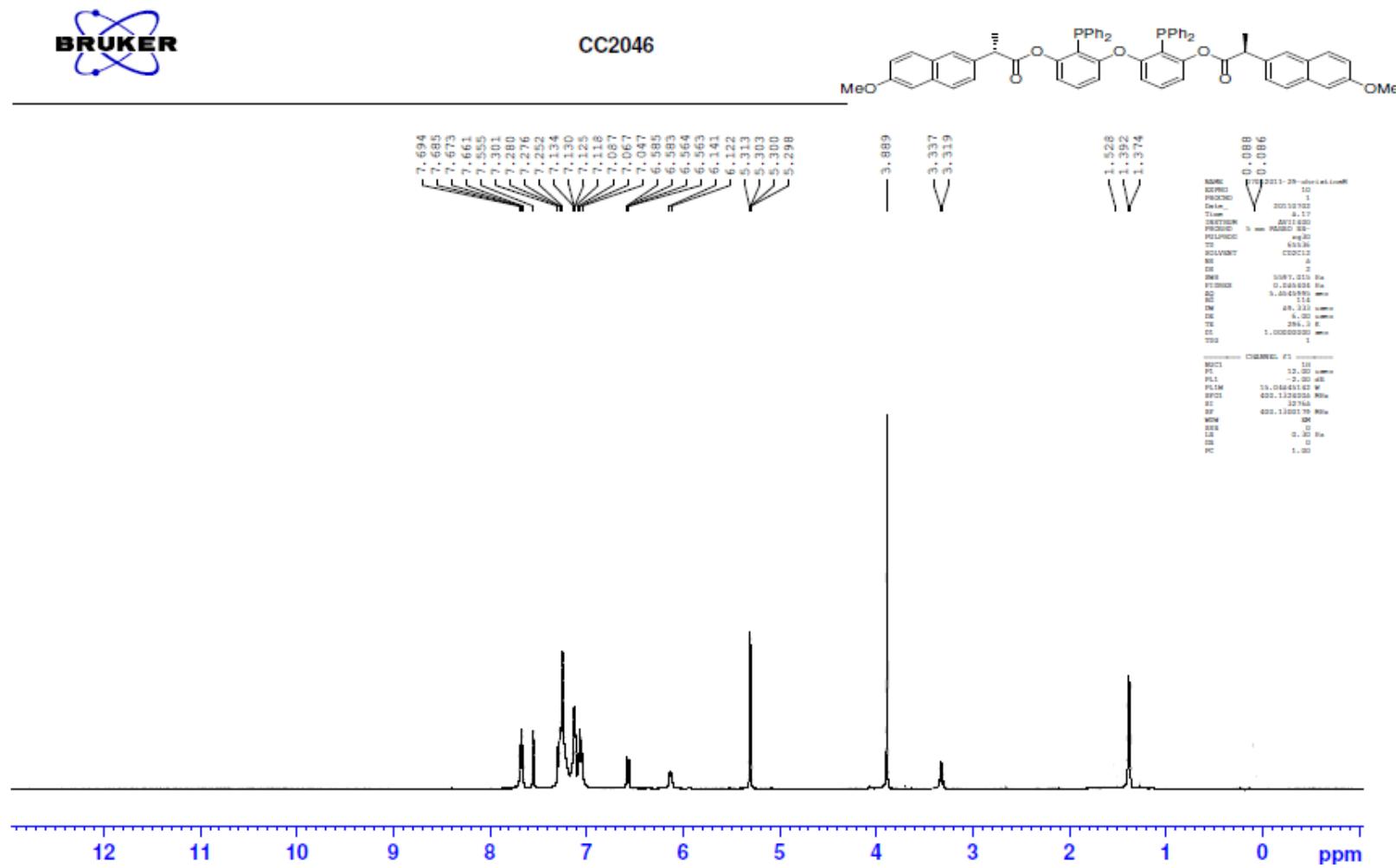


Figure S27  $^1\text{H}$  NMR spectrum of compound 17c (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CC2046

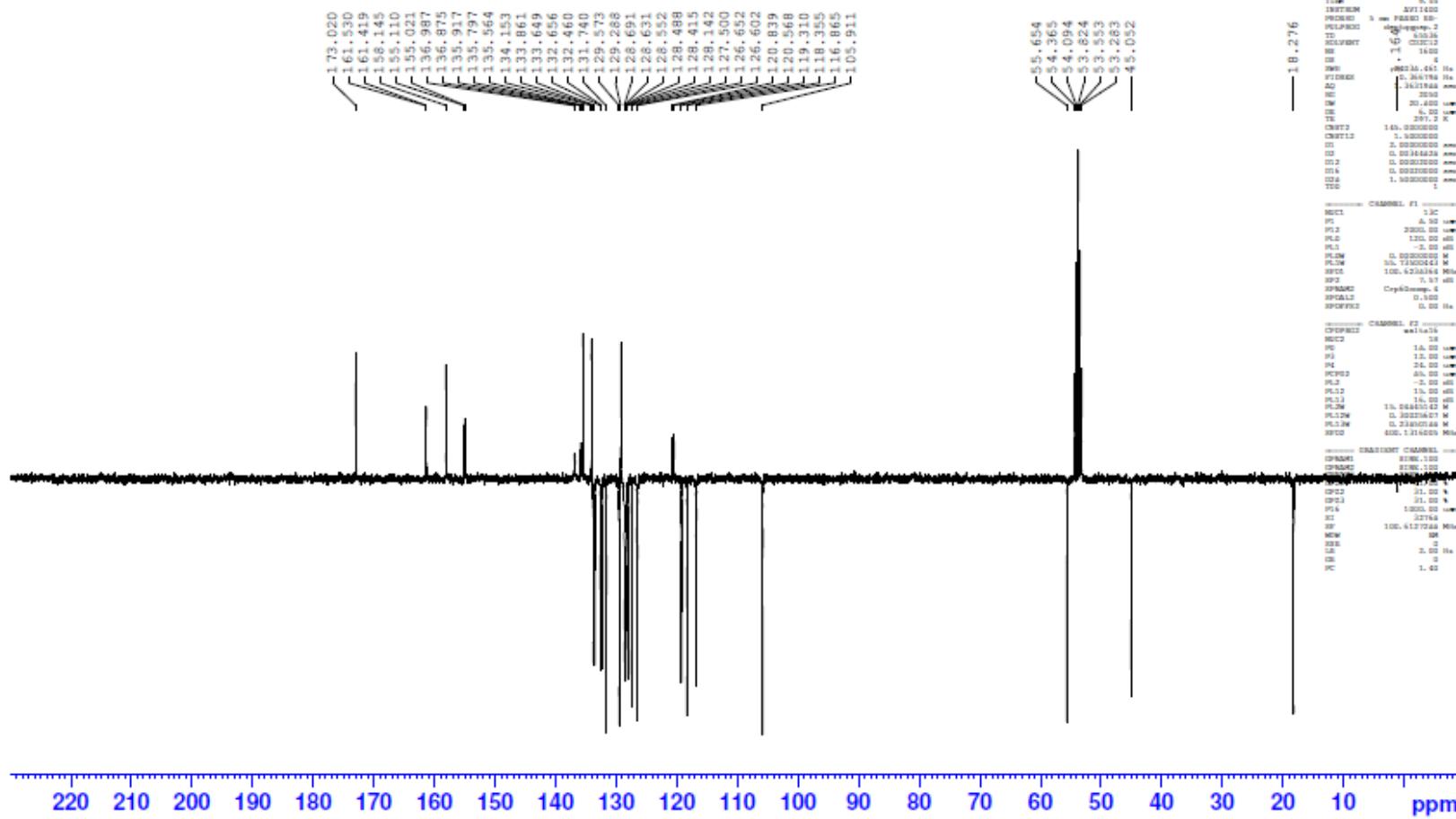
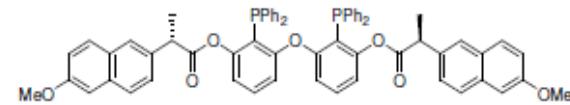


Figure S28  $^{13}\text{C}$  APT NMR spectrum of compound **17c** (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



CC2046

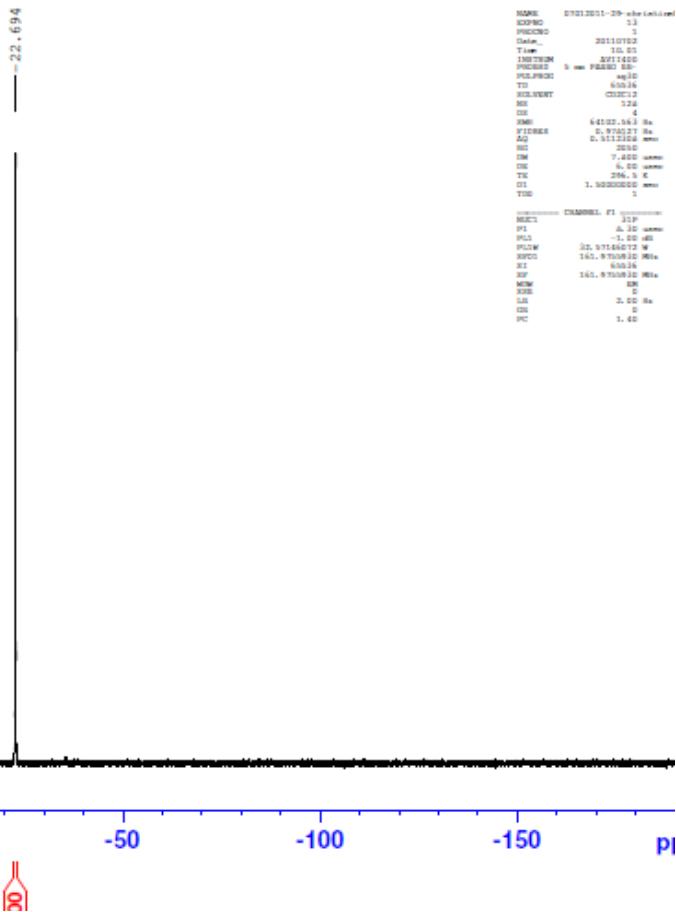
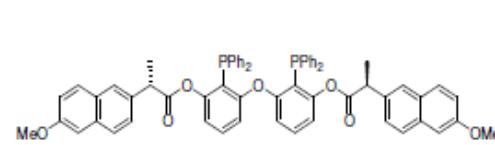


Figure S29  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 17c (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

## 11- Platinum Complexes

[PtCl<sub>2</sub>(15)]

01142015-20-pcjk-agj2-A.11.fid  
31P Observe with 1H decoupling  
agj1.119

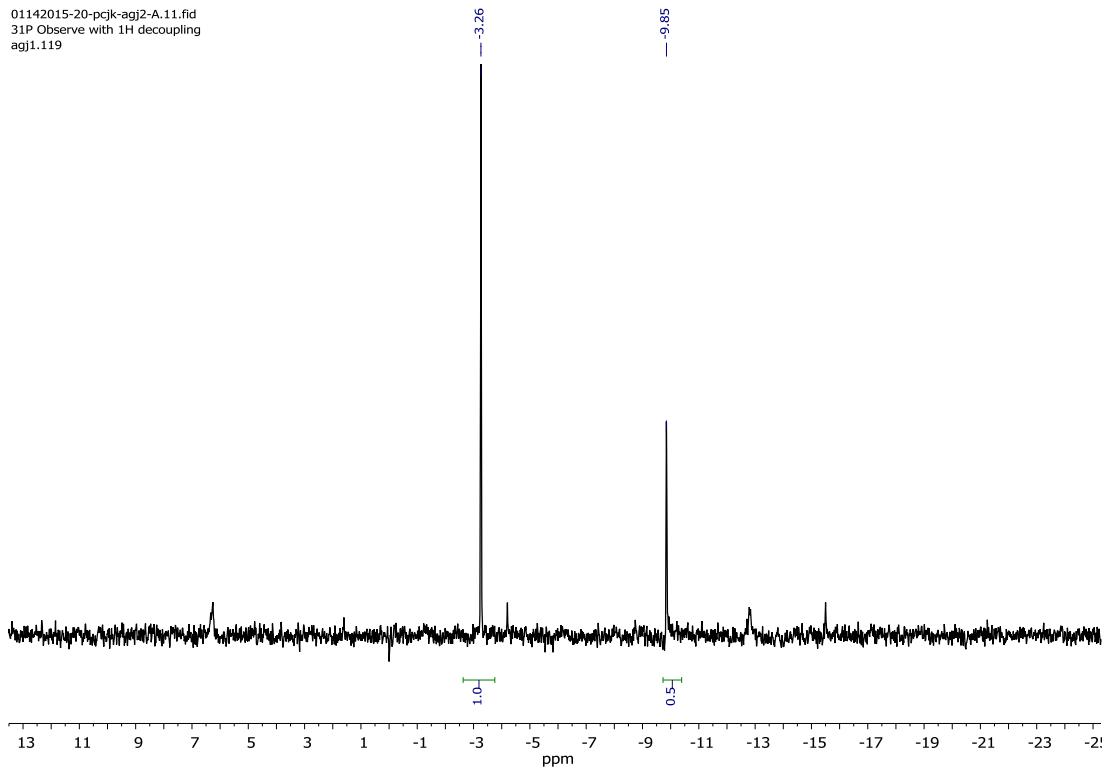
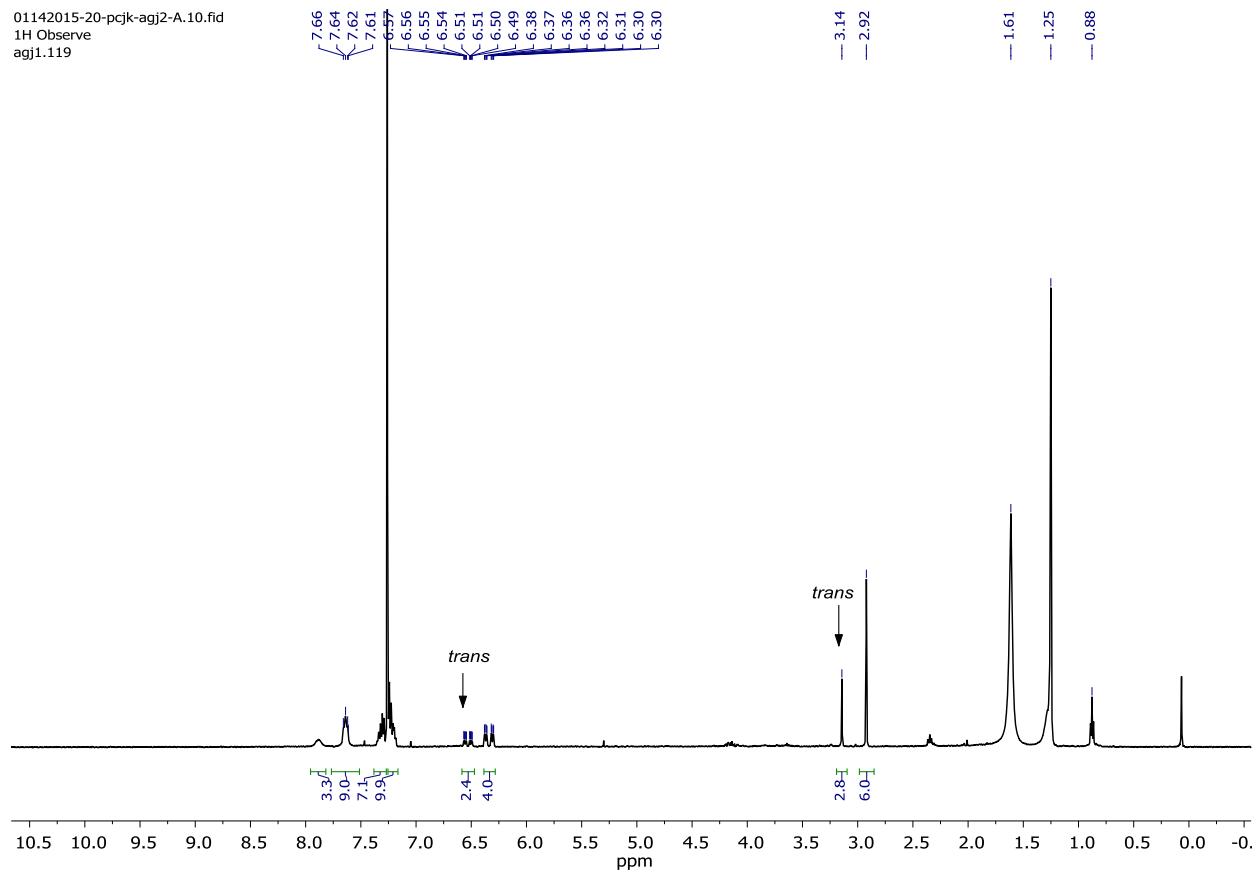
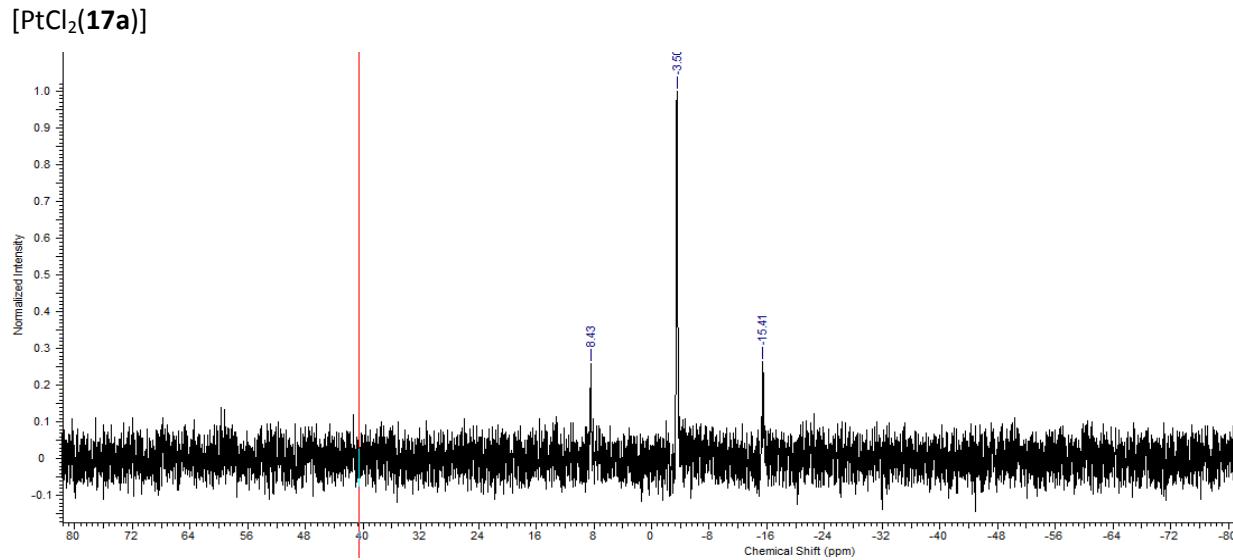


Figure S30: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(15) (202 MHz, CDCl<sub>3</sub>)



**Figure S31:**  $^1\text{H}$  NMR of  $\text{PtCl}_2(15)$  (500 MHz,  $\text{CDCl}_3$ ) (major product *cis*-isomer, minor product *trans*-isomer)



**Figure S32:**  $^{31}\text{P}\{^1\text{H}\}$  NMR of  $\text{PtCl}_2(17\text{a})$  (162 MHz,  $\text{CDCl}_3$ )

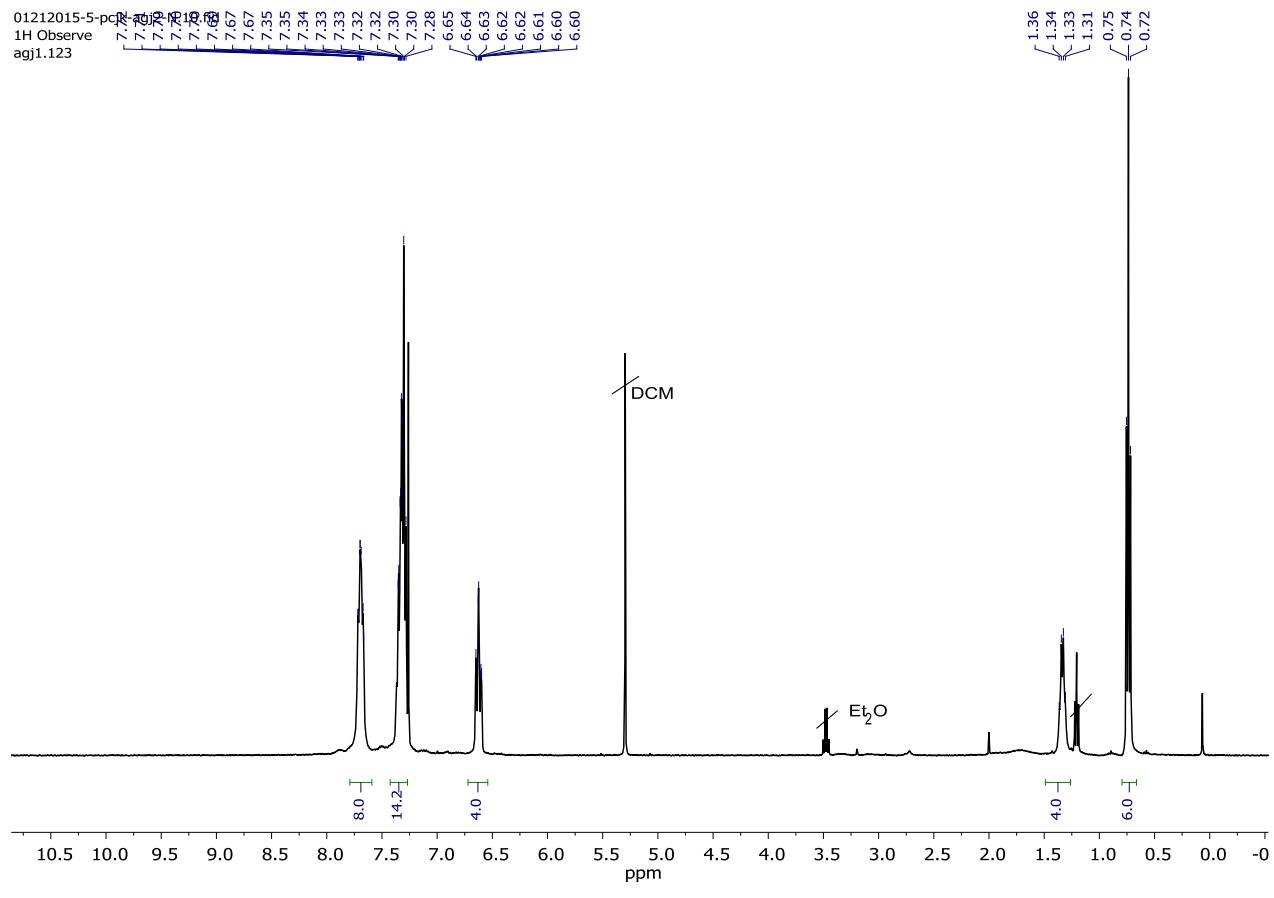


Figure S33:  $^1\text{H}$  NMR of  $\text{PtCl}_2(17\text{a})$  (400 MHz,  $\text{CDCl}_3$ )

[PtCl<sub>2</sub>(17b)]

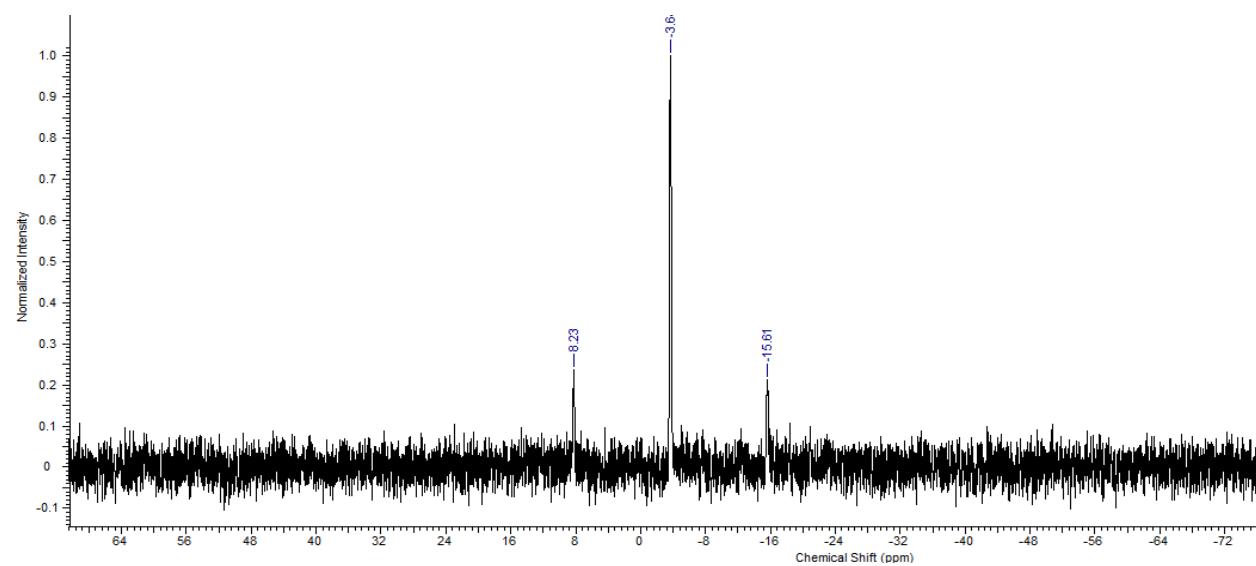


Figure S34: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(17b) (162 MHz, CDCl<sub>3</sub>)

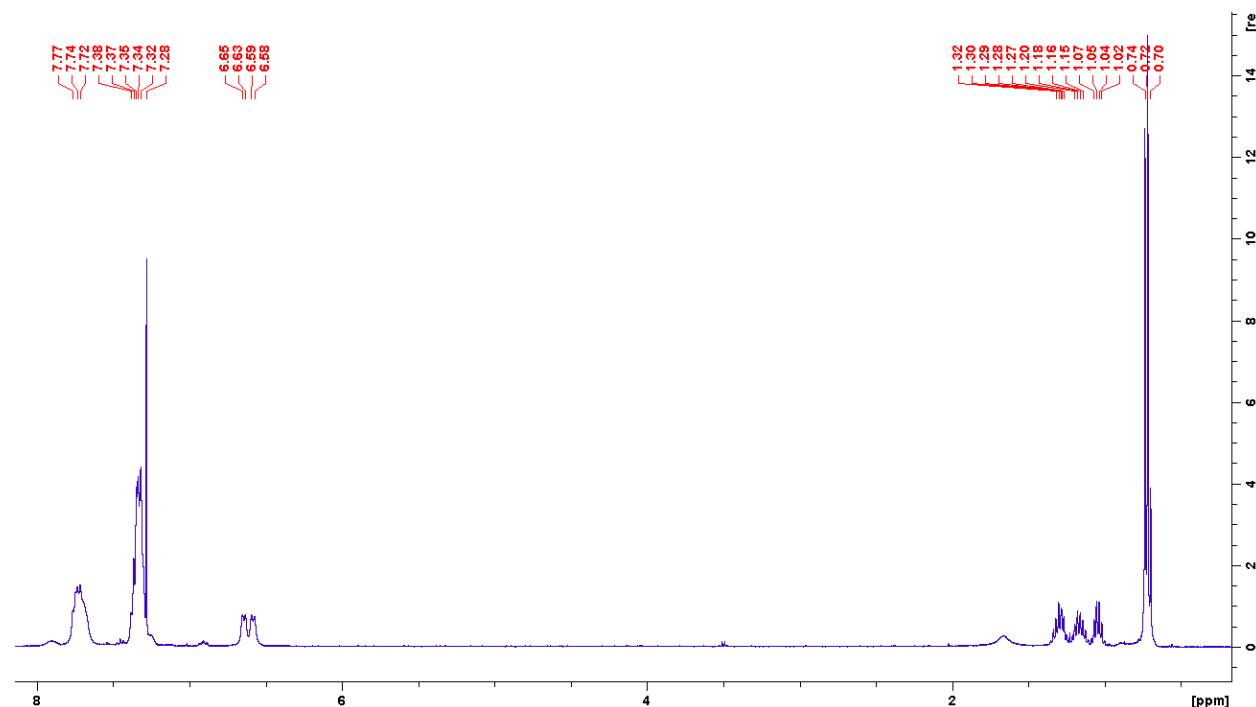


Figure S35: <sup>1</sup>H NMR of PtCl<sub>2</sub>(17b) (400 MHz, CDCl<sub>3</sub>)

[PtCl<sub>2</sub>(17c)]

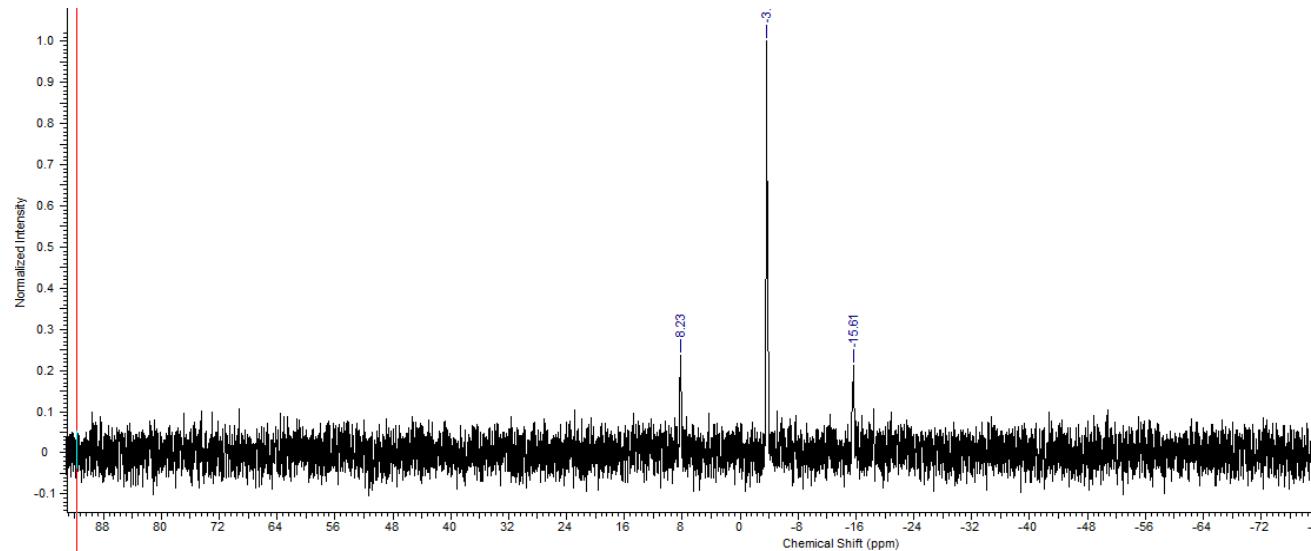


Figure S36: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(17c) (162 MHz, CDCl<sub>3</sub>)

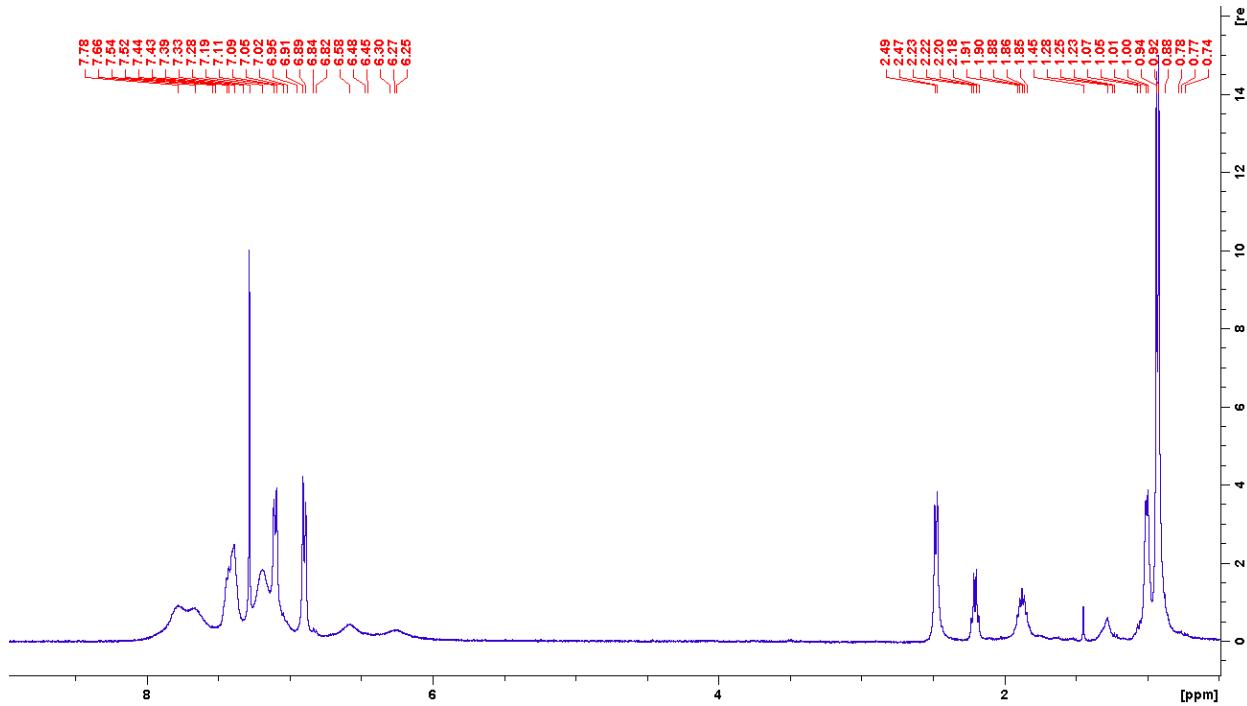


Figure S37: <sup>1</sup>H NMR of PtCl<sub>2</sub>(17c) (400 MHz, CDCl<sub>3</sub>)

## 12- Phosphine selenide compounds

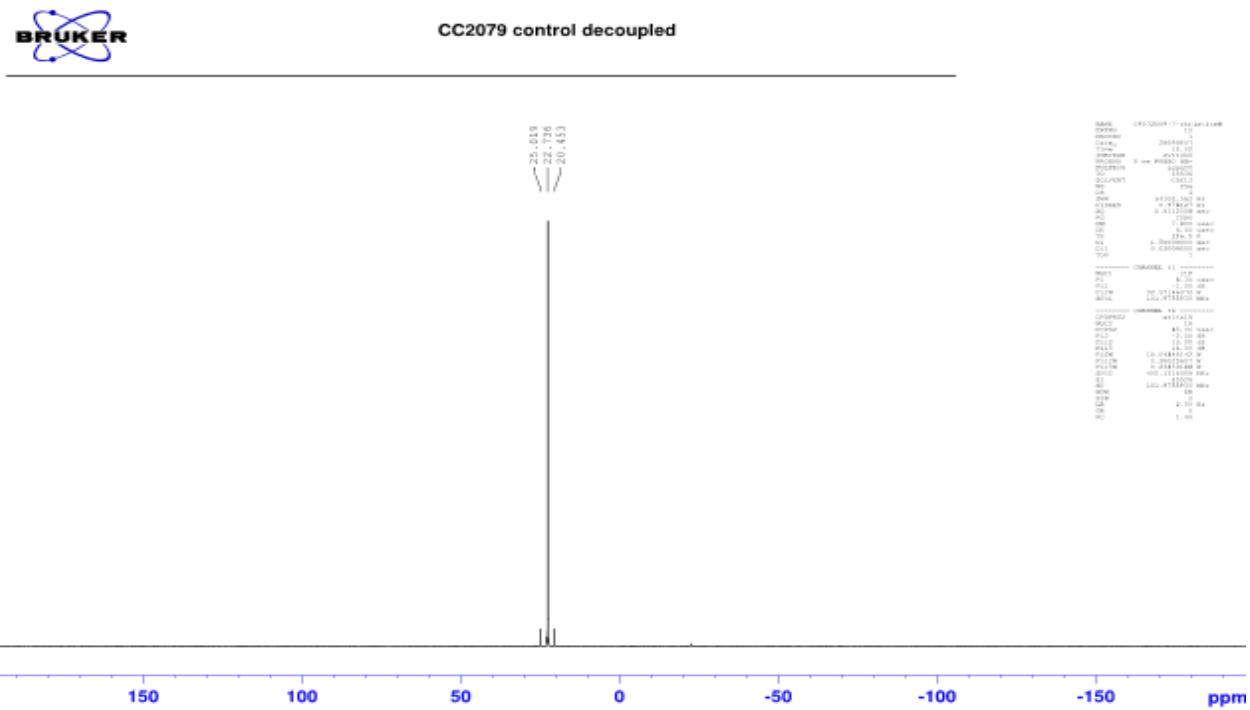
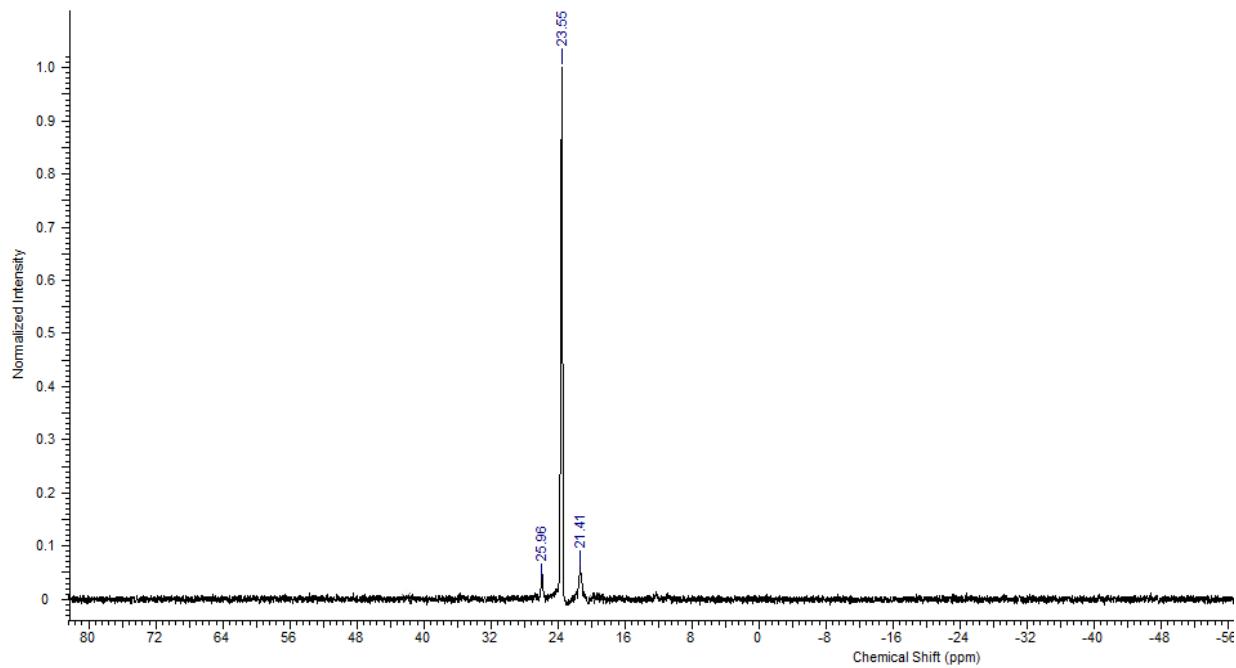
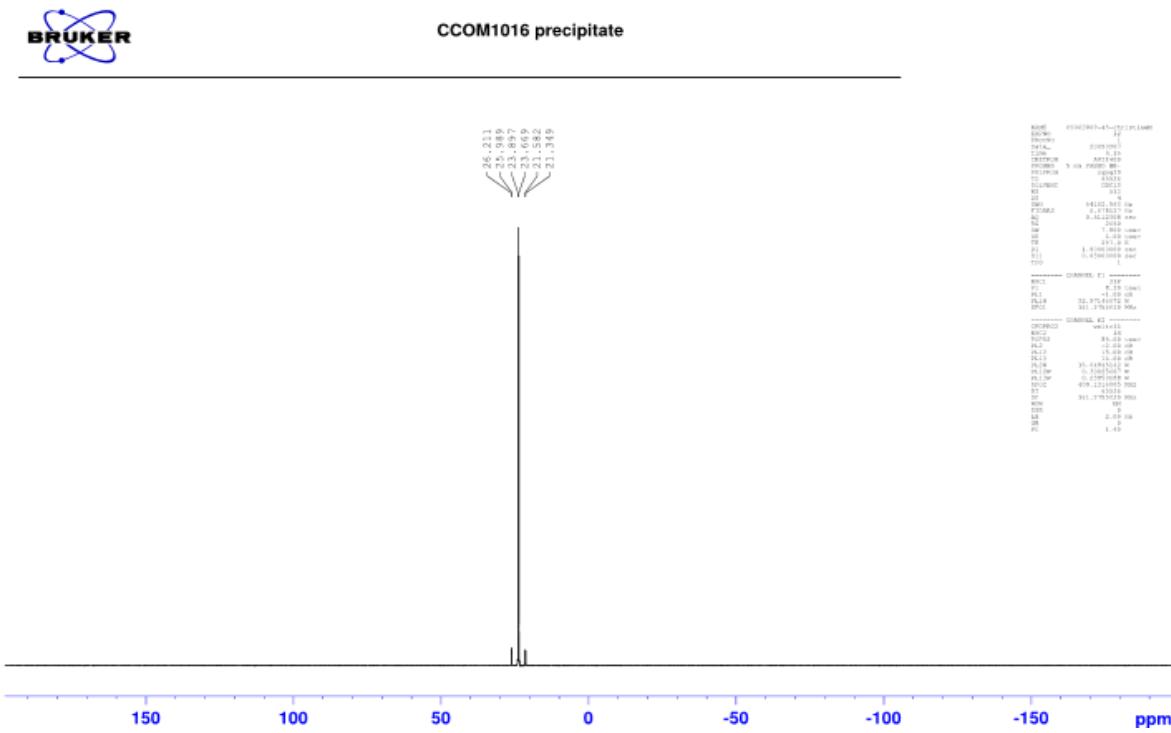


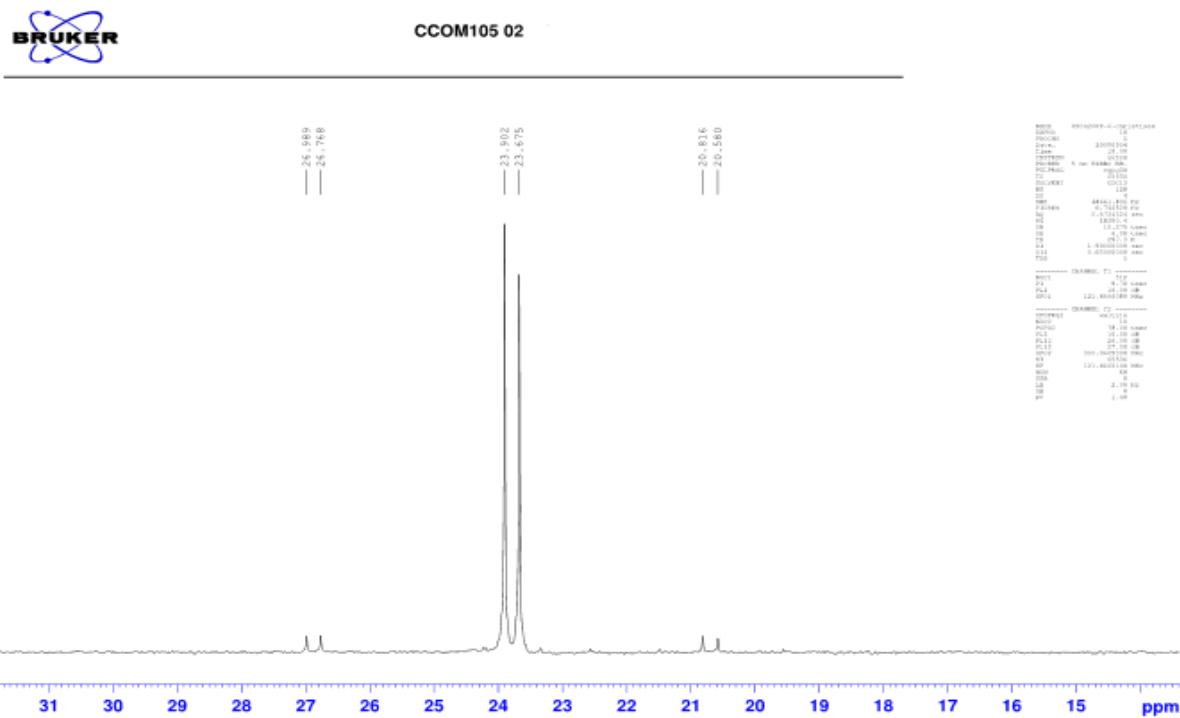
Figure S38      $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of diselenide of 15 (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



**Figure S39**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of diselenide of **17a** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

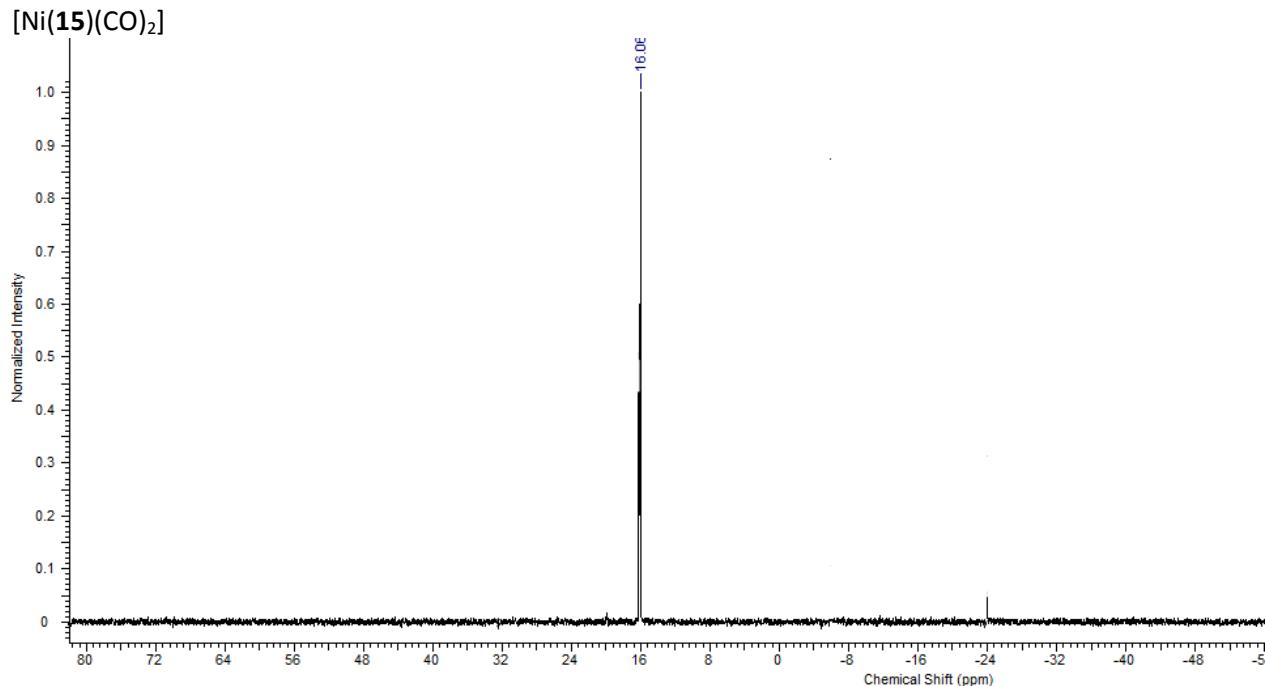


**Figure S40**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of diselenide of **17b** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

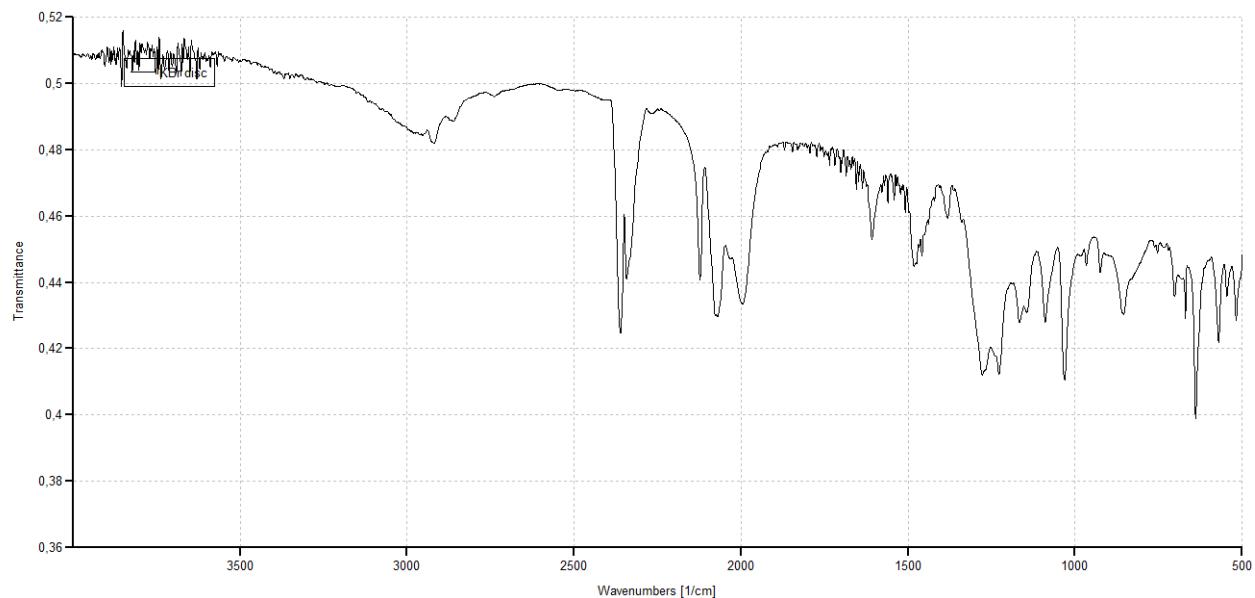


**Figure S41**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of diselenide of **17c** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

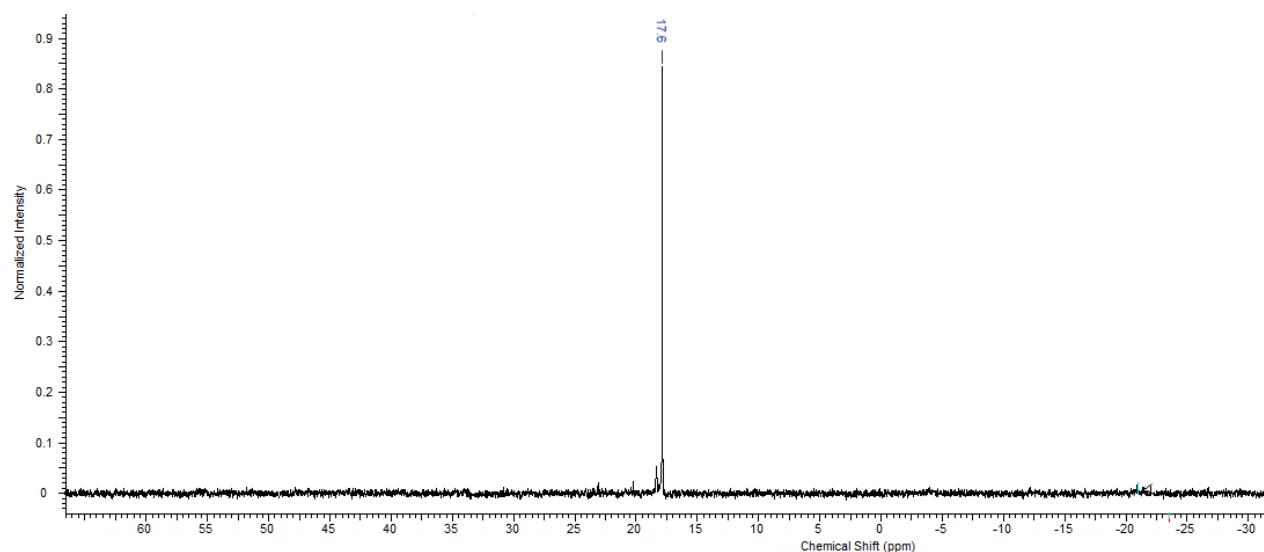
### 13- Nickel complexes



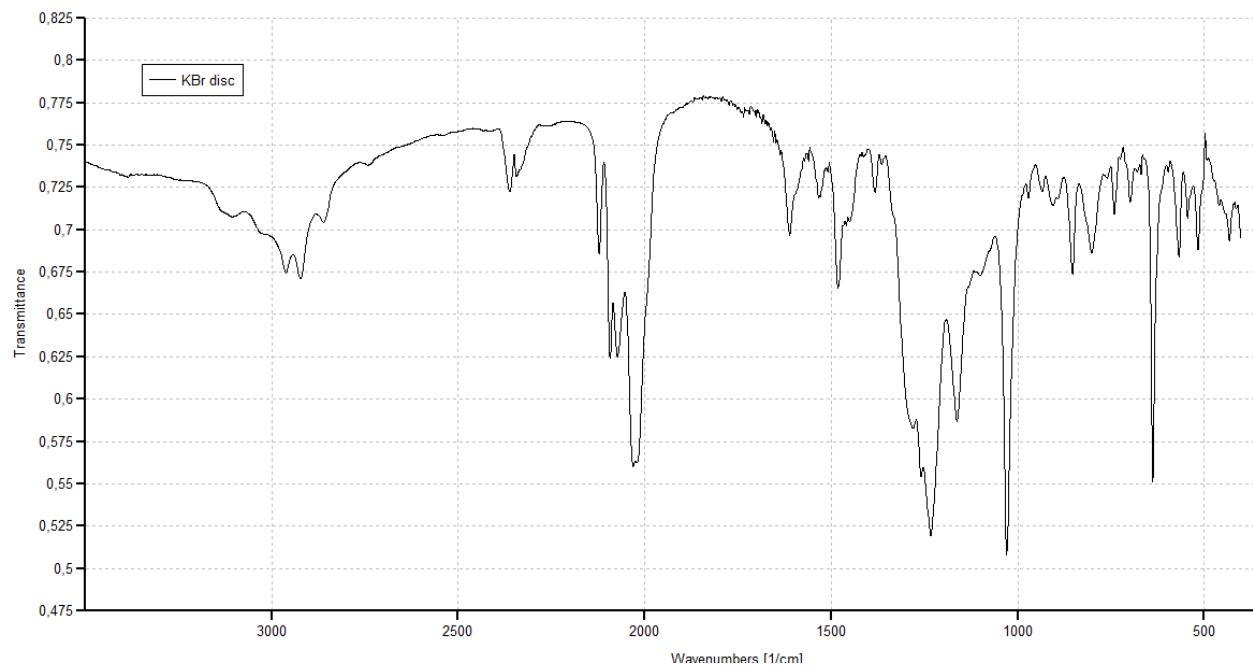
**Figure S42**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Ni}(15)(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



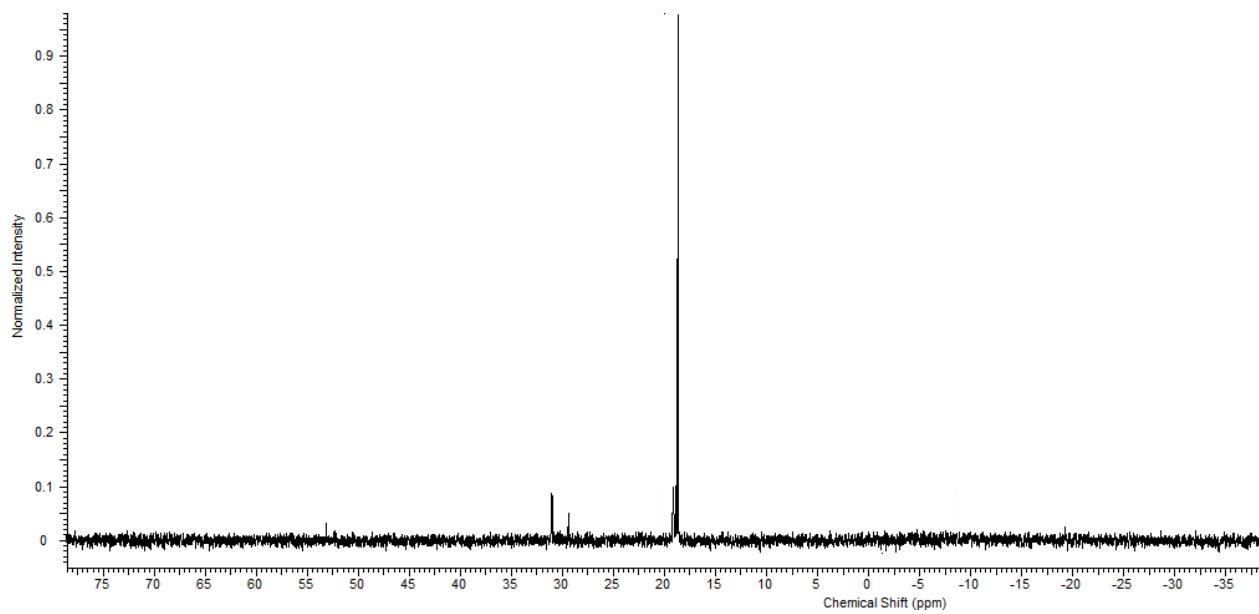
**Figure S43** IR spectrum of  $[\text{Ni}(15)(\text{CO})_2]$  (KBr)



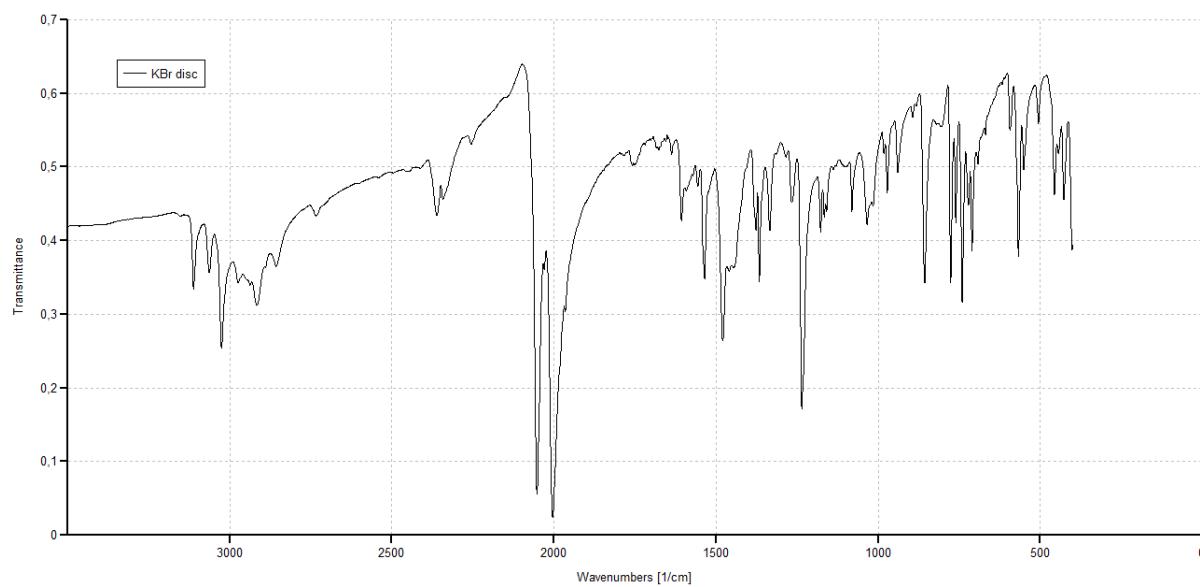
**Figure S44**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{a})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



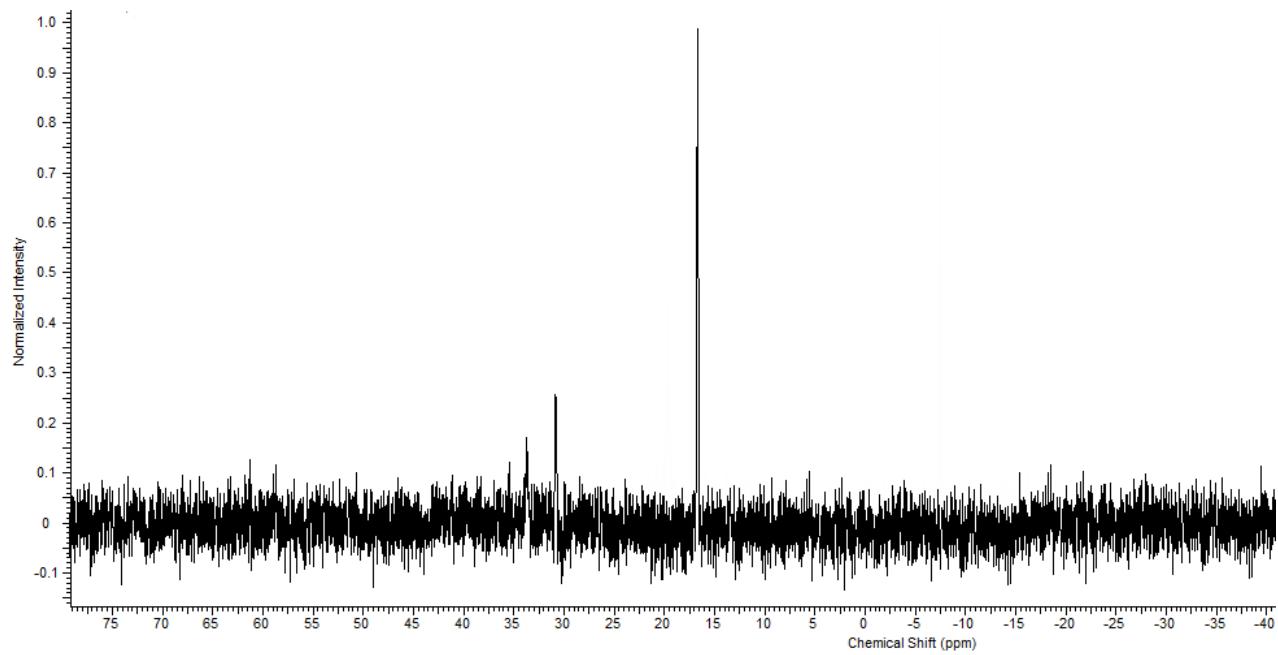
**Figure S45**      IR spectrum of  $[\text{Ni}(17\text{a})(\text{CO})_2]$  (KBr)



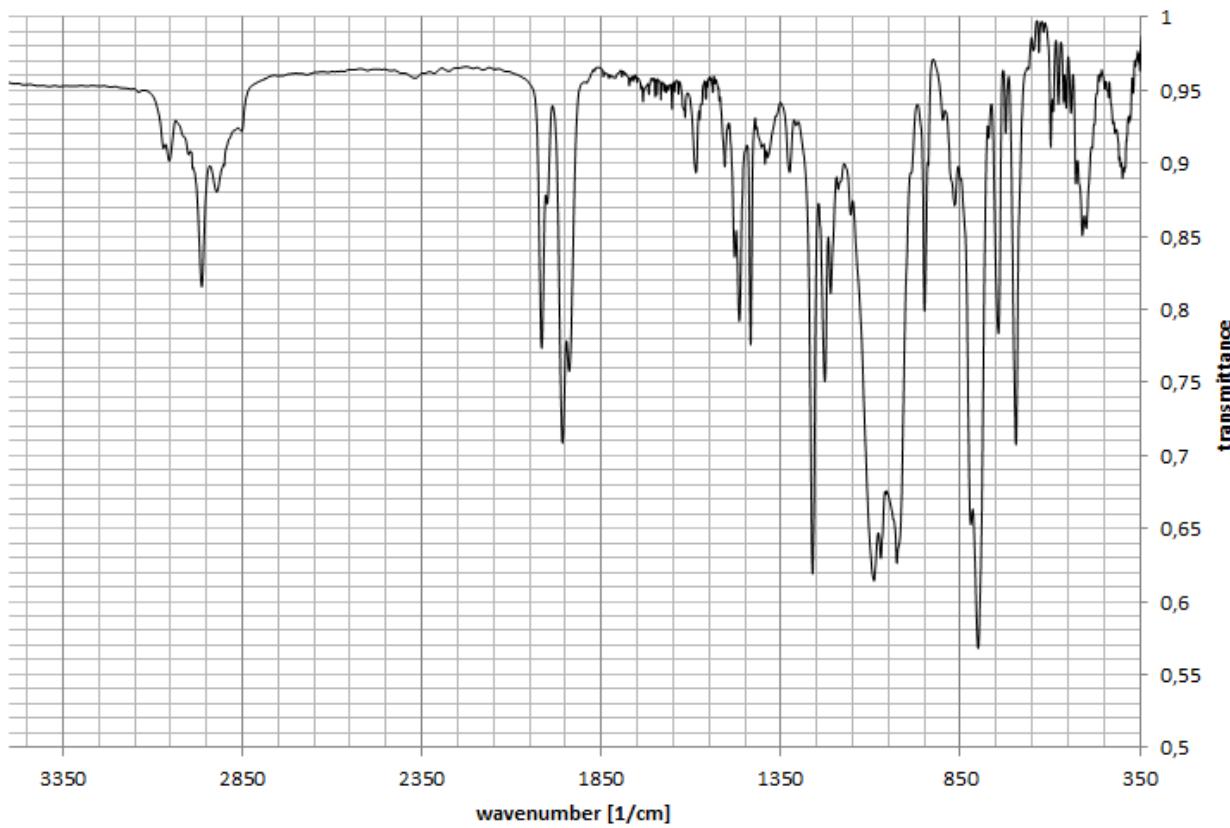
**Figure S46**       $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{b})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



**Figure S47**      IR spectrum of  $[\text{Ni}(17\text{b})(\text{CO})_2]$  (KBr)

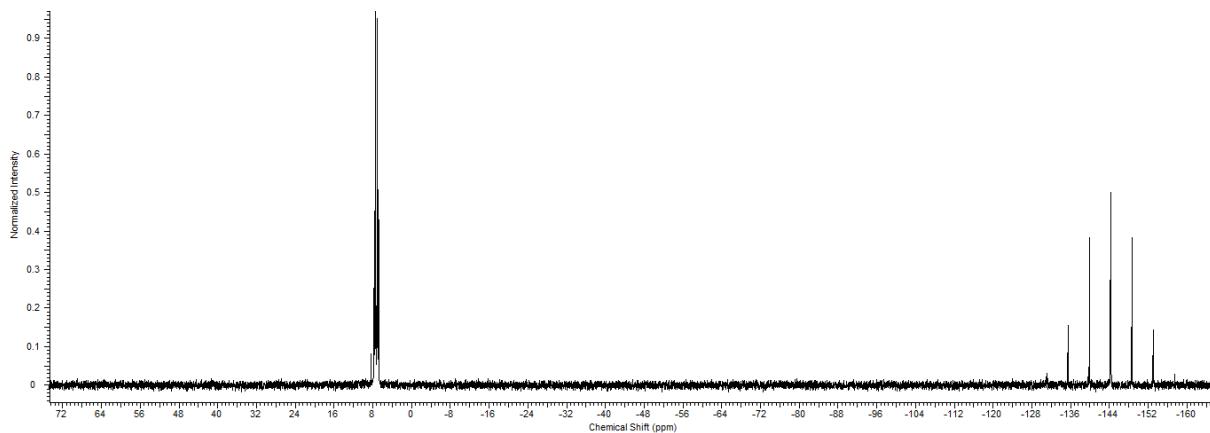


**Figure S48**       $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{c})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

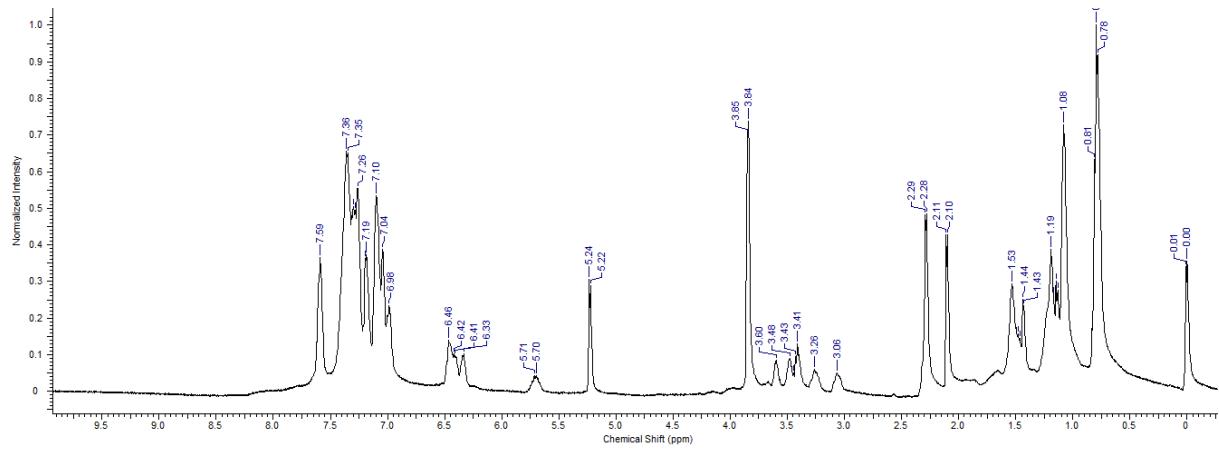


**Figure S49** IR spectrum of  $[\text{Ni}(17\text{c})(\text{CO})_2]$  (KBr)

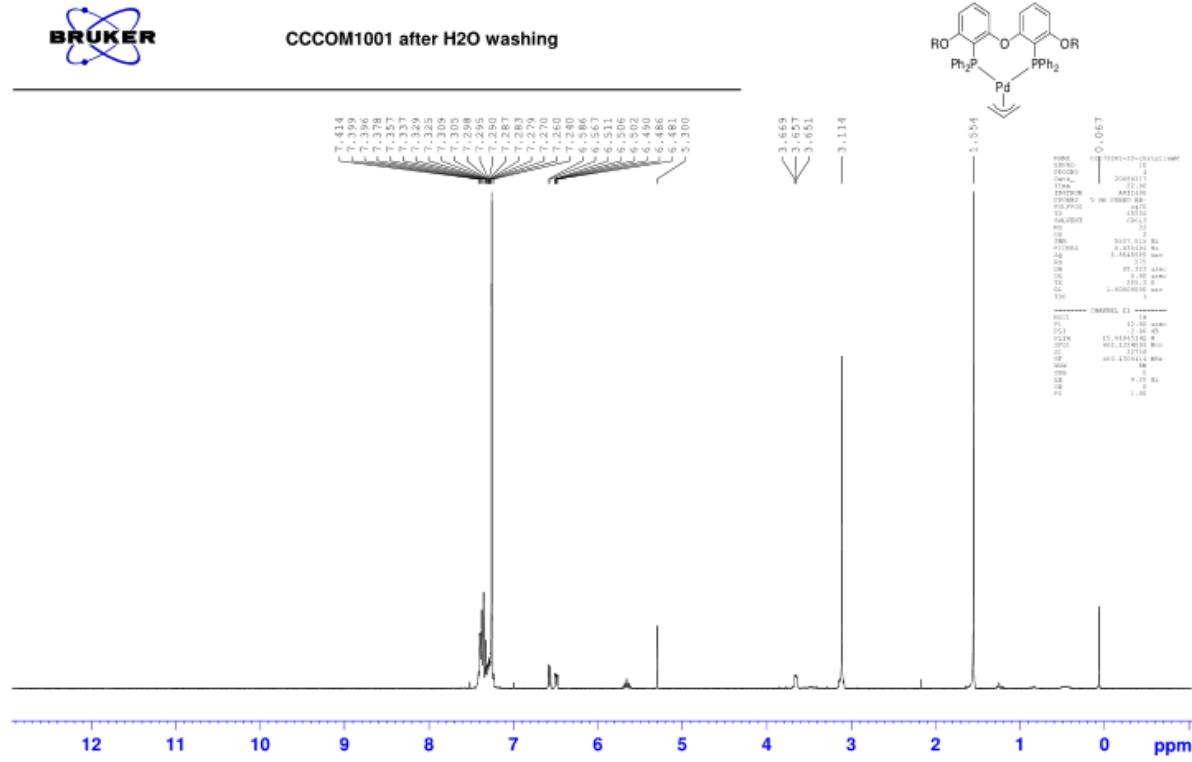
#### 14- Palladium complexes



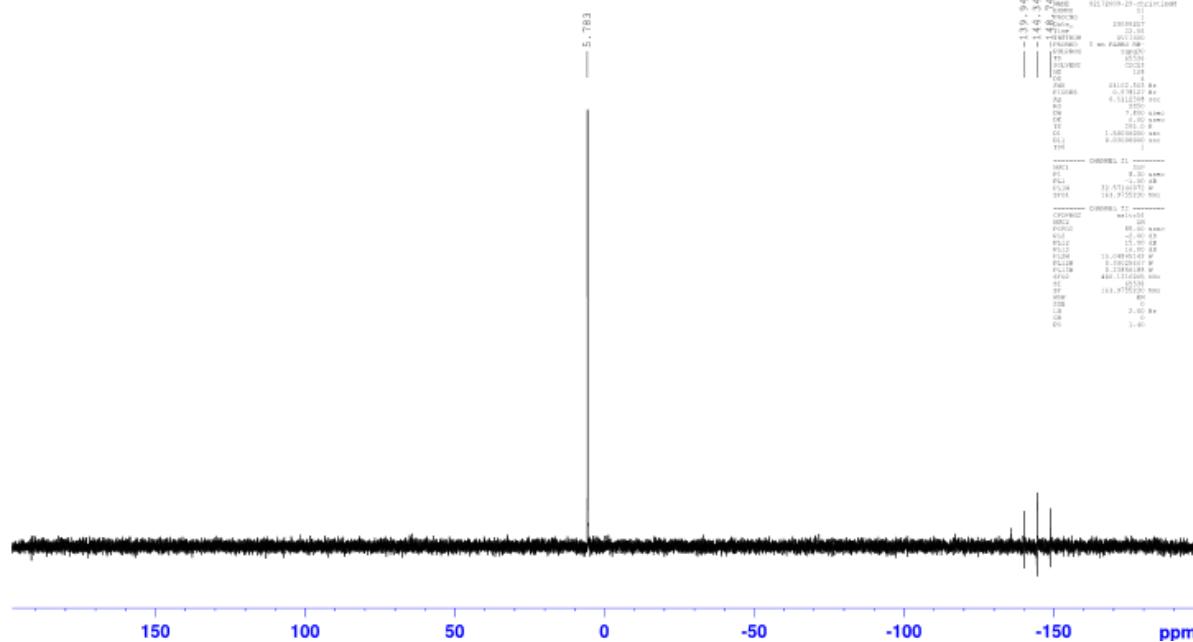
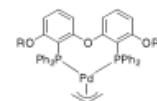
**Figure S50**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(14)]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



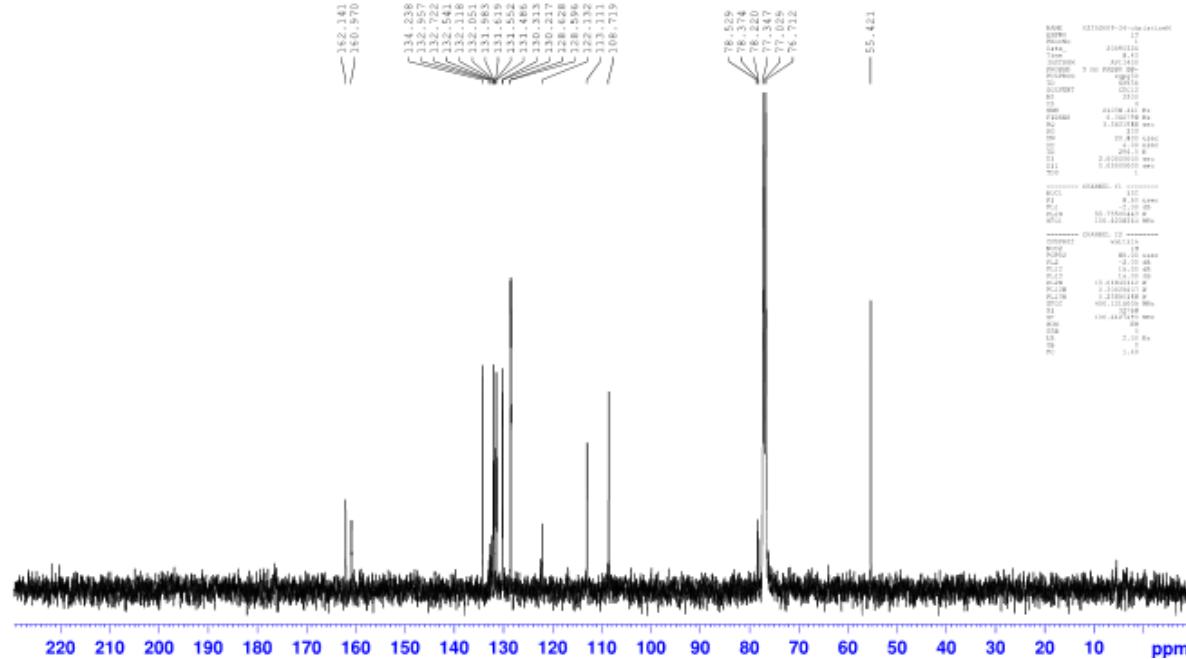
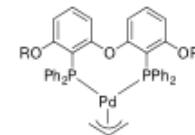
**Figure S51** <sup>1</sup>H NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(14)]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



**Figure S52** <sup>1</sup>H NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

CCCOM1001 after H<sub>2</sub>O washingFigure S53      $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$  (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

CCCOM1001

Figure S54      $^{13}\text{C}\{\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(15)]^+$  (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

**BRUKER**

CCCOM1004 after washing with H<sub>2</sub>O

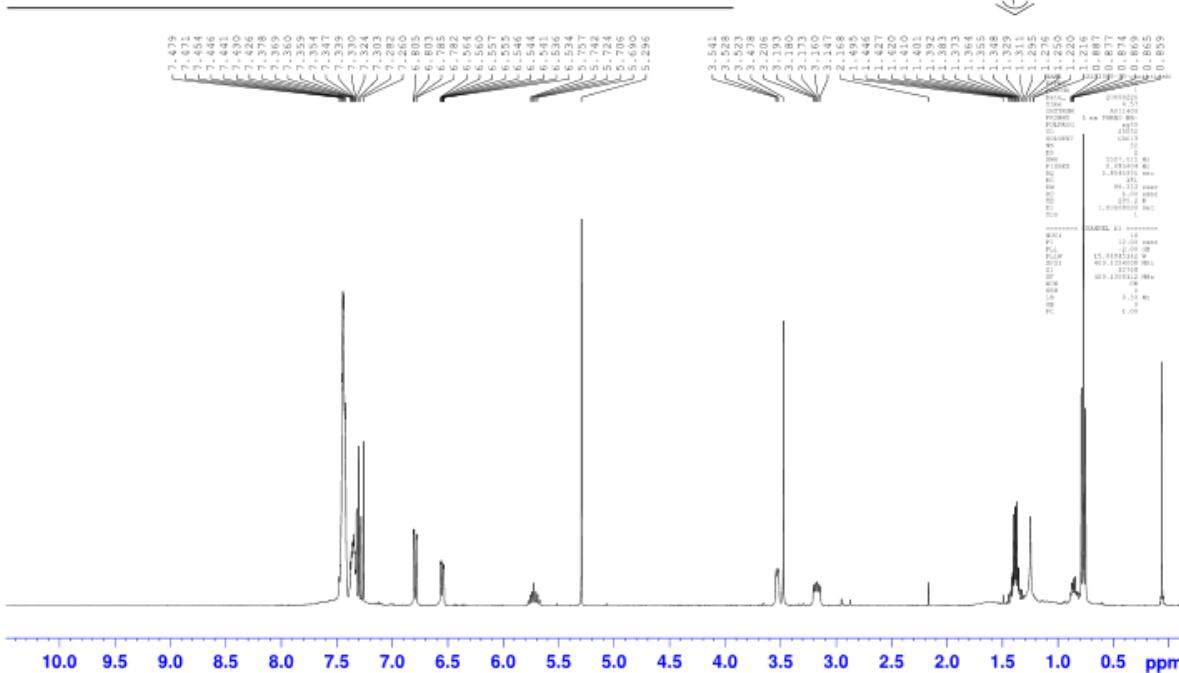
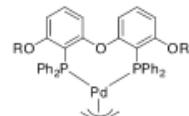


Figure S55 <sup>1</sup>H NMR spectrum of [Pd( $\eta^3$ -allyl)(17a)]<sup>+</sup> (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

**BRUKER**

CCCOM1004 after washing with H<sub>2</sub>O

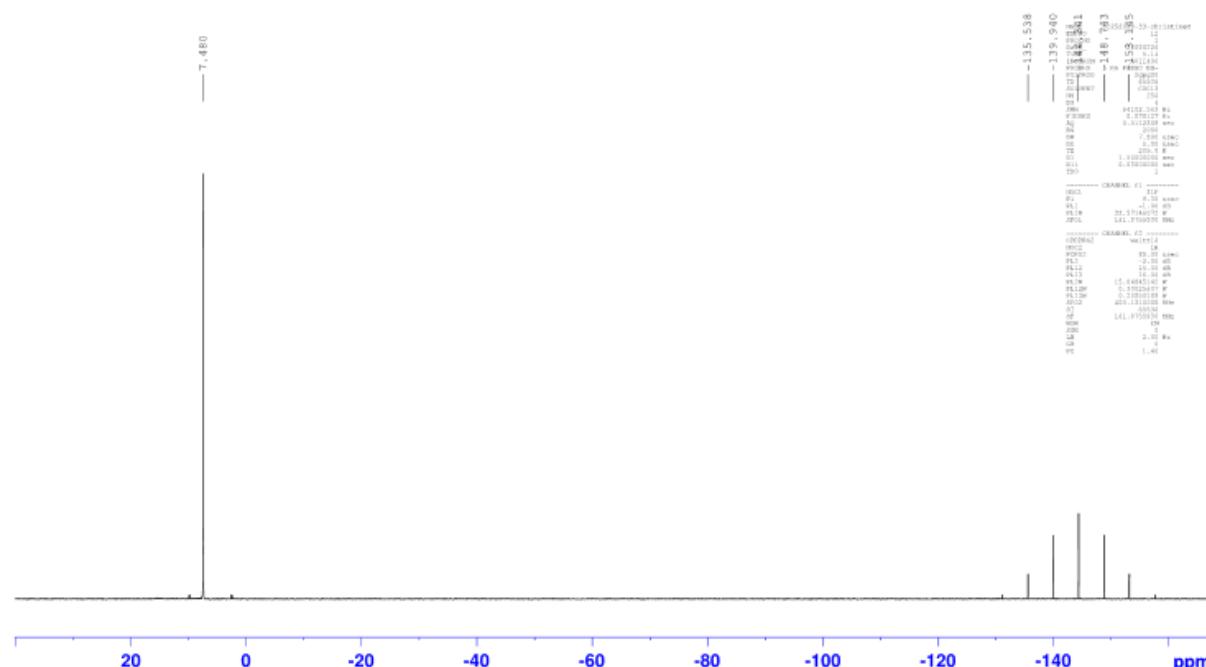
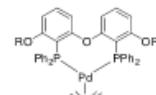


Figure S56 <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [Pd( $\eta^3$ -allyl)(17a)]<sup>+</sup> (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



1H Standard Sweep Width - 8 Scans  
13 ppm to -1 ppm

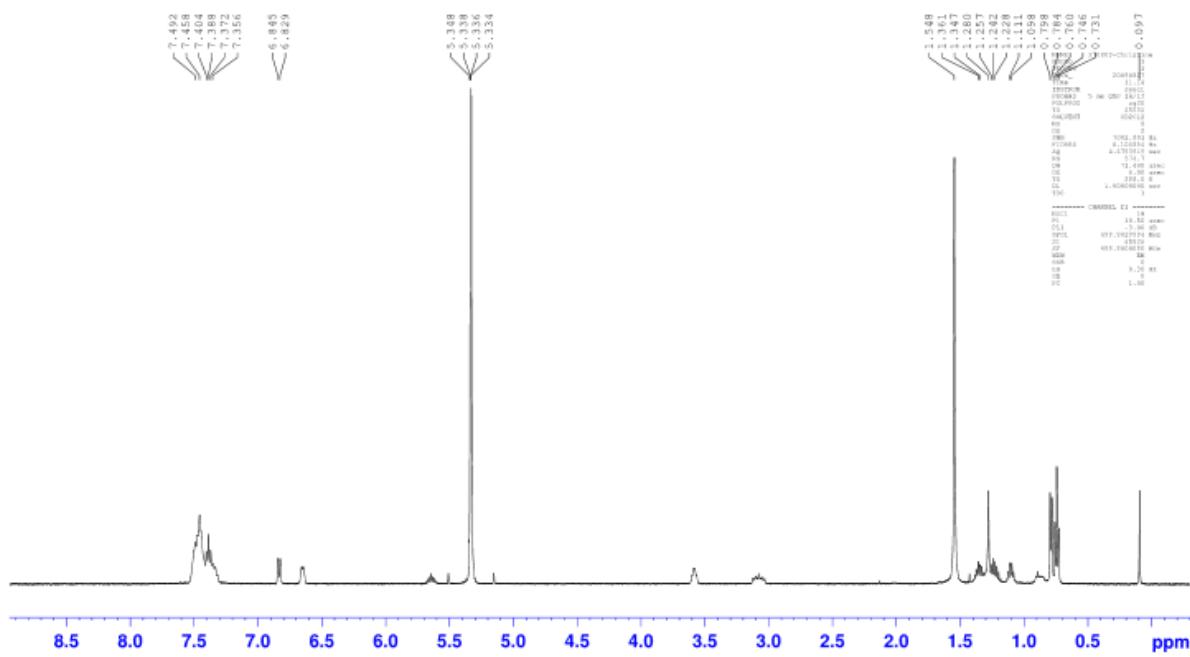
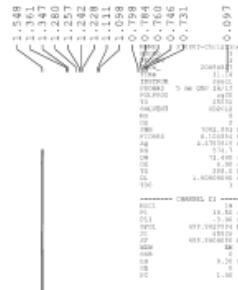
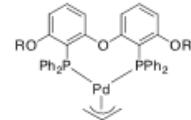


Figure S57  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{b})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



31P Standard Sweep Width - 1h Decoupled - 64 Scans  
200 ppm to -200 ppm

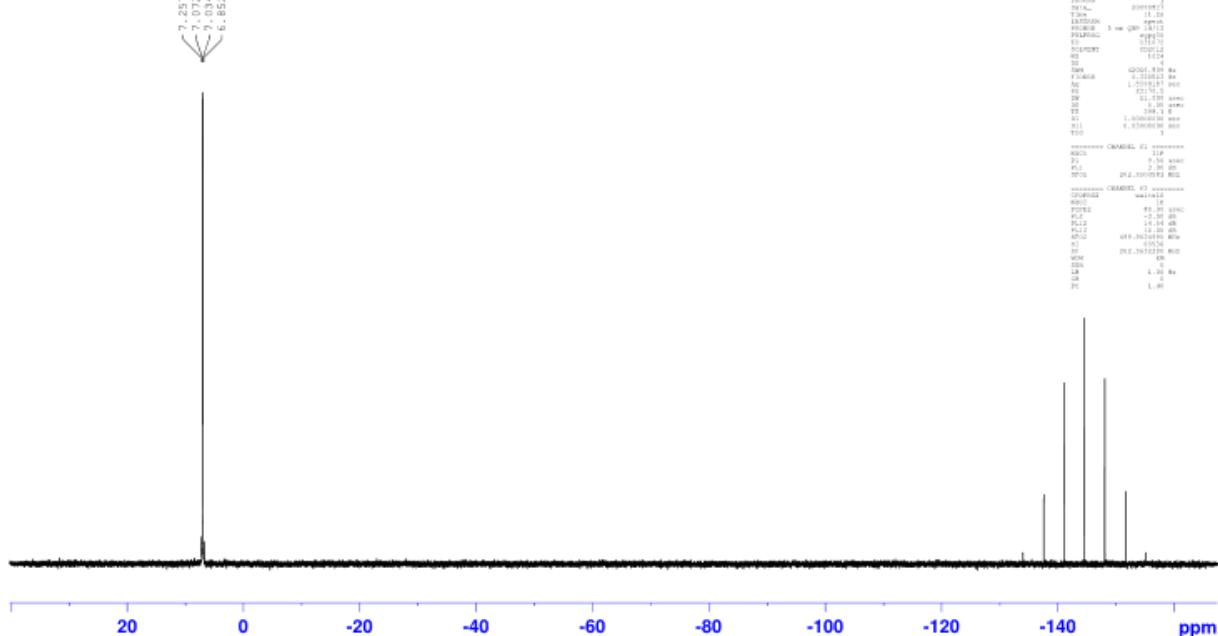
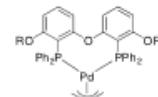


Figure S58  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{b})]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

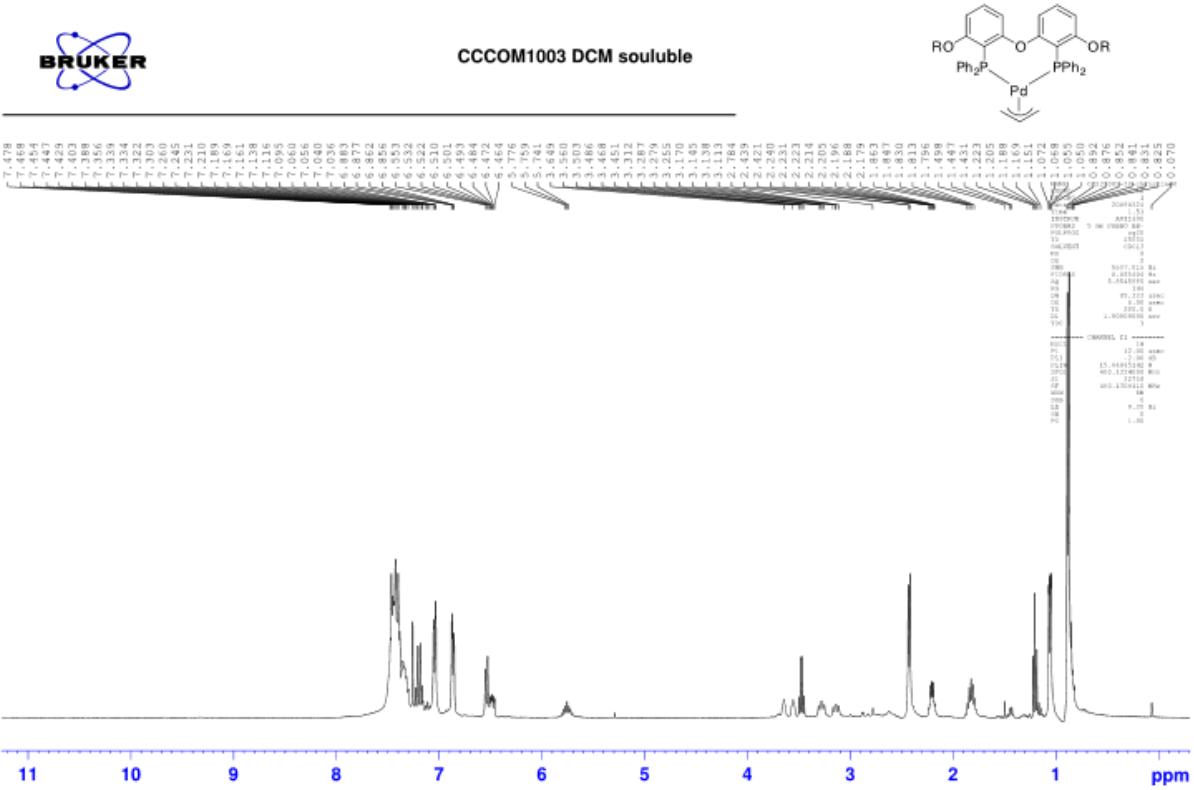


Figure S59       $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{c})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

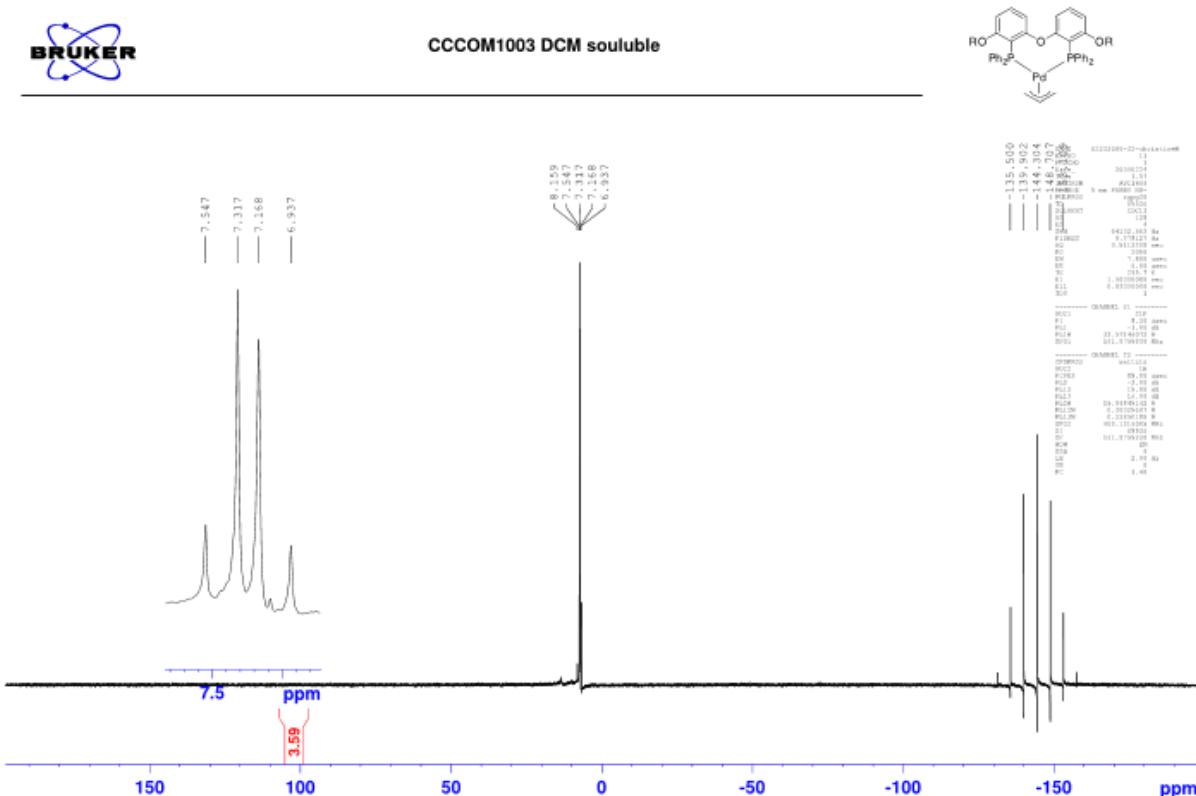
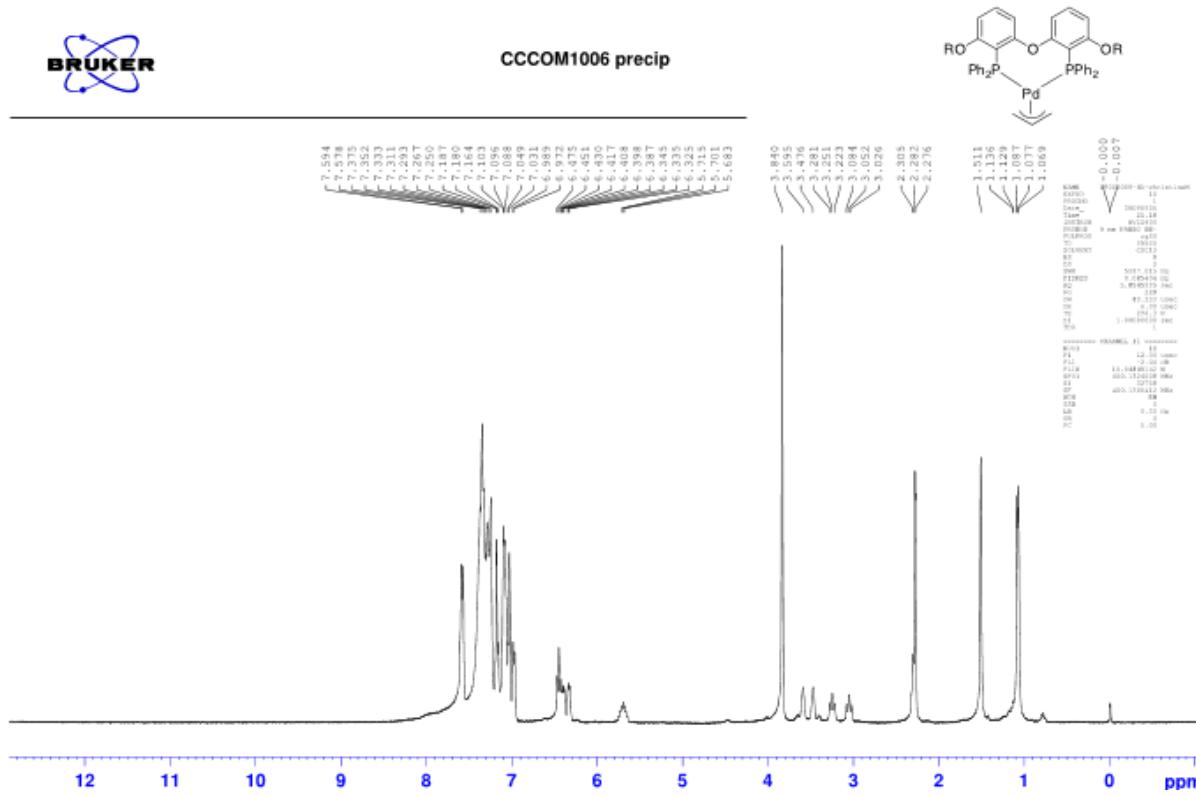
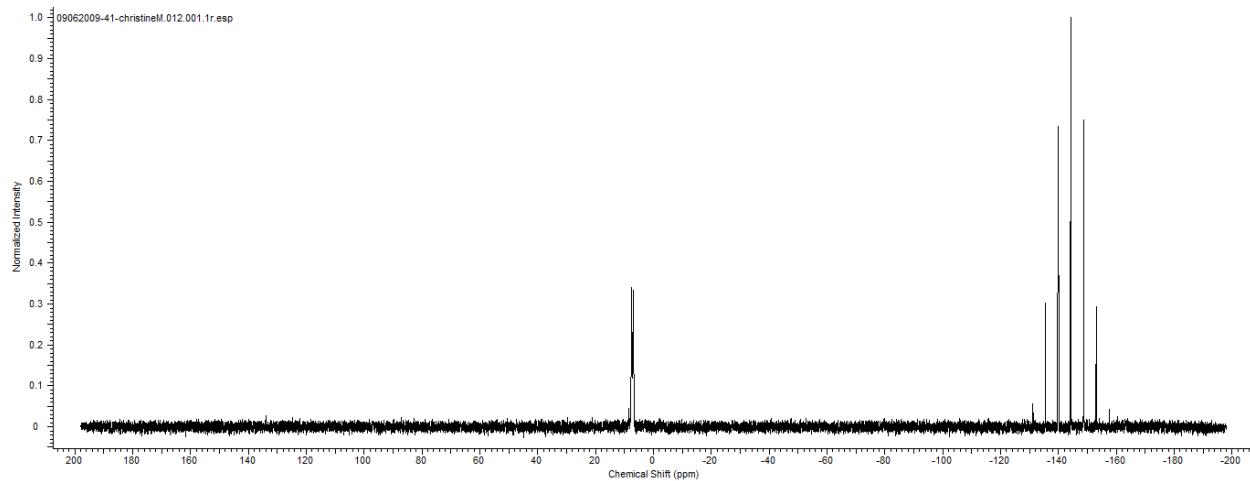


Figure S60       $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{c})]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

**BRUKER**



**Figure S61**  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{d})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



**Figure S62**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{d})]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)