

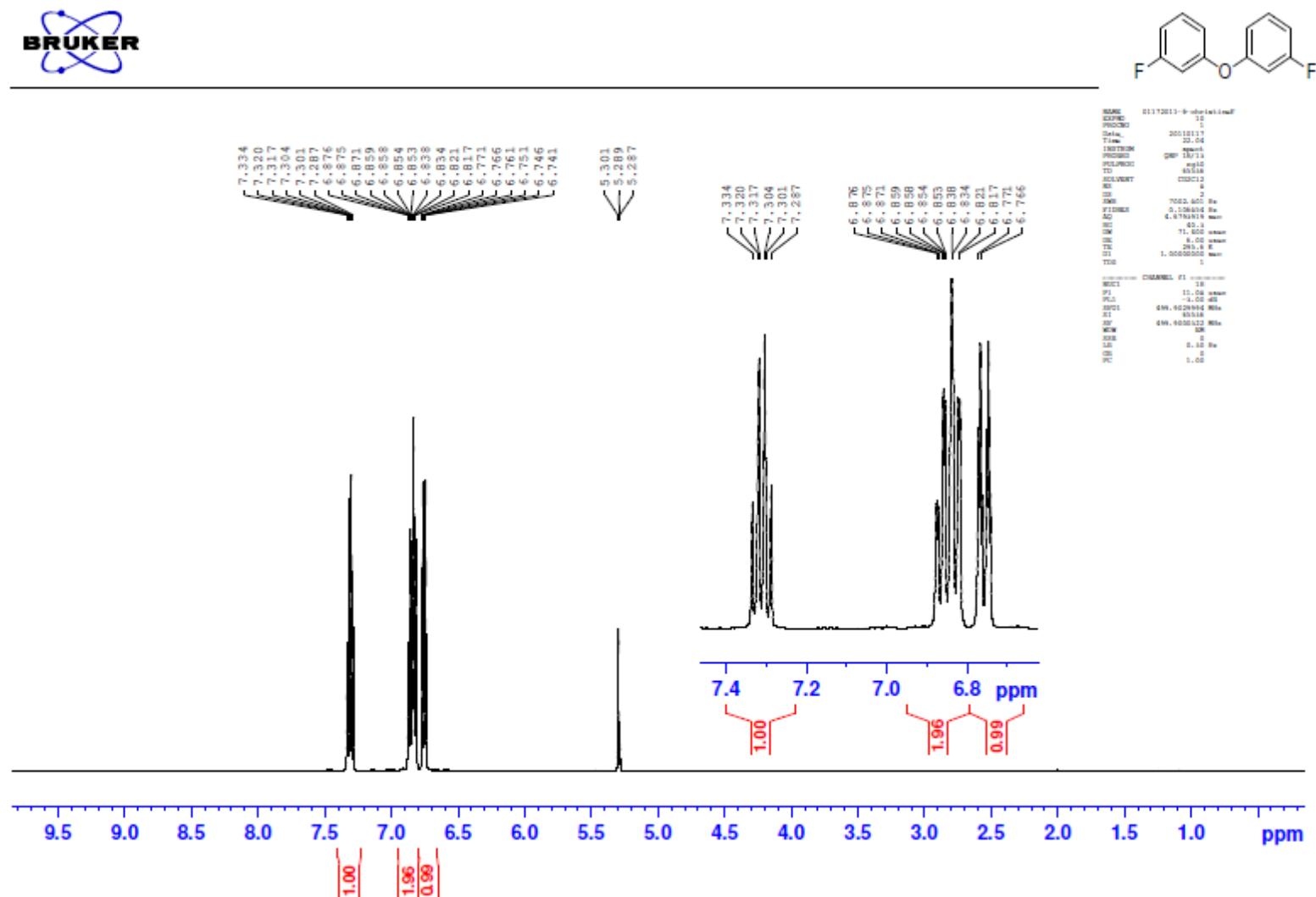
## Supporting Information

### 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

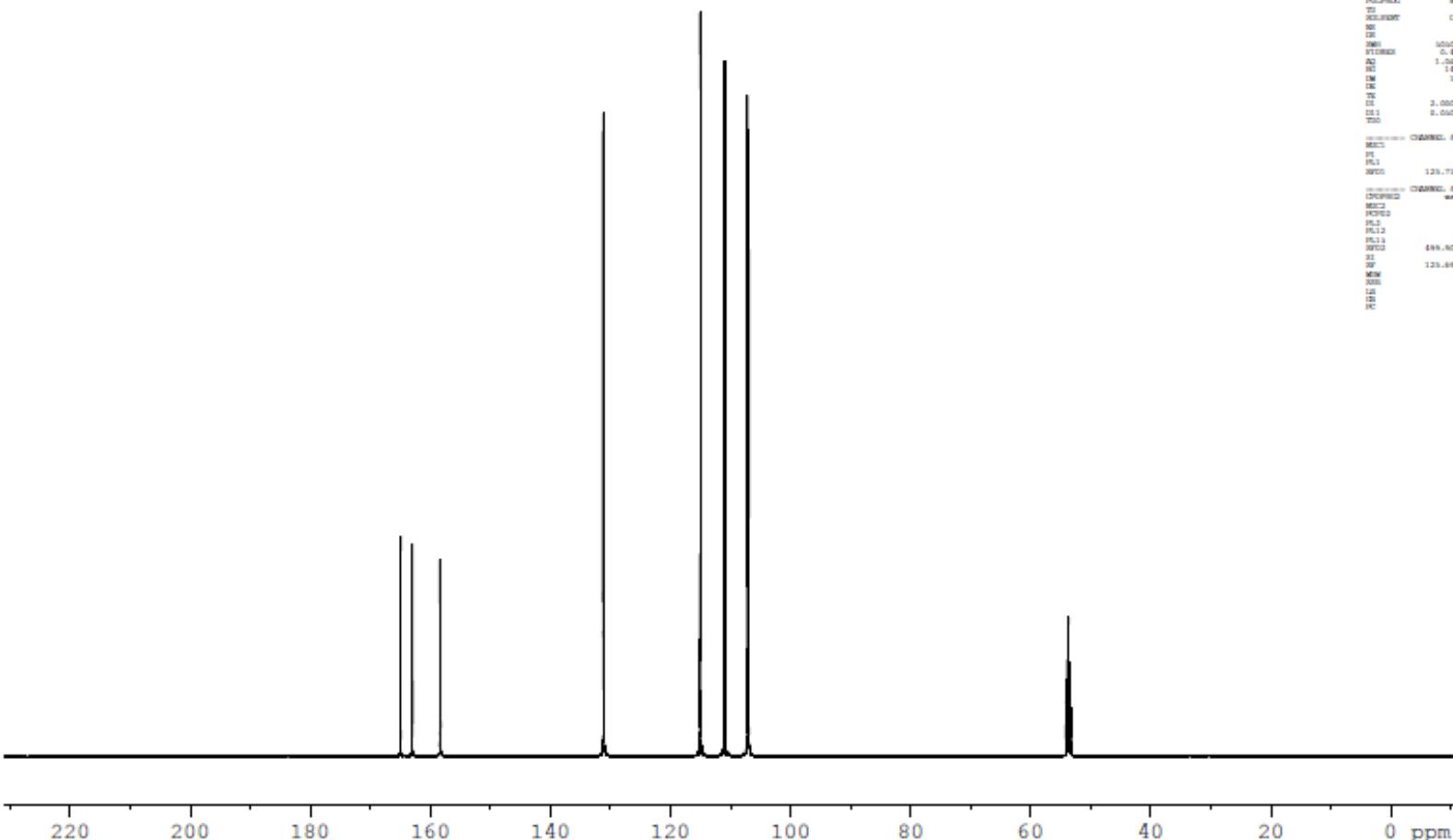
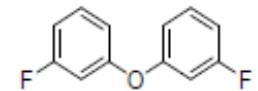
## 1- Compound 11F



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



CC5077



**Figure S2**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound 11F (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 295 K)



CC5077

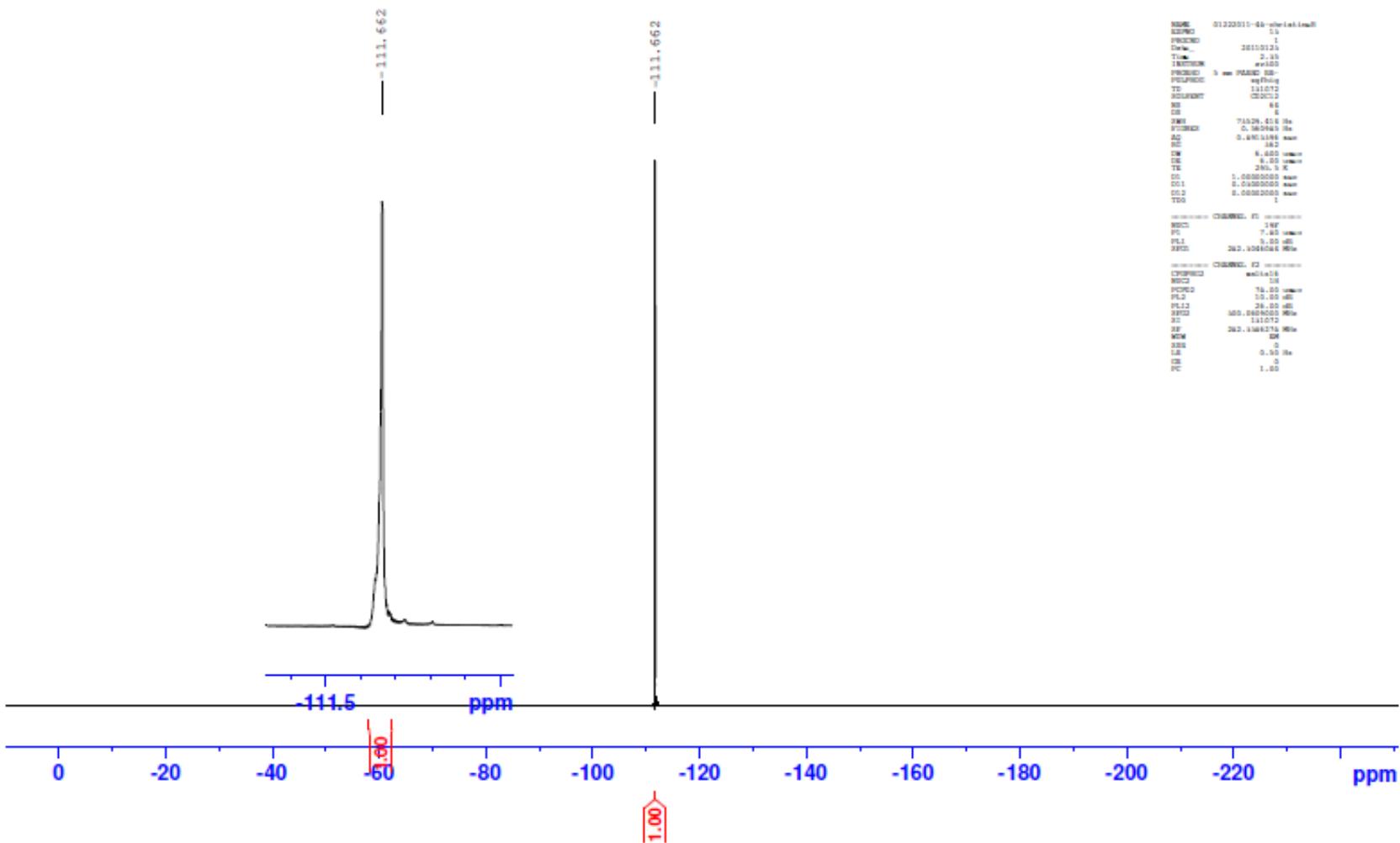
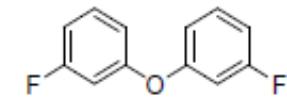


Figure S3 <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of compound 11F (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)

2- Compound 11OMe

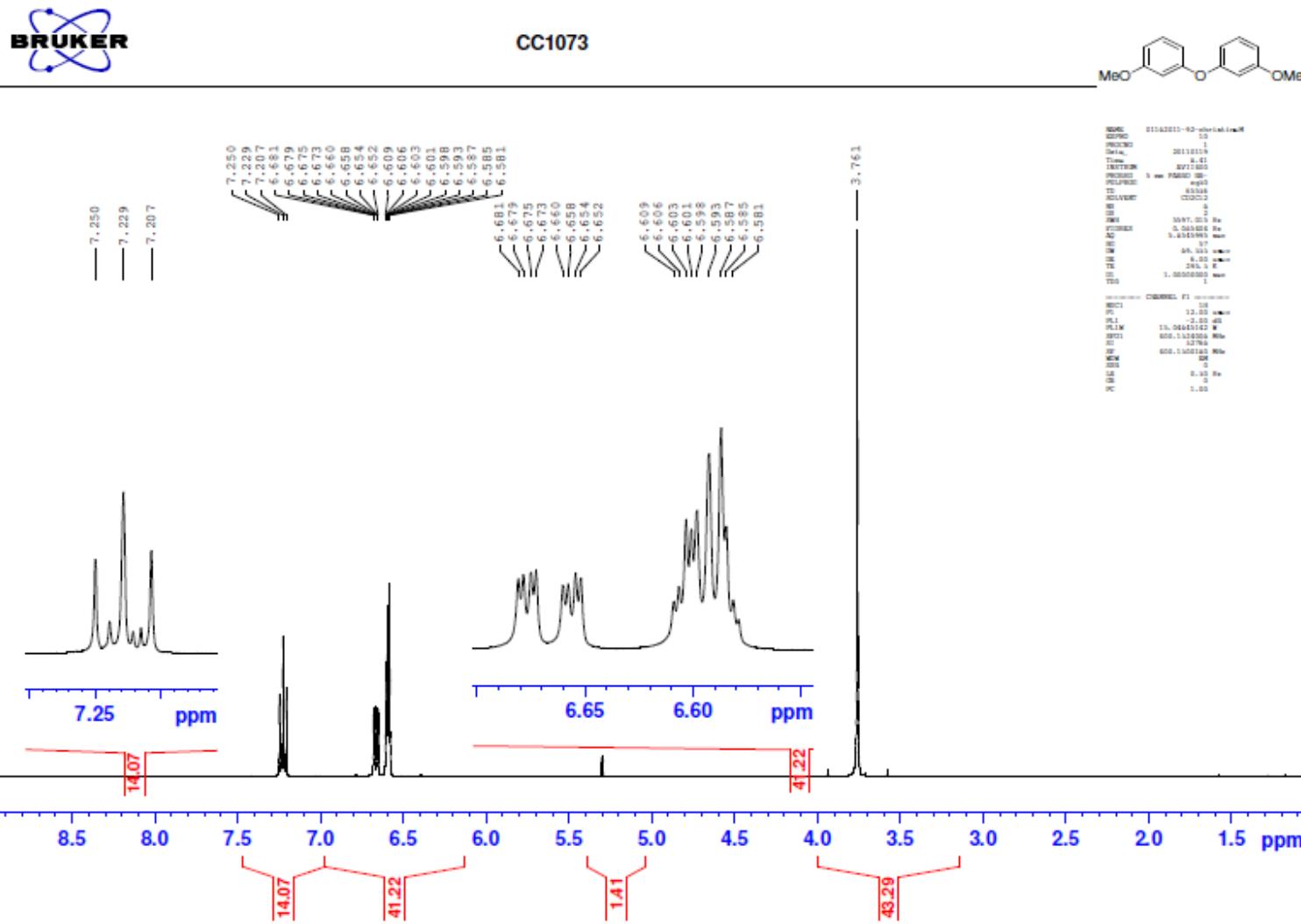
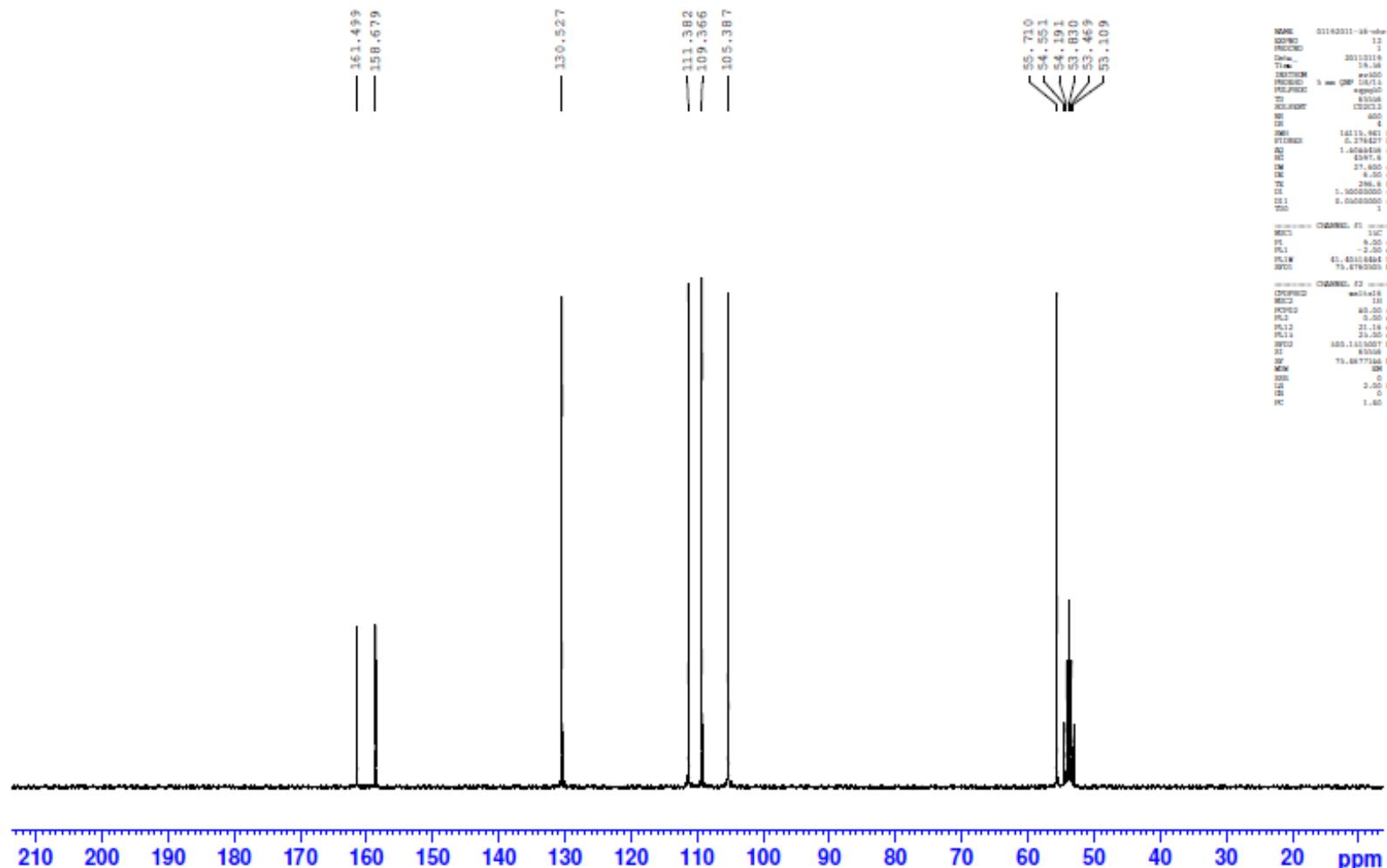
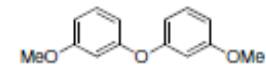


Figure S4 <sup>1</sup>H NMR spectrum of compound 11OMe (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)



CC1073





CC1073

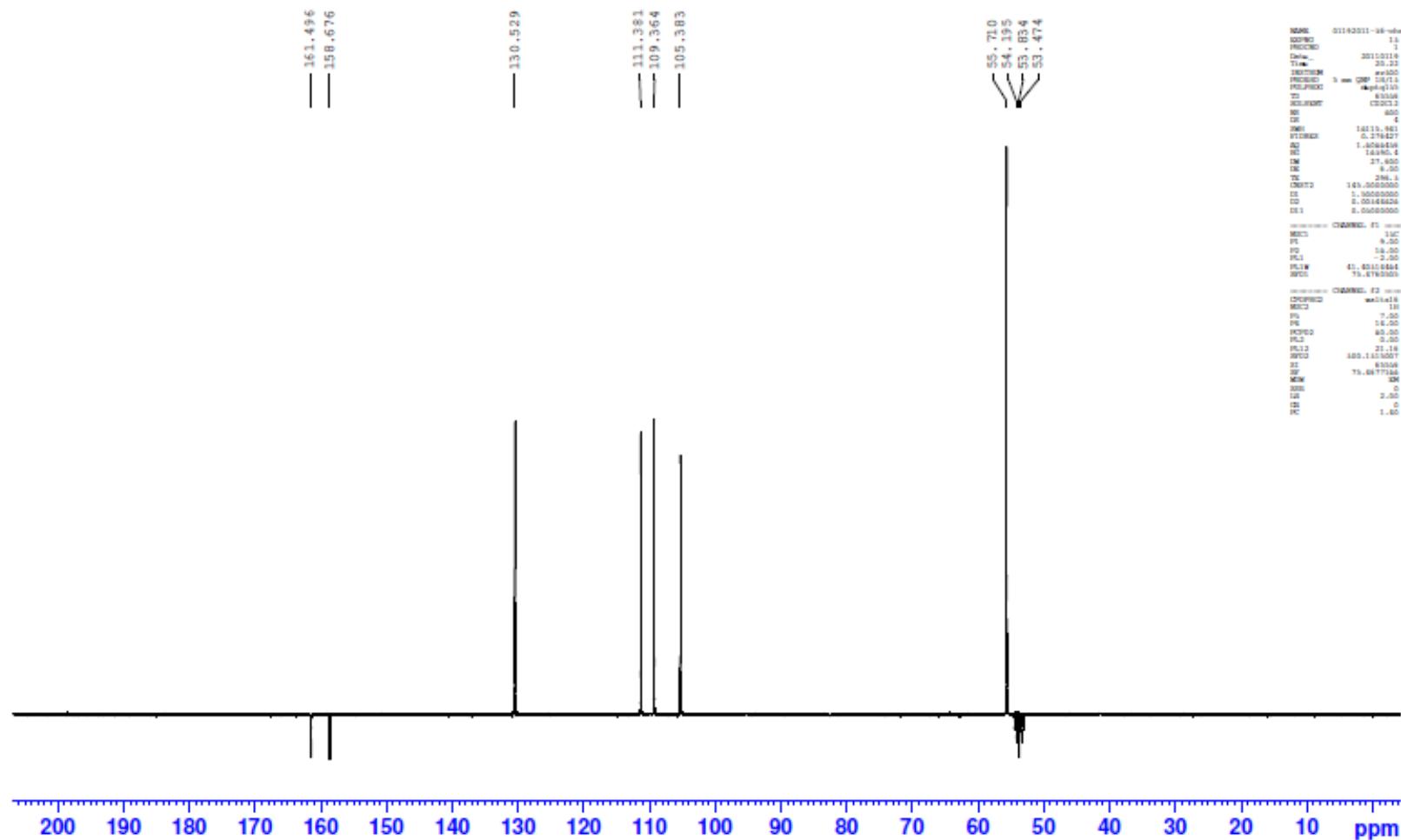
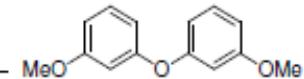


Figure S6 <sup>13</sup>C APT NMR spectrum of compound 11OMe (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)

3- Compound 12

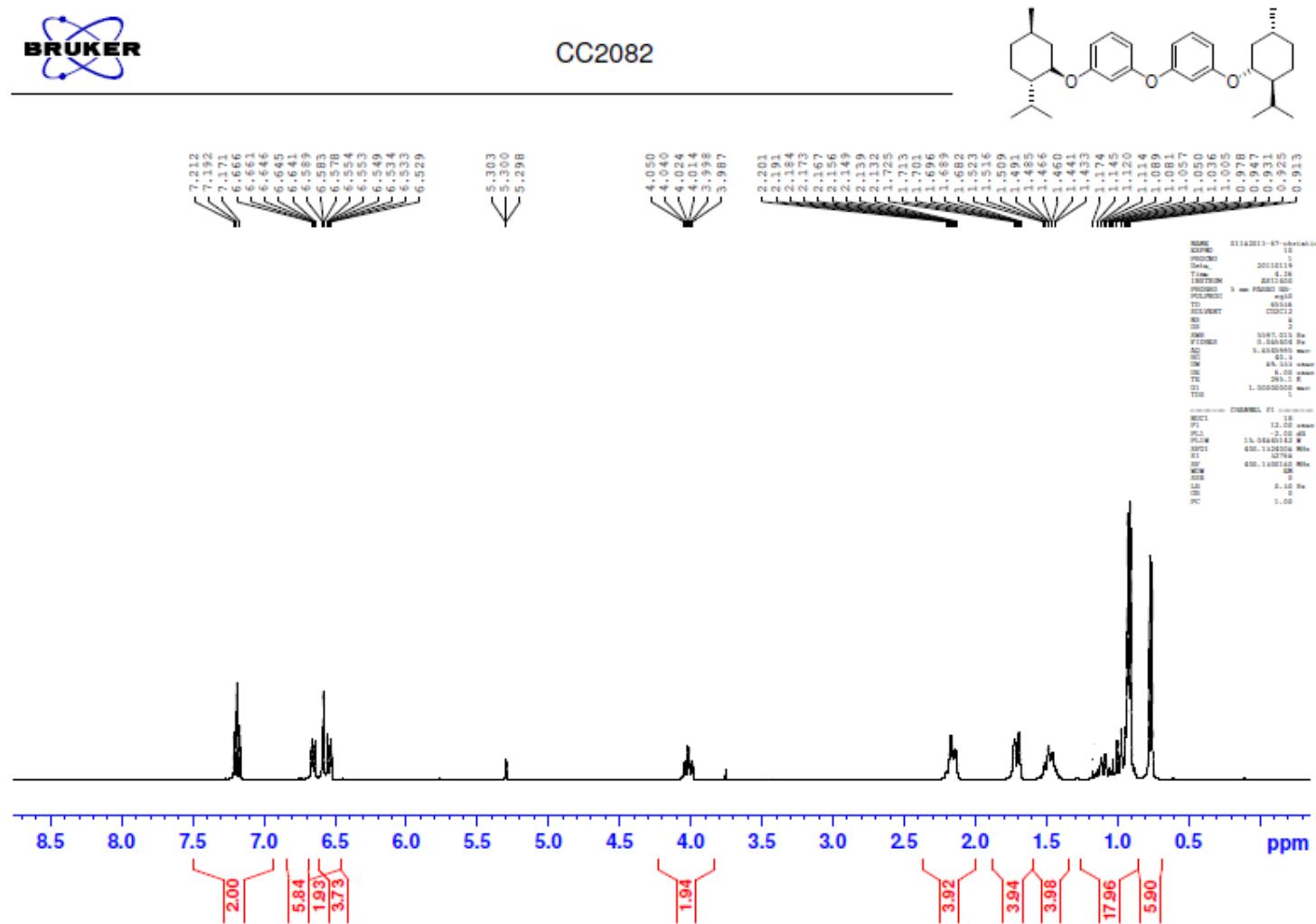
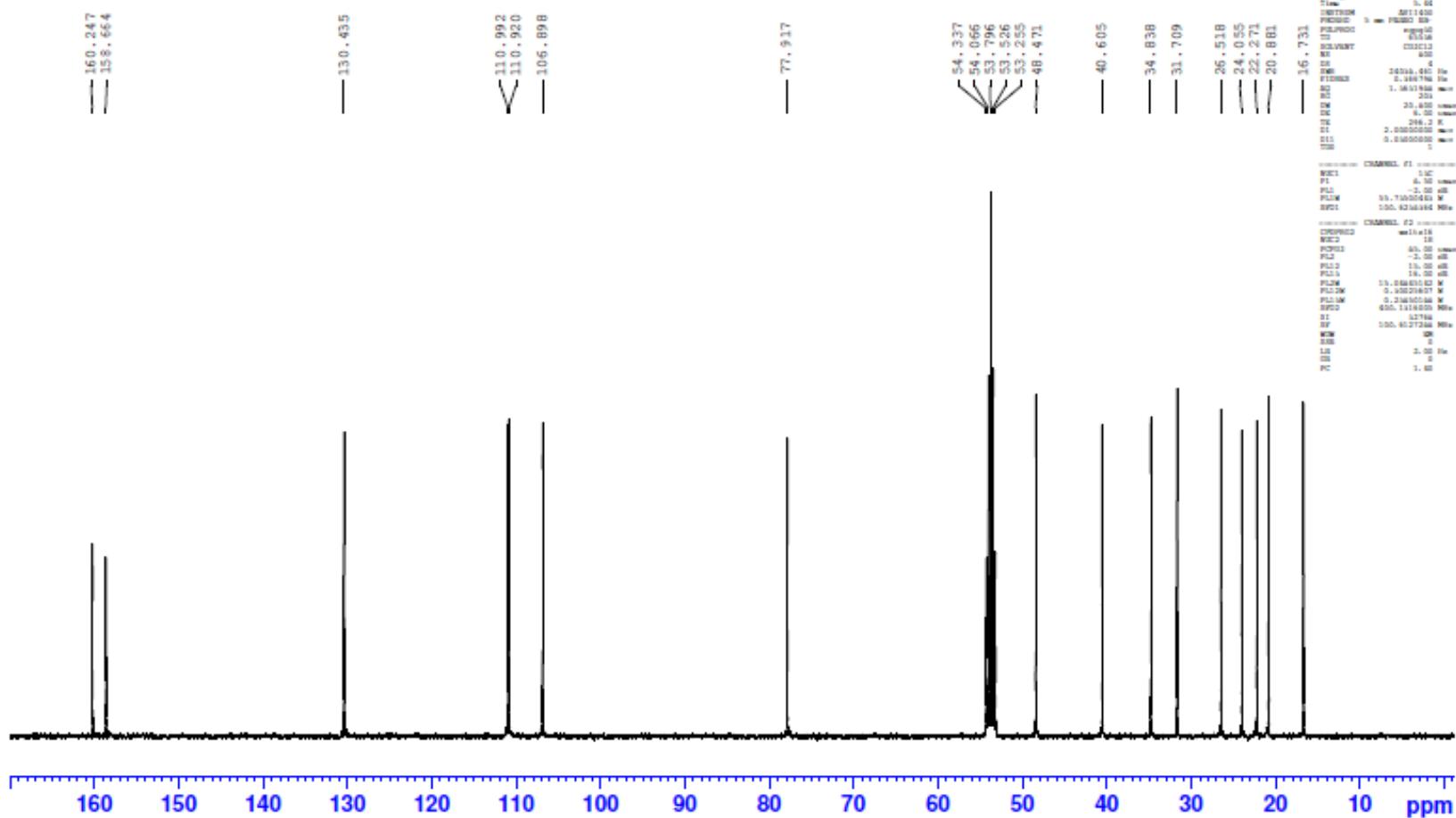


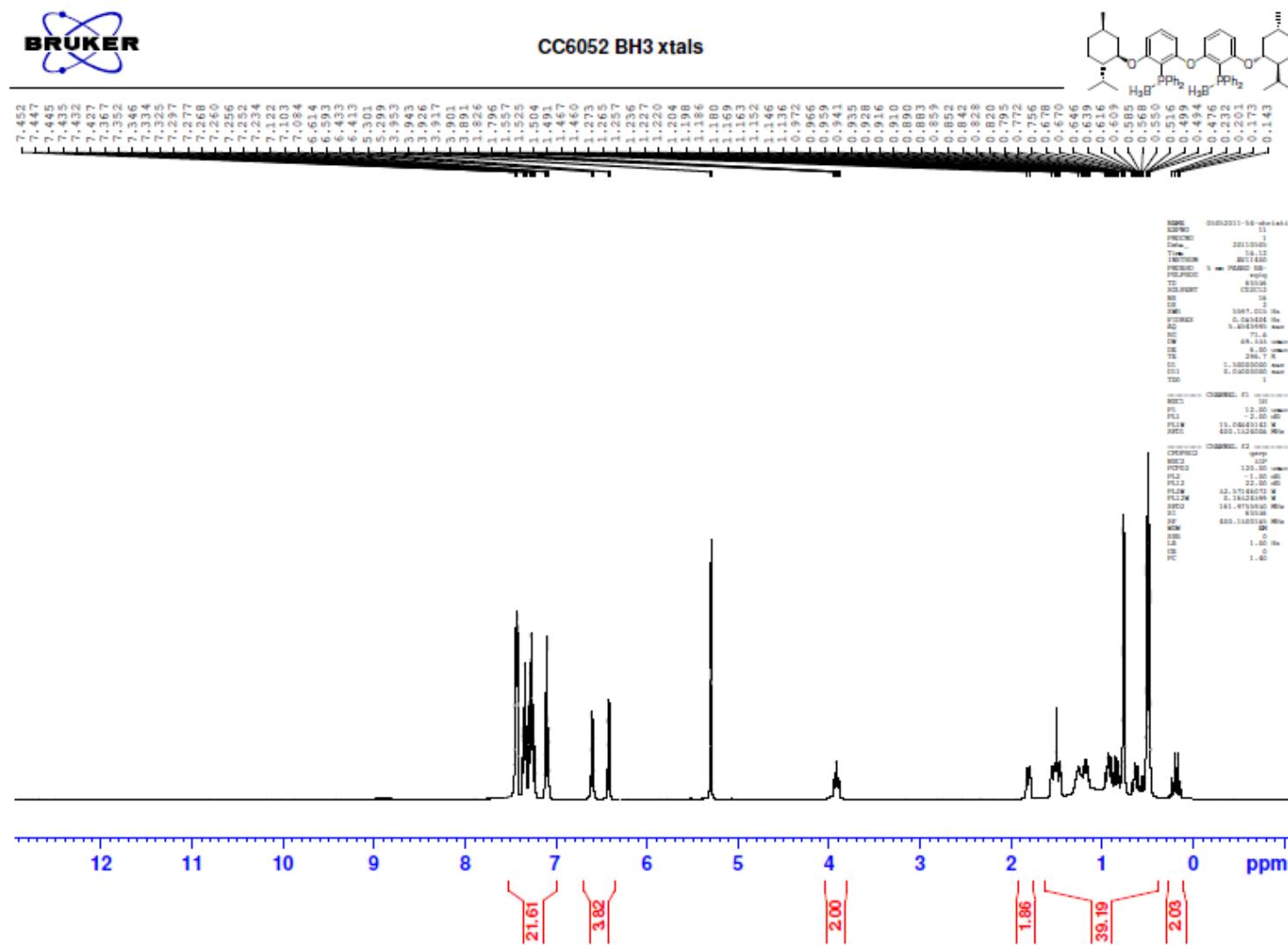
Figure S7      <sup>1</sup>H NMR spectrum of compound 12 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 295 K)



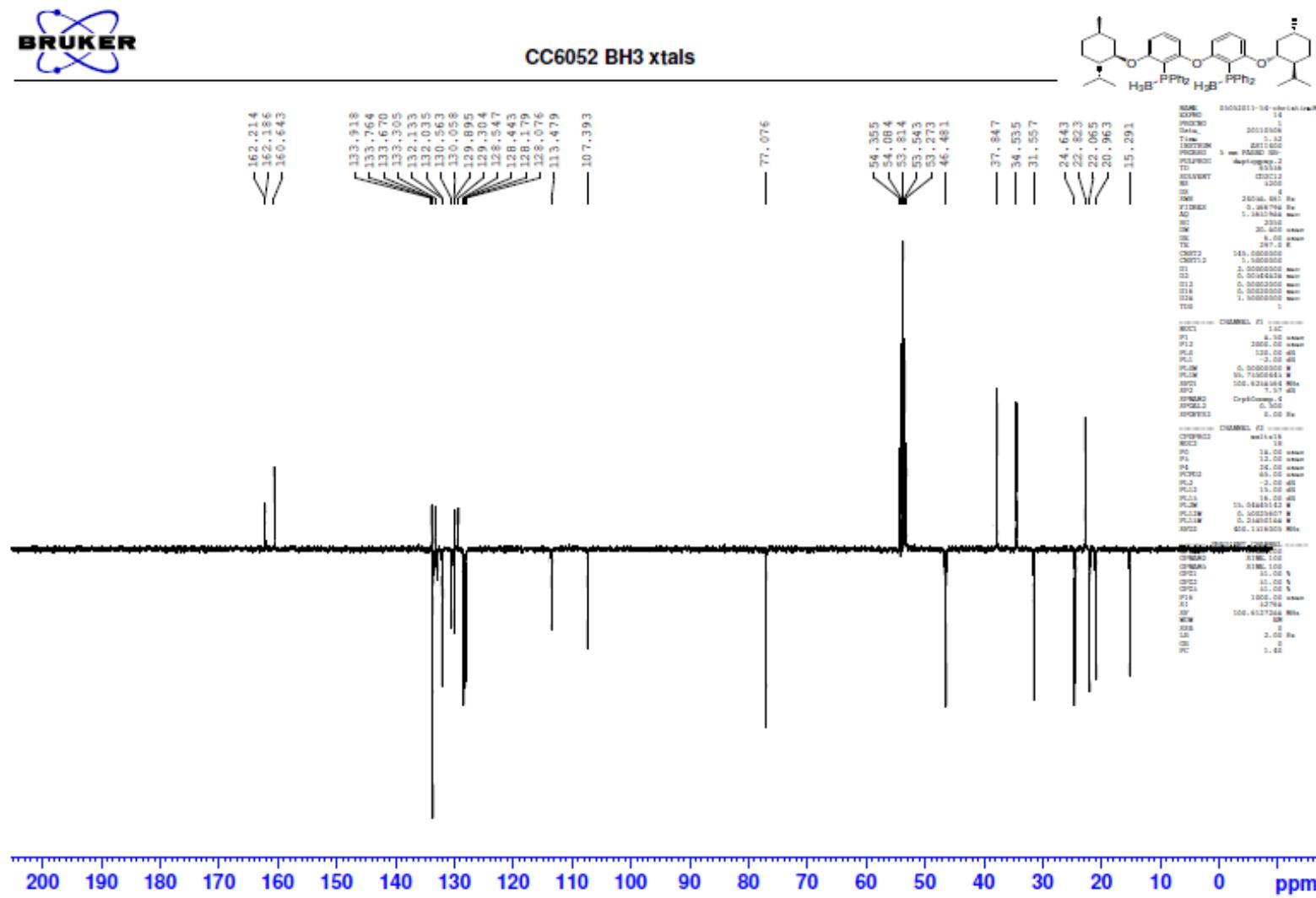
CC5082 after gCMS check

Figure S8     $^{13}\text{C}\{^1\text{H}\}$  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)



**Figure S10**  $^{13}\text{C}$  APT NMR spectrum of compound **13** (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



CC6052 BH3 xtals

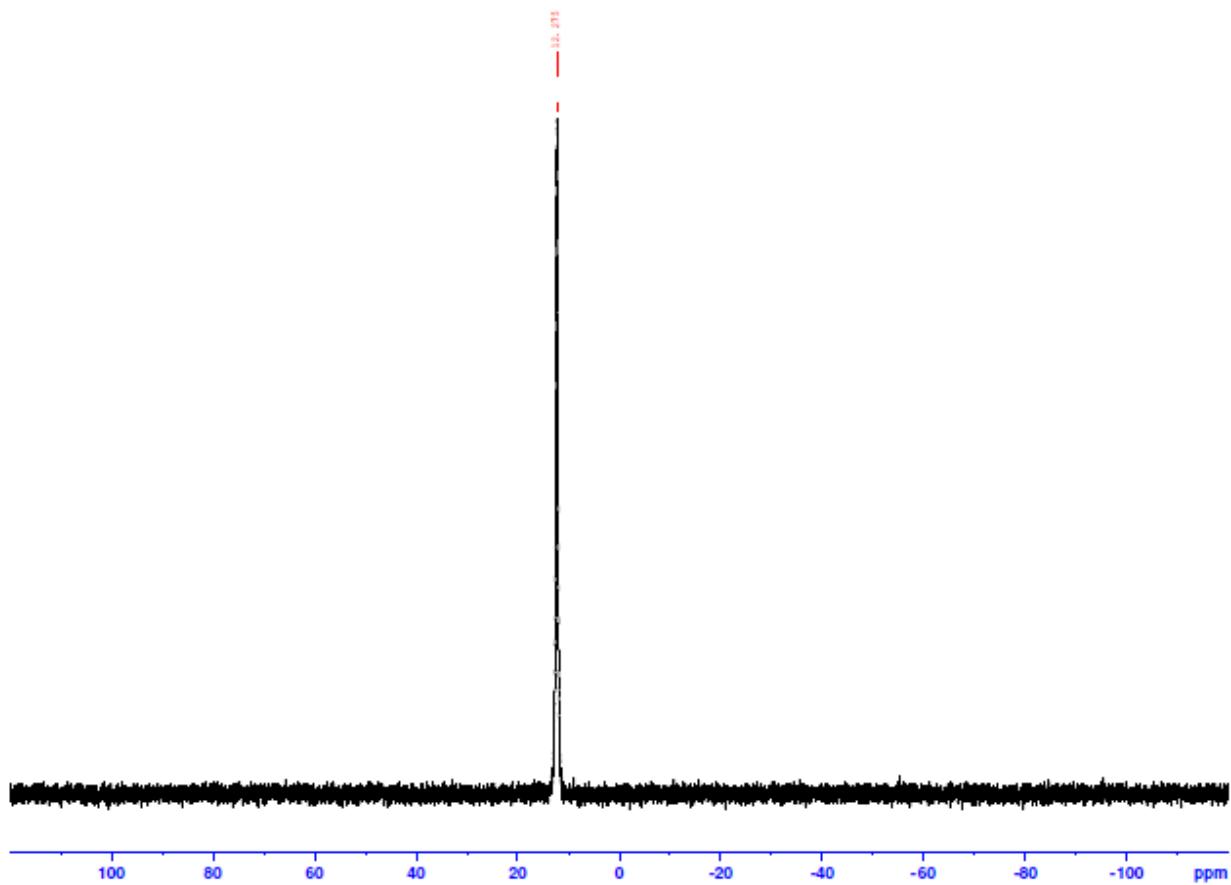
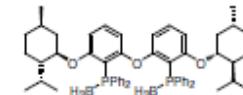


Figure S11  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 13 (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)

5- Compound 14

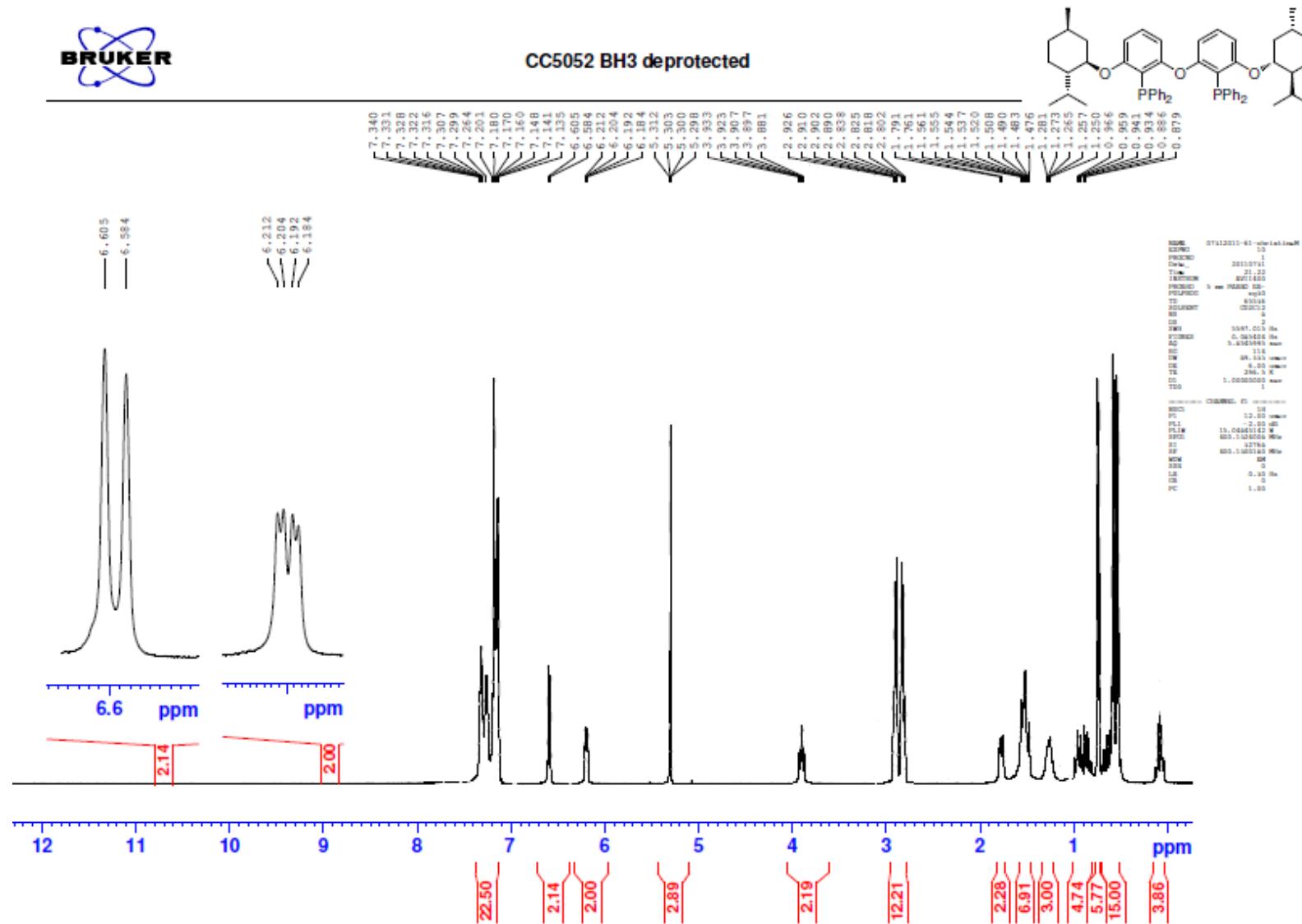
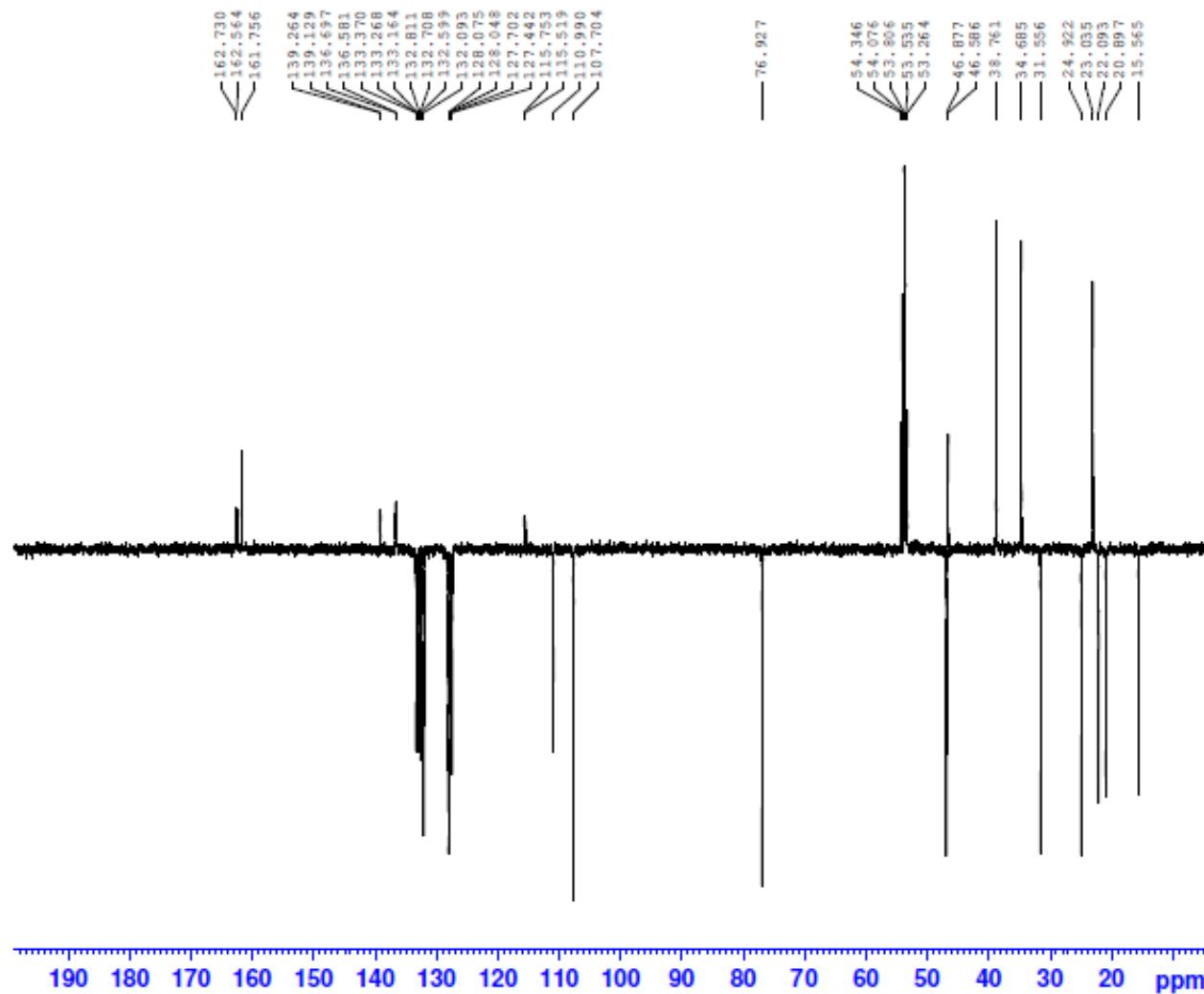
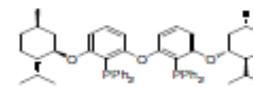


Figure S12  $^1\text{H}$  NMR spectrum of compound 14 (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 296 K)



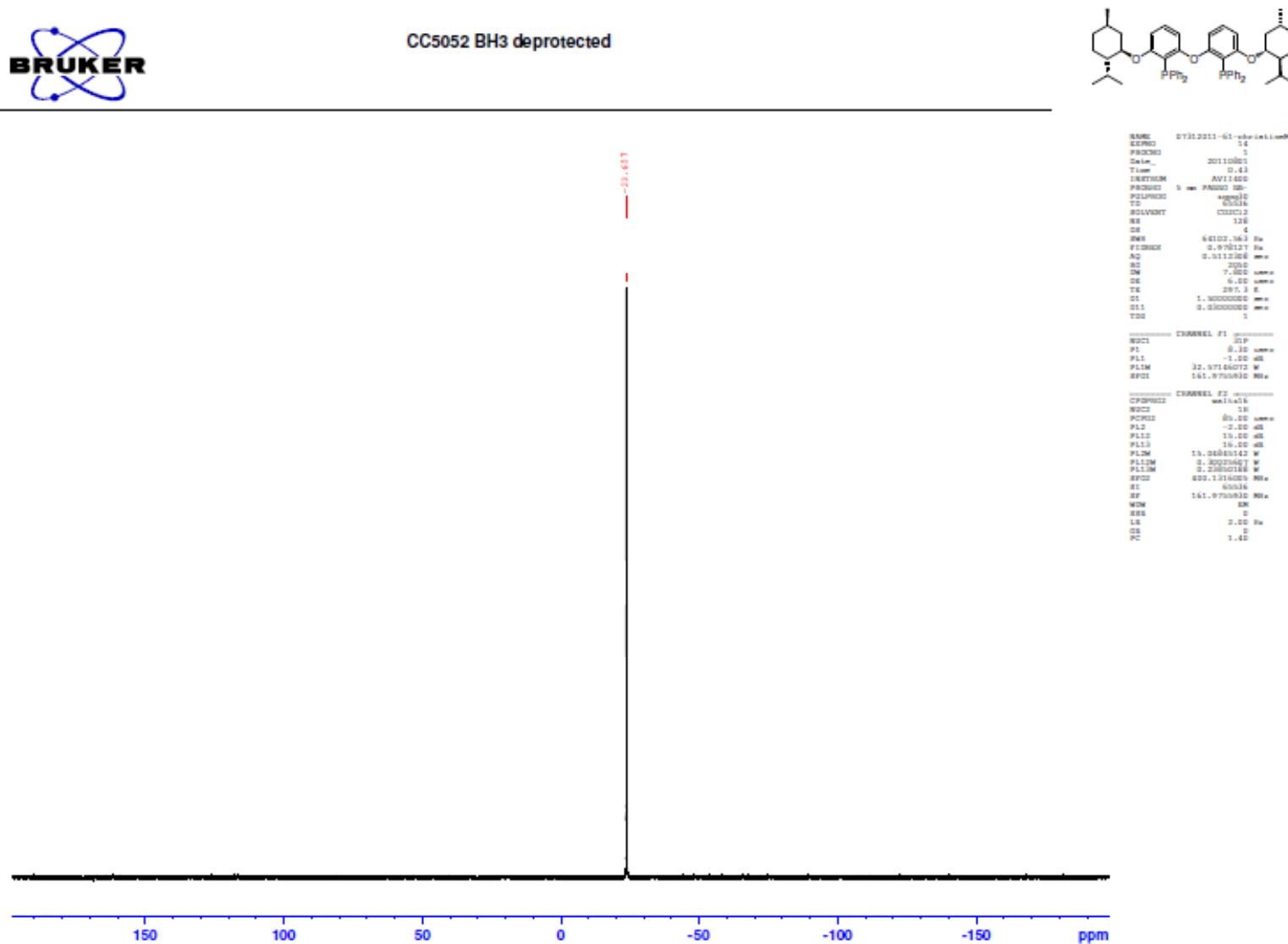
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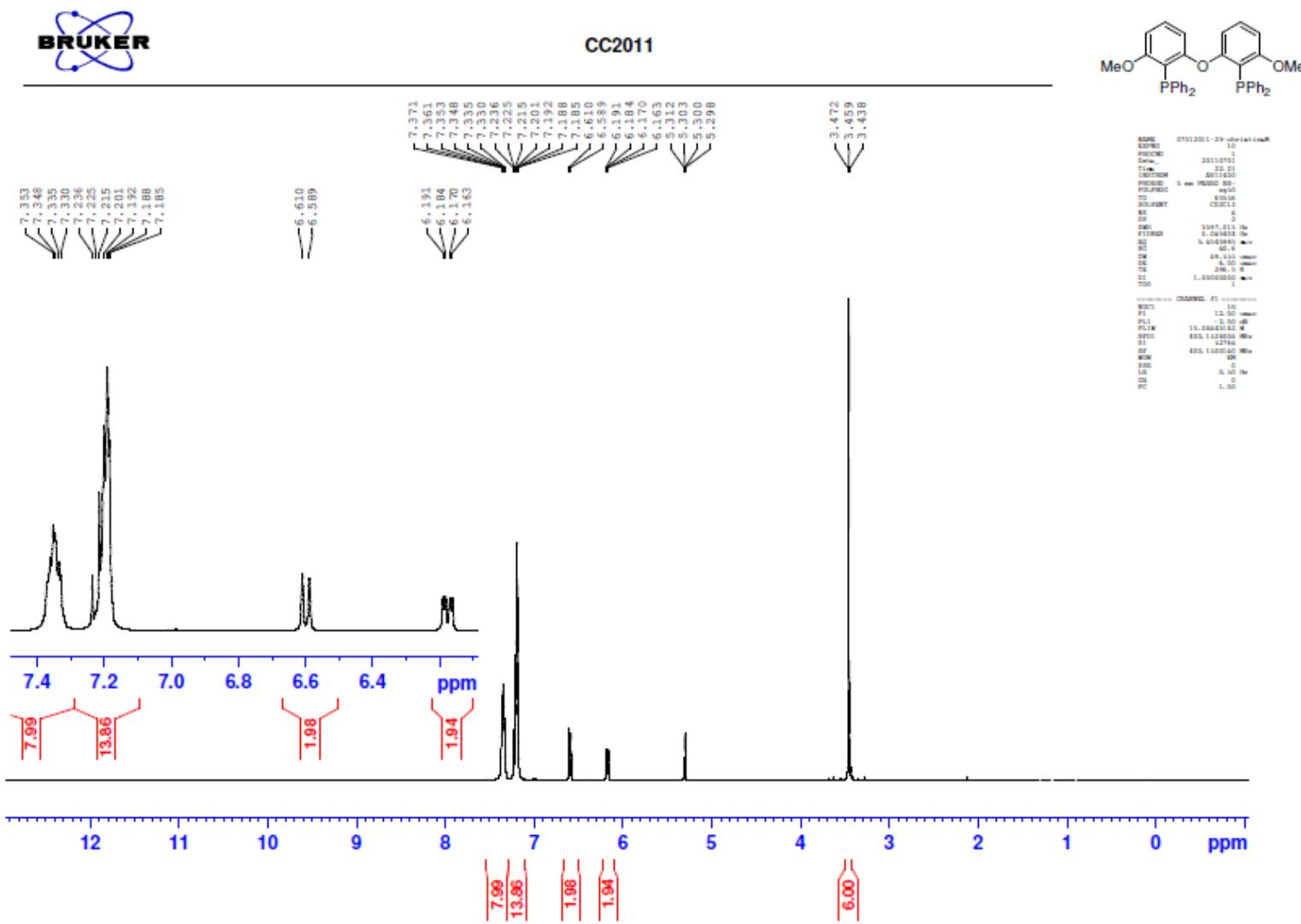
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POLARIZ: Depolariz,J  
TD: 65536  
SWEVENT: QCPMG  
NS: 1200  
DS: 200048, 161.4 Hz  
FIDRES: 2.000794 Hz  
AQ: 1.1815432 sec  
SW: 20.480 sec  
DW: 6.00 usec  
TE: 7.40 sec  
CR01: 143.0000000  
CR02: 1.0000000  
CR03: 1.0000000  
SI: 0.0044432 sec  
SI2: 0.0000250 sec  
SI4: 0.0000250 sec  
SI8: 1.0000000 sec  
TDR: 1  
SVD: CHANNEL F1 1.0000000  
NSC1: 14C  
PT1: 3000.00 wawa  
PL1: 125.00 dB  
PL2: 20.00 dB  
PLW: 0.0000000 W  
PLW1: 0.7435044 W  
SP1: 100.000000 Hz  
SP1L: 1.0000000 Hz  
SPW001: CryoDimen\_1  
SPW002: D\_100  
SPW003: 0.00 Hz  
SVD: CHANNEL F2 1.0000000  
NSC2: 14C  
PT2: 3000.00 wawa  
PL2: 125.00 dB  
PL12: 20.00 dB  
PL11: 14.00 dB  
PLW2: 0.0000000 W  
PL12W: 0.1000000 W  
PL11W: 0.2340000 W  
SP2: 0.0000000 Hz  
SVD: CHANNEL F3 1.0000000  
NSC3: 14C  
PT3: 3000.00 wawa  
PL3: 125.00 dB  
PL13: 20.00 dB  
PL12: 14.00 dB  
PLW3: 0.0000000 W  
PL13W: 0.1000000 W  
PL12W: 0.2340000 W  
SP3: 0.0000000 Hz  
SVD: CHANNEL F4 1.0000000  
NSC4: 14C  
PT4: 3000.00 wawa  
PL4: 125.00 dB  
PL14: 20.00 dB  
PL13: 14.00 dB  
PLW4: 0.0000000 W  
PL14W: 0.1000000 W  
PL13W: 0.2340000 W  
SP4: 0.0000000 Hz  
SVD: CHANNEL F5 1.0000000  
NSC5: 14C  
PT5: 3000.00 wawa  
PL5: 125.00 dB  
PL15: 20.00 dB  
PL14: 14.00 dB  
PLW5: 0.0000000 W  
PL15W: 0.1000000 W  
PL14W: 0.2340000 W  
SP5: 0.0000000 Hz  
SVD: CHANNEL F6 1.0000000  
NSC6: 14C  
PT6: 3000.00 wawa  
PL6: 125.00 dB  
PL16: 20.00 dB  
PL15: 14.00 dB  
PLW6: 0.0000000 W  
PL16W: 0.1000000 W  
PL15W: 0.2340000 W  
SP6: 0.0000000 Hz  
SVD: CHANNEL F7 1.0000000  
NSC7: 14C  
PT7: 3000.00 wawa  
PL7: 125.00 dB  
PL17: 20.00 dB  
PL16: 14.00 dB  
PLW7: 0.0000000 W  
PL17W: 0.1000000 W  
PL16W: 0.2340000 W  
SP7: 0.0000000 Hz  
SVD: CHANNEL F8 1.0000000  
NSC8: 14C  
PT8: 3000.00 wawa  
PL8: 125.00 dB  
PL18: 20.00 dB  
PL17: 14.00 dB  
PLW8: 0.0000000 W  
PL18W: 0.1000000 W  
PL17W: 0.2340000 W  
SP8: 0.0000000 Hz  
SVD: CHANNEL F9 1.0000000  
NSC9: 14C  
PT9: 3000.00 wawa  
PL9: 125.00 dB  
PL19: 20.00 dB  
PL18: 14.00 dB  
PLW9: 0.0000000 W  
PL19W: 0.1000000 W  
PL18W: 0.2340000 W  
SP9: 0.0000000 Hz  
SVD: CHANNEL F10 1.0000000  
NSC10: 14C  
PT10: 3000.00 wawa  
PL10: 125.00 dB  
PL20: 20.00 dB  
PL19: 14.00 dB  
PLW10: 0.0000000 W  
PL20W: 0.1000000 W  
PL19W: 0.2340000 W  
SP10: 0.0000000 Hz  
SVD: CHANNEL F11 1.0000000  
NSC11: 14C  
PT11: 3000.00 wawa  
PL11: 125.00 dB  
PL21: 20.00 dB  
PL20: 14.00 dB  
PLW11: 0.0000000 W  
PL21W: 0.1000000 W  
PL20W: 0.2340000 W  
SP11: 0.0000000 Hz  
SVD: CHANNEL F12 1.0000000  
NSC12: 14C  
PT12: 3000.00 wawa  
PL12: 125.00 dB  
PL22: 20.00 dB  
PL21: 14.00 dB  
PLW12: 0.0000000 W  
PL22W: 0.1000000 W  
PL21W: 0.2340000 W  
SP12: 0.0000000 Hz  
SVD: CHANNEL F13 1.0000000  
NSC13: 14C  
PT13: 3000.00 wawa  
PL13: 125.00 dB  
PL23: 20.00 dB  
PL22: 14.00 dB  
PLW13: 0.0000000 W  
PL23W: 0.1000000 W  
PL22W: 0.2340000 W  
SP13: 0.0000000 Hz  
SVD: CHANNEL F14 1.0000000  
NSC14: 14C  
PT14: 3000.00 wawa  
PL14: 125.00 dB  
PL24: 20.00 dB  
PL23: 14.00 dB  
PLW14: 0.0000000 W  
PL24W: 0.1000000 W  
PL23W: 0.2340000 W  
SP14: 0.0000000 Hz  
SVD: CHANNEL F15 1.0000000  
NSC15: 14C  
PT15: 3000.00 wawa  
PL15: 125.00 dB  
PL25: 20.00 dB  
PL24: 14.00 dB  
PLW15: 0.0000000 W  
PL25W: 0.1000000 W  
PL24W: 0.2340000 W  
SP15: 0.0000000 Hz  
SVD: CHANNEL F16 1.0000000  
NSC16: 14C  
PT16: 3000.00 wawa  
PL16: 125.00 dB  
PL26: 20.00 dB  
PL25: 14.00 dB  
PLW16: 0.0000000 W  
PL26W: 0.1000000 W  
PL25W: 0.2340000 W  
SP16: 0.0000000 Hz  
SVD: CHANNEL F17 1.0000000  
NSC17: 14C  
PT17: 3000.00 wawa  
PL17: 125.00 dB  
PL27: 20.00 dB  
PL26: 14.00 dB  
PLW17: 0.0000000 W  
PL27W: 0.1000000 W  
PL26W: 0.2340000 W  
SP17: 0.0000000 Hz  
SVD: CHANNEL F18 1.0000000  
NSC18: 14C  
PT18: 3000.00 wawa  
PL18: 125.00 dB  
PL28: 20.00 dB  
PL27: 14.00 dB  
PLW18: 0.0000000 W  
PL28W: 0.1000000 W  
PL27W: 0.2340000 W  
SP18: 0.0000000 Hz  
SVD: CHANNEL F19 1.0000000  
NSC19: 14C  
PT19: 3000.00 wawa  
PL19: 125.00 dB  
PL29: 20.00 dB  
PL28: 14.00 dB  
PLW19: 0.0000000 W  
PL29W: 0.1000000 W  
PL28W: 0.2340000 W  
SP19: 0.0000000 Hz  
SVD: CHANNEL F20 1.0000000  
NSC20: 14C  
PT20: 3000.00 wawa  
PL20: 125.00 dB  
PL30: 20.00 dB  
PL29: 14.00 dB  
PLW20: 0.0000000 W  
PL30W: 0.1000000 W  
PL29W: 0.2340000 W  
SP20: 0.0000000 Hz  
SVD: CHANNEL F21 1.0000000  
NSC21: 14C  
PT21: 3000.00 wawa  
PL21: 125.00 dB  
PL31: 20.00 dB  
PL30: 14.00 dB  
PLW21: 0.0000000 W  
PL31W: 0.1000000 W  
PL30W: 0.2340000 W  
SP21: 0.0000000 Hz  
SVD: CHANNEL F22 1.0000000  
NSC22: 14C  
PT22: 3000.00 wawa  
PL22: 125.00 dB  
PL32: 20.00 dB  
PL31: 14.00 dB  
PLW22: 0.0000000 W  
PL32W: 0.1000000 W  
PL31W: 0.2340000 W  
SP22: 0.0000000 Hz  
SVD: CHANNEL F23 1.0000000  
NSC23: 14C  
PT23: 3000.00 wawa  
PL23: 125.00 dB  
PL33: 20.00 dB  
PL32: 14.00 dB  
PLW23: 0.0000000 W  
PL33W: 0.1000000 W  
PL32W: 0.2340000 W  
SP23: 0.0000000 Hz  
SVD: CHANNEL F24 1.0000000  
NSC24: 14C  
PT24: 3000.00 wawa  
PL24: 125.00 dB  
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PL33: 14.00 dB  
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NSC25: 14C  
PT25: 3000.00 wawa  
PL25: 125.00 dB  
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PL34: 14.00 dB  
PLW25: 0.0000000 W  
PL35W: 0.1000000 W  
PL34W: 0.2340000 W  
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SVD: CHANNEL F26 1.0000000  
NSC26: 14C  
PT26: 3000.00 wawa  
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PL35: 14.00 dB  
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SVD: CHANNEL F27 1.0000000  
NSC27: 14C  
PT27: 3000.00 wawa  
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PL36: 14.00 dB  
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SP27: 0.0000000 Hz  
SVD: CHANNEL F28 1.0000000  
NSC28: 14C  
PT28: 3000.00 wawa  
PL28: 125.00 dB  
PL38: 20.00 dB  
PL37: 14.00 dB  
PLW28: 0.0000000 W  
PL38W: 0.1000000 W  
PL37W: 0.2340000 W  
SP28: 0.0000000 Hz  
SVD: CHANNEL F29 1.0000000  
NSC29: 14C  
PT29: 3000.00 wawa  
PL29: 125.00 dB  
PL39: 20.00 dB  
PL38: 14.00 dB  
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PL38W: 0.2340000 W  
SP29: 0.0000000 Hz  
SVD: CHANNEL F30 1.0000000  
NSC30: 14C  
PT30: 3000.00 wawa  
PL30: 125.00 dB  
PL40: 20.00 dB  
PL39: 14.00 dB  
PLW30: 0.0000000 W  
PL40W: 0.1000000 W  
PL39W: 0.2340000 W  
SP30: 0.0000000 Hz  
SVD: CHANNEL F31 1.0000000  
NSC31: 14C  
PT31: 3000.00 wawa  
PL31: 125.00 dB  
PL41: 20.00 dB  
PL40: 14.00 dB  
PLW31: 0.0000000 W  
PL41W: 0.1000000 W  
PL40W: 0.2340000 W  
SP31: 0.0000000 Hz  
SVD: CHANNEL F32 1.0000000  
NSC32: 14C  
PT32: 3000.00 wawa  
PL32: 125.00 dB  
PL42: 20.00 dB  
PL41: 14.00 dB  
PLW32: 0.0000000 W  
PL42W: 0.1000000 W  
PL41W: 0.2340000 W  
SP32: 0.0000000 Hz  
SVD: CHANNEL F33 1.0000000  
NSC33: 14C  
PT33: 3000.00 wawa  
PL33: 125.00 dB  
PL43: 20.00 dB  
PL42: 14.00 dB  
PLW33: 0.0000000 W  
PL43W: 0.1000000 W  
PL42W: 0.2340000 W  
SP33: 0.0000000 Hz  
SVD: CHANNEL F34 1.0000000  
NSC34: 14C  
PT34: 3000.00 wawa  
PL34: 125.00 dB  
PL44: 20.00 dB  
PL43: 14.00 dB  
PLW34: 0.0000000 W  
PL44W: 0.1000000 W  
PL43W: 0.2340000 W  
SP34: 0.0000000 Hz  
SVD: CHANNEL F35 1.0000000  
NSC35: 14C  
PT35: 3000.00 wawa  
PL35: 125.00 dB  
PL45: 20.00 dB  
PL44: 14.00 dB  
PLW35: 0.0000000 W  
PL45W: 0.1000000 W  
PL44W: 0.2340000 W  
SP35: 0.0000000 Hz  
SVD: CHANNEL F36 1.0000000  
NSC36: 14C  
PT36: 3000.00 wawa  
PL36: 125.00 dB  
PL46: 20.00 dB  
PL45: 14.00 dB  
PLW36: 0.0000000 W  
PL46W: 0.1000000 W  
PL45W: 0.2340000 W  
SP36: 0.0000000 Hz  
SVD: CHANNEL F37 1.0000000  
NSC37: 14C  
PT37: 3000.00 wawa  
PL37: 125.00 dB  
PL47: 20.00 dB  
PL46: 14.00 dB  
PLW37: 0.0000000 W  
PL47W: 0.1000000 W  
PL46W: 0.2340000 W  
SP37: 0.0000000 Hz  
SVD: CHANNEL F38 1.0000000  
NSC38: 14C  
PT38: 3000.00 wawa  
PL38: 125.00 dB  
PL48: 20.00 dB  
PL47: 14.00 dB  
PLW38: 0.0000000 W  
PL48W: 0.1000000 W  
PL47W: 0.2340000 W  
SP38: 0.0000000 Hz  
SVD: CHANNEL F39 1.0000000  
NSC39: 14C  
PT39: 3000.00 wawa  
PL39: 125.00 dB  
PL49: 20.00 dB  
PL48: 14.00 dB  
PLW39: 0.0000000 W  
PL49W: 0.1000000 W  
PL48W: 0.2340000 W  
SP39: 0.0000000 Hz  
SVD: CHANNEL F40 1.0000000  
NSC40: 14C  
PT40: 3000.00 wawa  
PL40: 125.00 dB  
PL50: 20.00 dB  
PL49: 14.00 dB  
PLW40: 0.0000000 W  
PL50W: 0.1000000 W  
PL49W: 0.2340000 W  
SP40: 0.0000000 Hz  
SVD: CHANNEL F41 1.0000000  
NSC41: 14C  
PT41: 3000.00 wawa  
PL41: 125.00 dB  
PL51: 20.00 dB  
PL50: 14.00 dB  
PLW41: 0.0000000 W  
PL51W: 0.1000000 W  
PL50W: 0.2340000 W  
SP41: 0.0000000 Hz  
SVD: CHANNEL F42 1.0000000  
NSC42: 14C  
PT42: 3000.00 wawa  
PL42: 125.00 dB  
PL52: 20.00 dB  
PL51: 14.00 dB  
PLW42: 0.0000000 W  
PL52W: 0.1000000 W  
PL51W: 0.2340000 W  
SP42: 0.0000000 Hz  
SVD: CHANNEL F43 1.0000000  
NSC43: 14C  
PT43: 3000.00 wawa  
PL43: 125.00 dB  
PL53: 20.00 dB  
PL52: 14.00 dB  
PLW43: 0.0000000 W  
PL53W: 0.1000000 W  
PL52W: 0.2340000 W  
SP43: 0.0000000 Hz  
SVD: CHANNEL F44 1.0000000  
NSC44: 14C  
PT44: 3000.00 wawa  
PL44: 125.00 dB  
PL54: 20.00 dB  
PL53: 14.00 dB  
PLW44: 0.0000000 W  
PL54W: 0.1000000 W  
PL53W: 0.2340000 W  
SP44: 0.0000000 Hz  
SVD: CHANNEL F45 1.0000000  
NSC45: 14C  
PT45: 3000.00 wawa  
PL45: 125.00 dB  
PL55: 20.00 dB  
PL54: 14.00 dB  
PLW45: 0.0000000 W  
PL55W: 0.1000000 W  
PL54W: 0.2340000 W  
SP45: 0.0000000 Hz  
SVD: CHANNEL F46 1.0000000  
NSC46: 14C  
PT46: 3000.00 wawa  
PL46: 125.00 dB  
PL56: 20.00 dB  
PL55: 14.00 dB  
PLW46: 0.0000000 W  
PL56W: 0.1000000 W  
PL55W: 0.2340000 W  
SP46: 0.0000000 Hz  
SVD: CHANNEL F47 1.0000000  
NSC47: 14C  
PT47: 3000.00 wawa  
PL47: 125.00 dB  
PL57: 20.00 dB  
PL56: 14.00 dB  
PLW47: 0.0000000 W  
PL57W: 0.1000000 W  
PL56W: 0.2340000 W  
SP47: 0.0000000 Hz  
SVD: CHANNEL F48 1.0000000  
NSC48: 14C  
PT48: 3000.00 wawa  
PL48: 125.00 dB  
PL58: 20.00 dB  
PL57: 14.00 dB  
PLW48: 0.0000000 W  
PL58W: 0.1000000 W  
PL57W: 0.2340000 W  
SP48: 0.0000000 Hz  
SVD: CHANNEL F49 1.0000000  
NSC49: 14C  
PT49: 3000.00 wawa  
PL49: 125.00 dB  
PL59: 20.00 dB  
PL58: 14.00 dB  
PLW49: 0.0000000 W  
PL59W: 0.1000000 W  
PL58W: 0.2340000 W  
SP49: 0.0000000 Hz  
SVD: CHANNEL F50 1.0000000  
NSC50: 14C  
PT50: 3000.00 wawa  
PL50: 125.00 dB  
PL60: 20.00 dB  
PL59: 14.00 dB  
PLW50: 0.0000000 W  
PL60W: 0.1000000 W  
PL59W: 0.2340000 W  
SP50: 0.0000000 Hz  
SVD: CHANNEL F51 1.0000000  
NSC51: 14C  
PT51: 3000.00 wawa  
PL51: 125.00 dB  
PL61: 20.00 dB  
PL60: 14.00 dB  
PLW51: 0.0000000 W  
PL61W: 0.1000000 W  
PL60W: 0.2340000 W  
SP51: 0.0000000 Hz  
SVD: CHANNEL F52 1.0000000  
NSC52: 14C  
PT52: 3000.00 wawa  
PL52: 125.00 dB  
PL62: 20.00 dB  
PL61: 14.00 dB  
PLW52: 0.0000000 W  
PL62W: 0.1000000 W  
PL61W: 0.2340000 W  
SP52: 0.0000000 Hz  
SVD: CHANNEL F53 1.0000000  
NSC53: 14C  
PT53: 3000.00 wawa  
PL53: 125.00 dB  
PL63: 20.00 dB  
PL62: 14.00 dB  
PLW53: 0.0000000 W  
PL63W: 0.1000000 W  
PL62W: 0.2340000 W  
SP53: 0.0000000 Hz  
SVD: CHANNEL F54 1.0000000  
NSC54: 14C  
PT54: 3000.00 wawa  
PL54: 125.00 dB  
PL64: 20.00 dB  
PL63: 14.00 dB  
PLW54: 0.0000000 W  
PL64W: 0.1000000 W  
PL63W: 0.2340000 W  
SP54: 0.0000000 Hz  
SVD: CHANNEL F55 1.0000000  
NSC55: 14C  
PT55: 3000.00 wawa  
PL55: 125.00 dB  
PL65: 20.00 dB  
PL64: 14.00 dB  
PLW55: 0.0000000 W  
PL65W: 0.1000000 W  
PL64W: 0.2340000 W  
SP55: 0.0000000 Hz  
SVD: CHANNEL F56 1.0000000  
NSC56: 14C  
PT56: 3000.00 wawa  
PL56: 125.00 dB  
PL66: 20.00 dB  
PL65: 14.00 dB  
PLW56: 0.0000000 W  
PL66W: 0.1000000 W  
PL65W: 0.2340000 W  
SP56: 0.0000000 Hz  
SVD: CHANNEL F57 1.0000000  
NSC57: 14C  
PT57: 3000.00 wawa  
PL57: 125.00 dB  
PL67: 20.00 dB  
PL66: 14.00 dB  
PLW57: 0.0000000 W  
PL67W: 0.1000000 W  
PL66W: 0.2340000 W  
SP57: 0.0000000 Hz  
SVD: CHANNEL F58 1.0000000  
NSC58: 14C  
PT58: 3000.00 wawa  
PL58: 125.00 dB  
PL68: 20.00 dB  
PL67: 14.00 dB  
PLW58: 0.0000000 W  
PL68W: 0.1000000 W  
PL67W: 0.2340000 W  
SP58: 0.0000000 Hz  
SVD: CHANNEL F59 1.0000000  
NSC59: 14C  
PT59: 3000.00 wawa  
PL59: 125.00 dB  
PL69: 20.00 dB  
PL68: 14.00 dB  
PLW59: 0.0000000 W  
PL69W: 0.1000000 W  
PL68W: 0.2340000 W  
SP59: 0.0000000 Hz  
SVD: CHANNEL F60 1.0000000  
NSC60: 14C  
PT60: 3000.00 wawa  
PL60: 125.00 dB  
PL70: 20.00 dB  
PL69: 14.00 dB  
PLW60: 0.0000000 W  
PL70W: 0.1000000 W  
PL69W: 0.2340000 W  
SP60: 0.0000000 Hz  
SVD: CHANNEL F61 1.0000000  
NSC61: 14C  
PT61: 3000.00 wawa  
PL61: 125.00 dB  
PL71: 20.00 dB  
PL70: 14.00 dB  
PLW61: 0.0000000 W  
PL71W: 0.1000000 W  
PL70W: 0.2340000 W  
SP61: 0.0000000 Hz  
SVD: CHANNEL F62 1.0000000  
NSC62: 14C  
PT62: 3000.00 wawa  
PL62: 125.00 dB  
PL72: 20.00 dB  
PL71: 14.00 dB  
PLW62: 0.0000000 W  
PL72W: 0.1000000 W  
PL71W: 0.2340000 W  
SP62: 0.0000000 Hz  
SVD: CHANNEL F63 1.0000000  
NSC63: 14C  
PT63: 3000.00 wawa  
PL63: 125.00 dB  
PL73: 20.00 dB  
PL72: 14.00 dB  
PLW63: 0.0000000 W  
PL73W: 0.1000000 W  
PL72W: 0.2340000 W  
SP63: 0.0000000 Hz  
SVD: CHANNEL F64 1.0000000  
NSC64: 14C  
PT64: 3000.00 wawa  
PL64: 125.00 dB  
PL74: 20.00 dB  
PL73: 14.00 dB  
PLW64: 0.0000000 W  
PL74W: 0.1000000 W  
PL73W: 0.2340000 W  
SP64: 0.0000000 Hz  
SVD: CHANNEL F65 1.0000000  
NSC65: 14C  
PT65: 3000.00 wawa  
PL65: 125.00 dB  
PL75: 20.00 dB  
PL74: 14.00 dB  
PLW65: 0.0000000 W  
PL75W: 0.1000000 W  
PL74W: 0.2340000 W  
SP65: 0.0000000 Hz  
SVD: CHANNEL F66 1.0000000  
NSC66: 14C  
PT66: 3000.00 wawa  
PL66: 125.00 dB  
PL76: 20.00 dB  
PL75: 14.00 dB  
PLW66: 0.0000000 W  
PL76W: 0.1000000 W  
PL75W: 0.2340000 W  
SP66: 0.0000000 Hz  
SVD: CHANNEL F67 1.0000000  
NSC67: 14C  
PT67: 3000.00 wawa  
PL67: 125.00 dB  
PL77: 20.00 dB  
PL76: 14.00 dB  
PLW67: 0.0000000 W  
PL77W: 0.1000000 W  
PL76W: 0.2340000 W  
SP67: 0.0000000 Hz  
SVD: CHANNEL F68 1.0000000  
NSC68: 14C  
PT68: 3000.00 wawa  
PL68: 125.00 dB  
PL78



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)

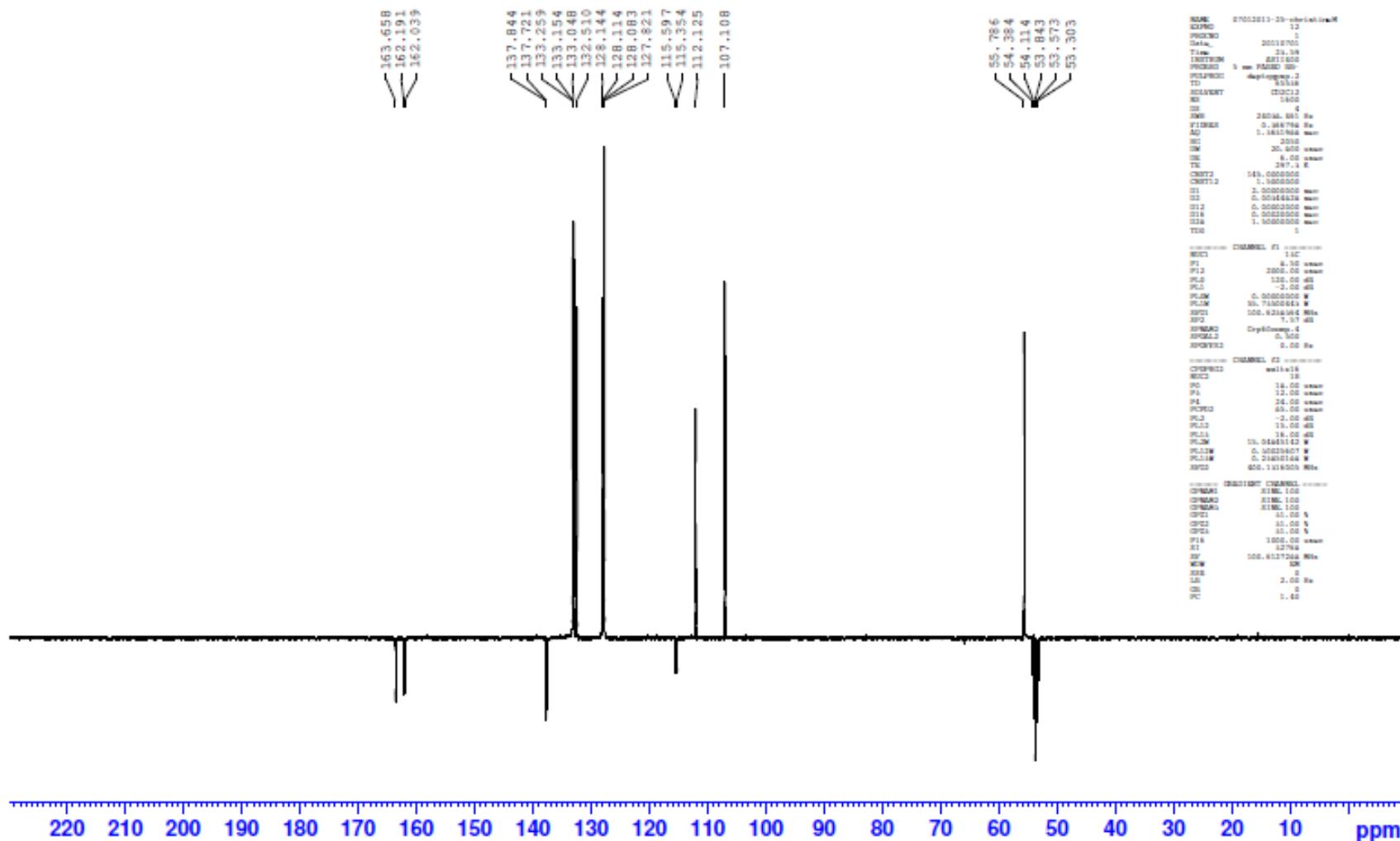
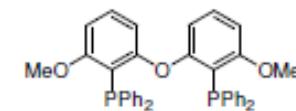
## 6- Compound 15



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



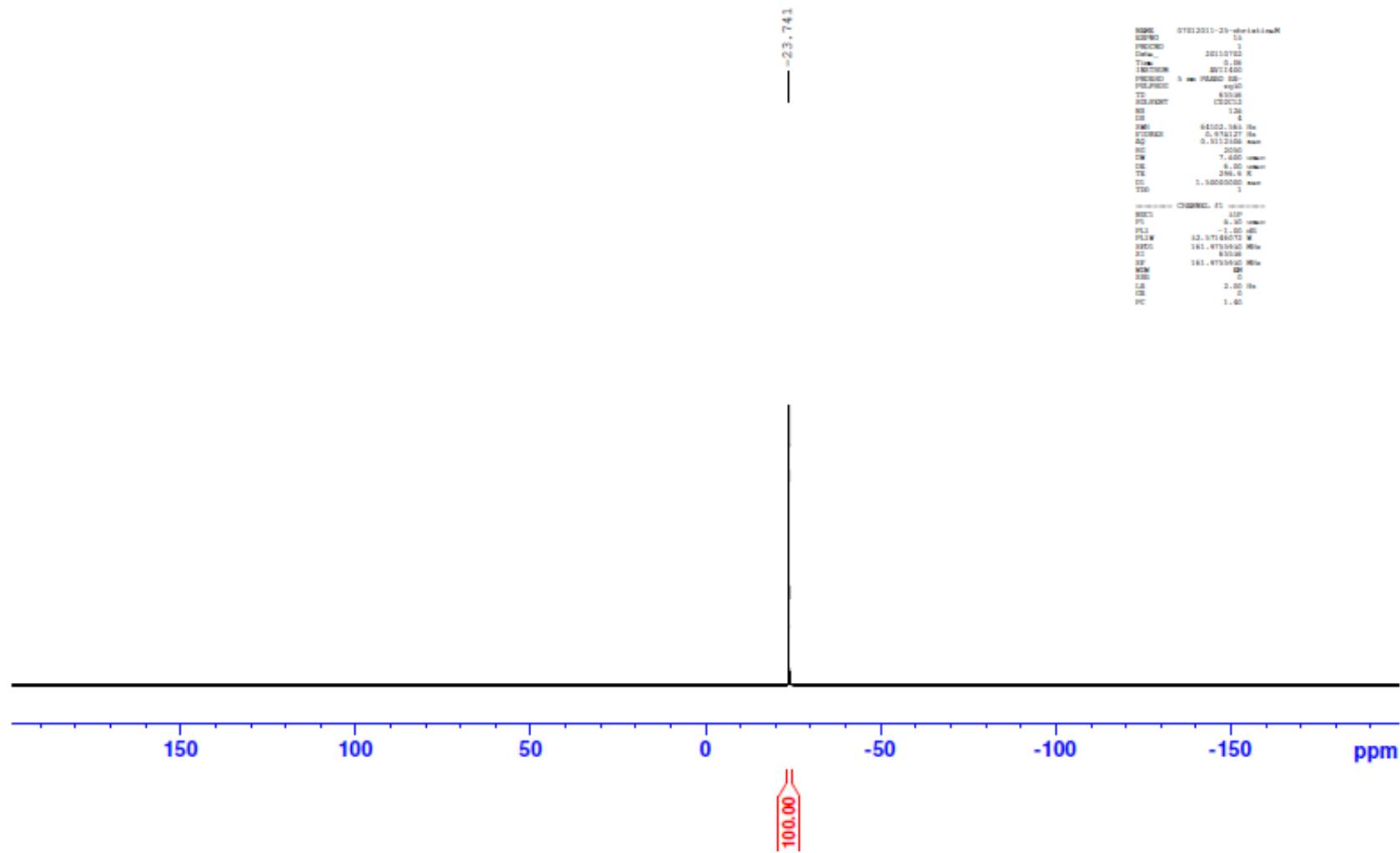
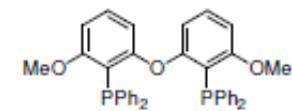
CC2011



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

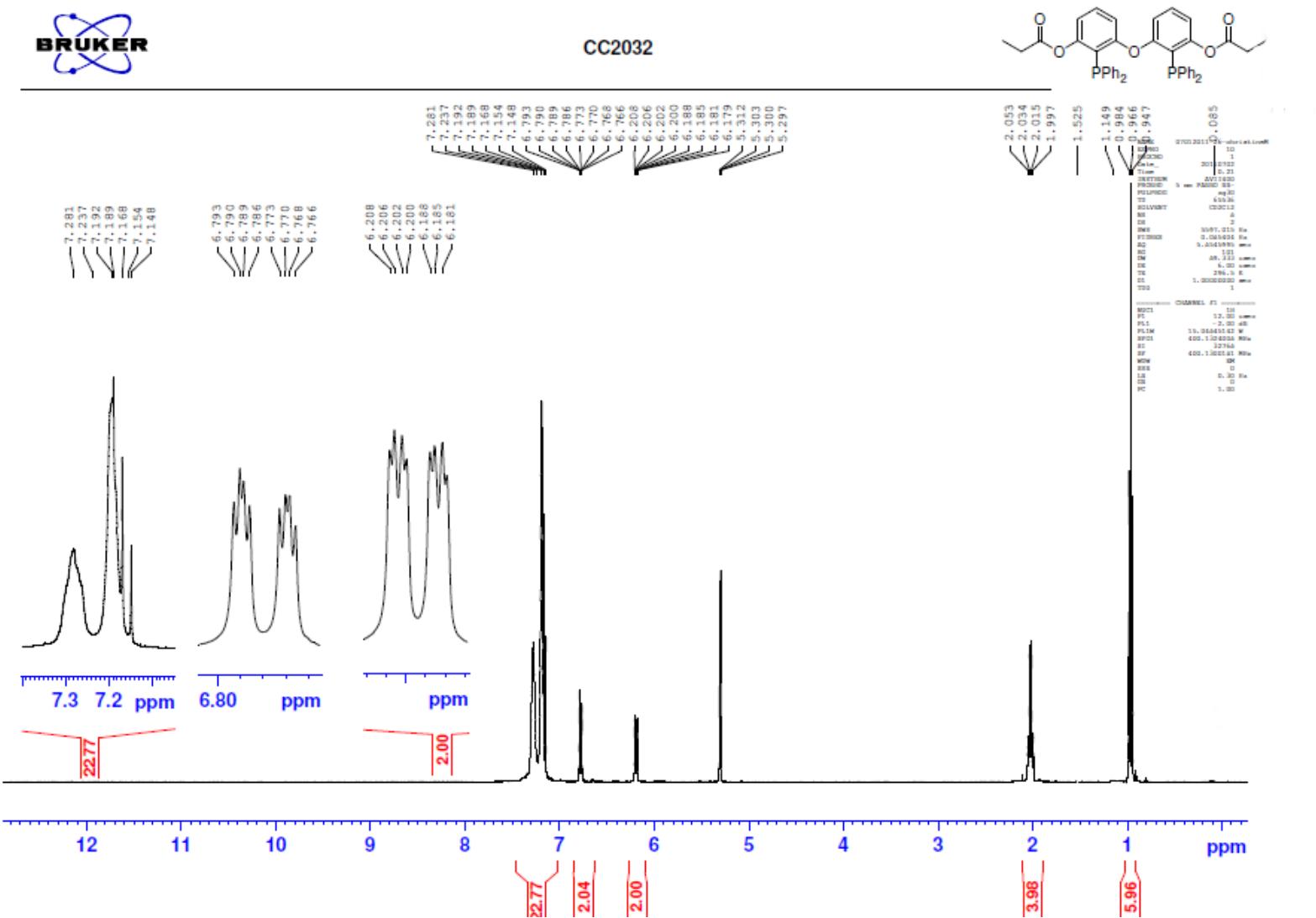


CC2011



**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



**Figure S18**  $^1\text{H}$  NMR spectrum of compound **17a** (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

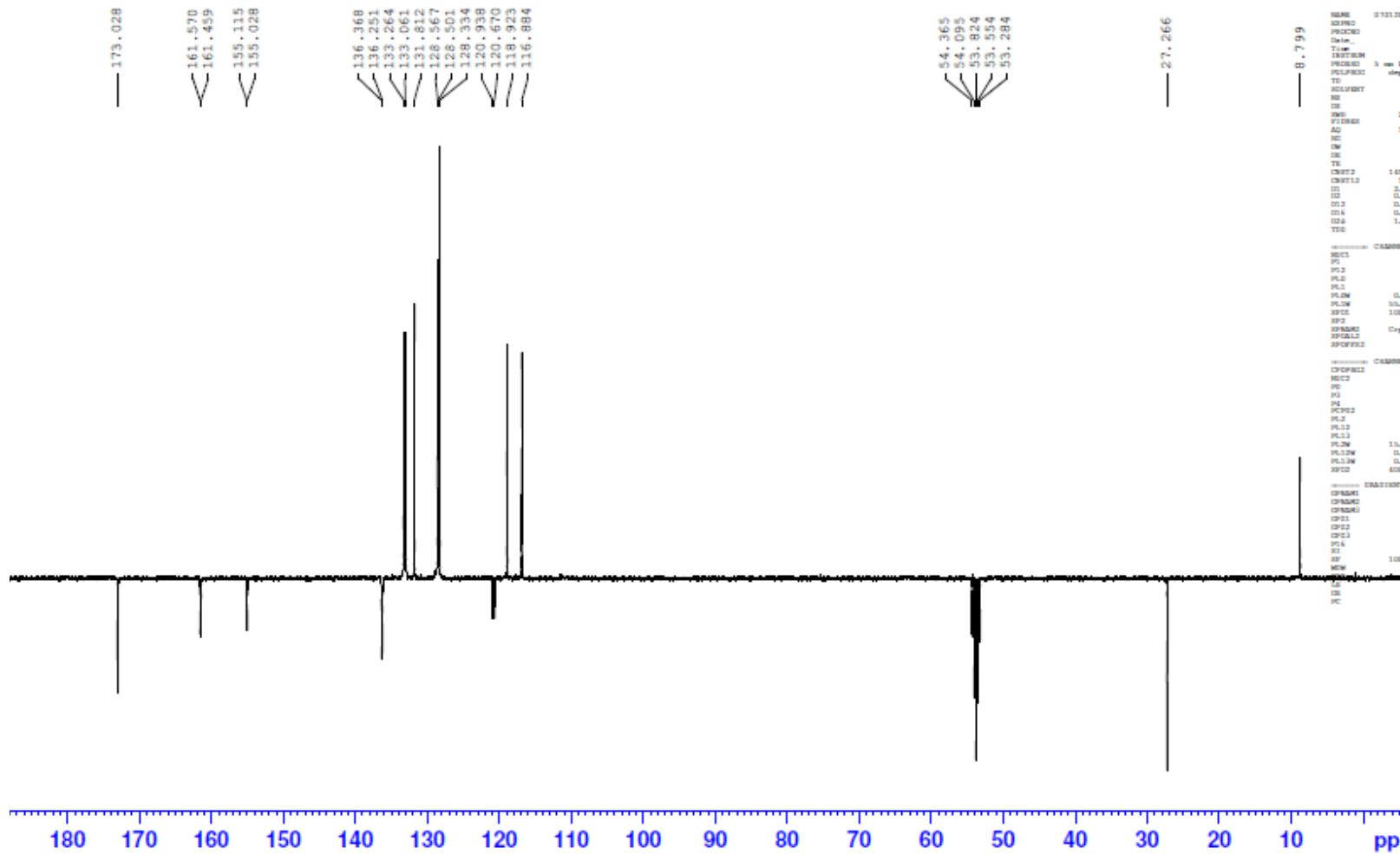
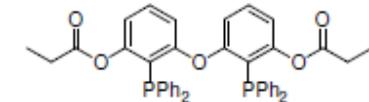


Figure S19 <sup>13</sup>C APT NMR spectrum of compound 17a (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



CC2032

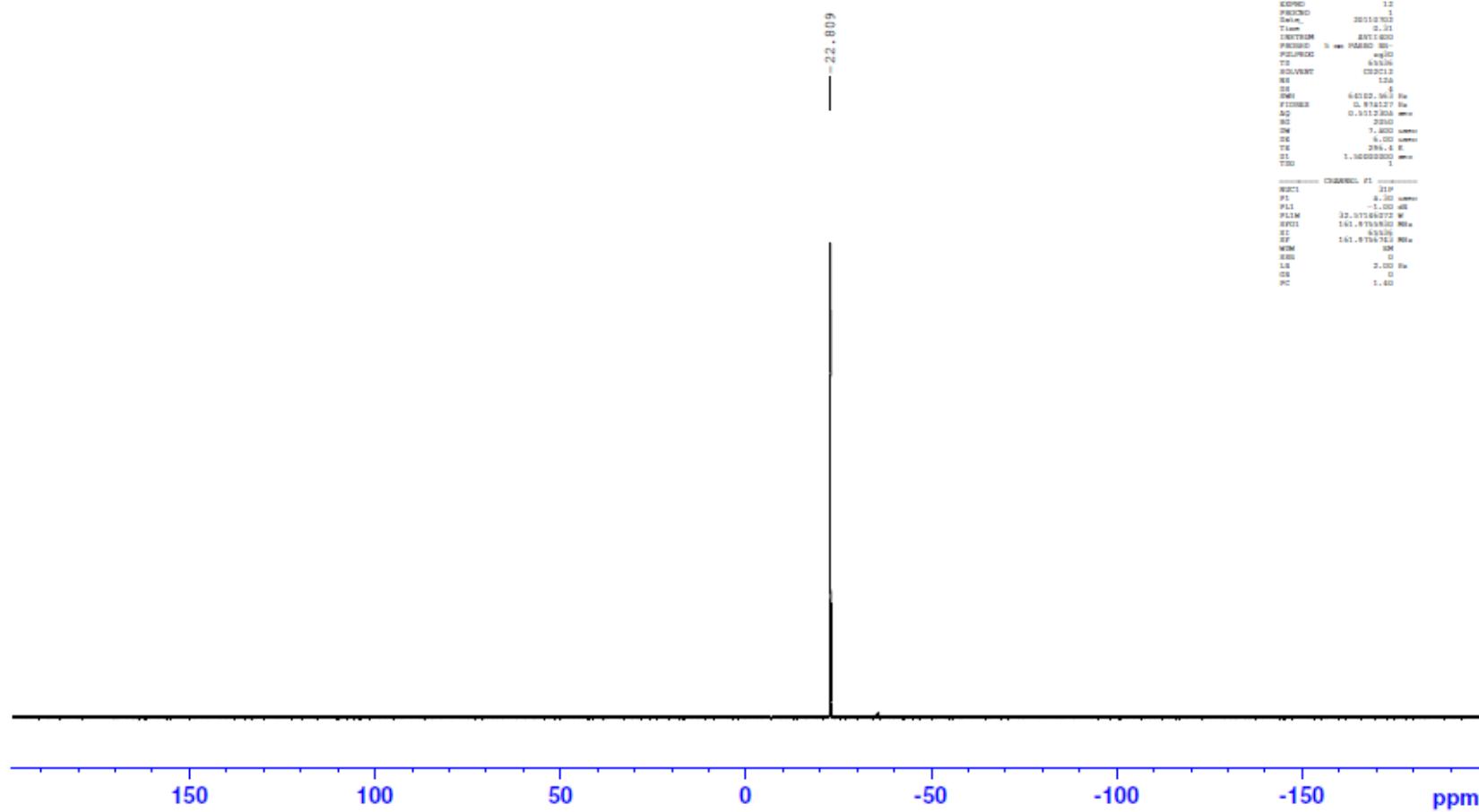
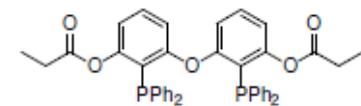


Figure S20  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 17a (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

8- Compound 17a

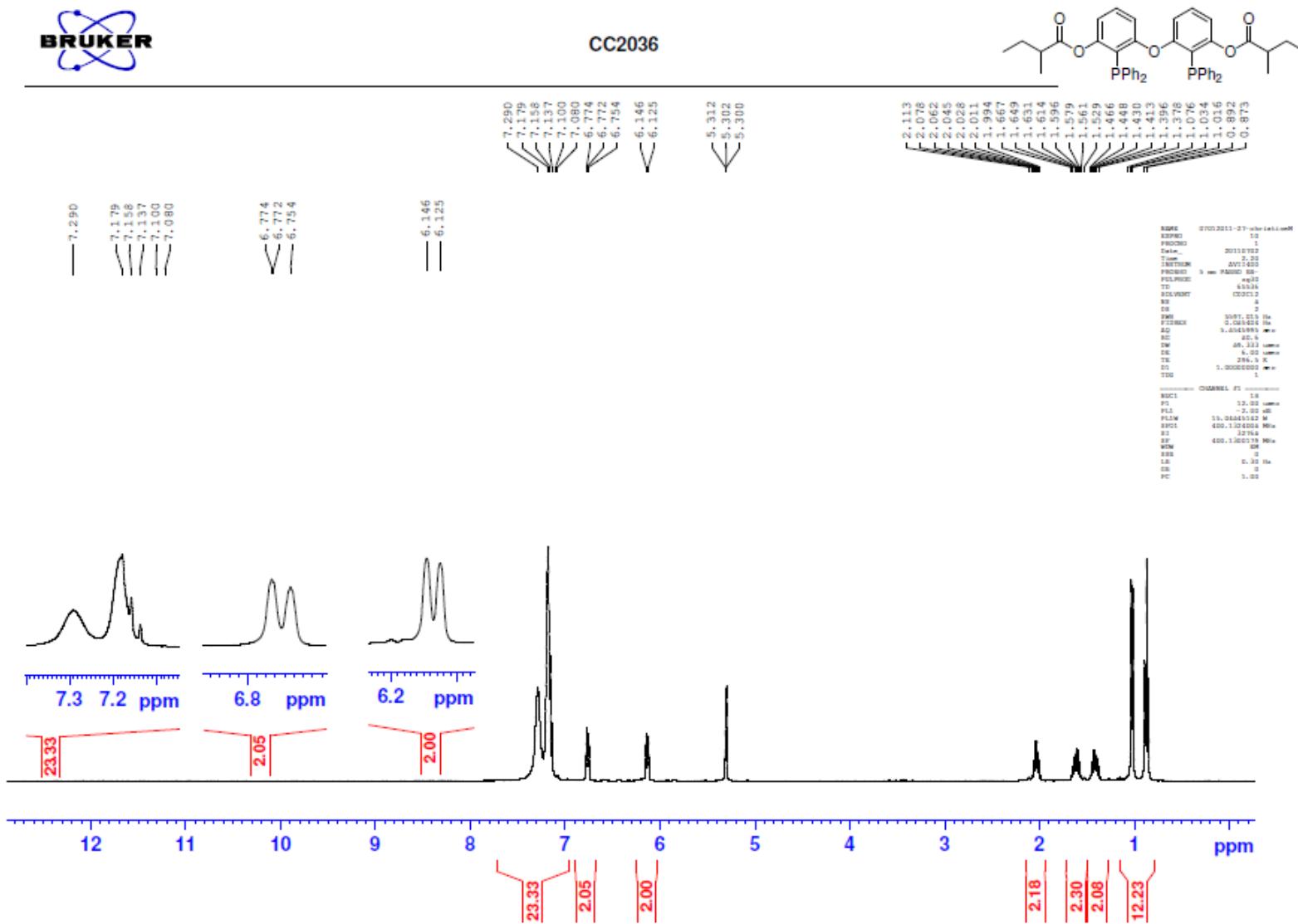
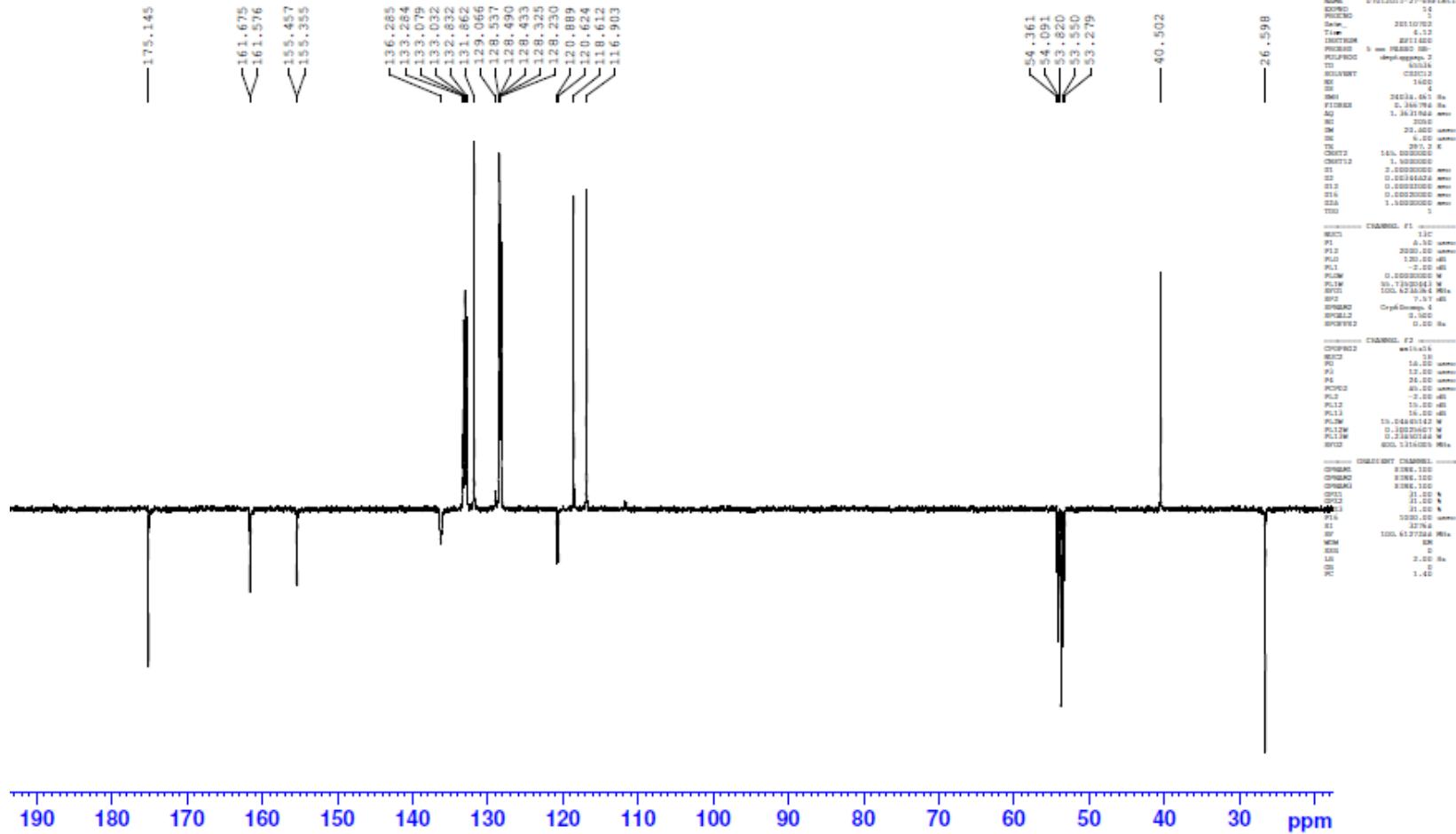


Figure S21 <sup>1</sup>H NMR spectrum of compound 17b (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)

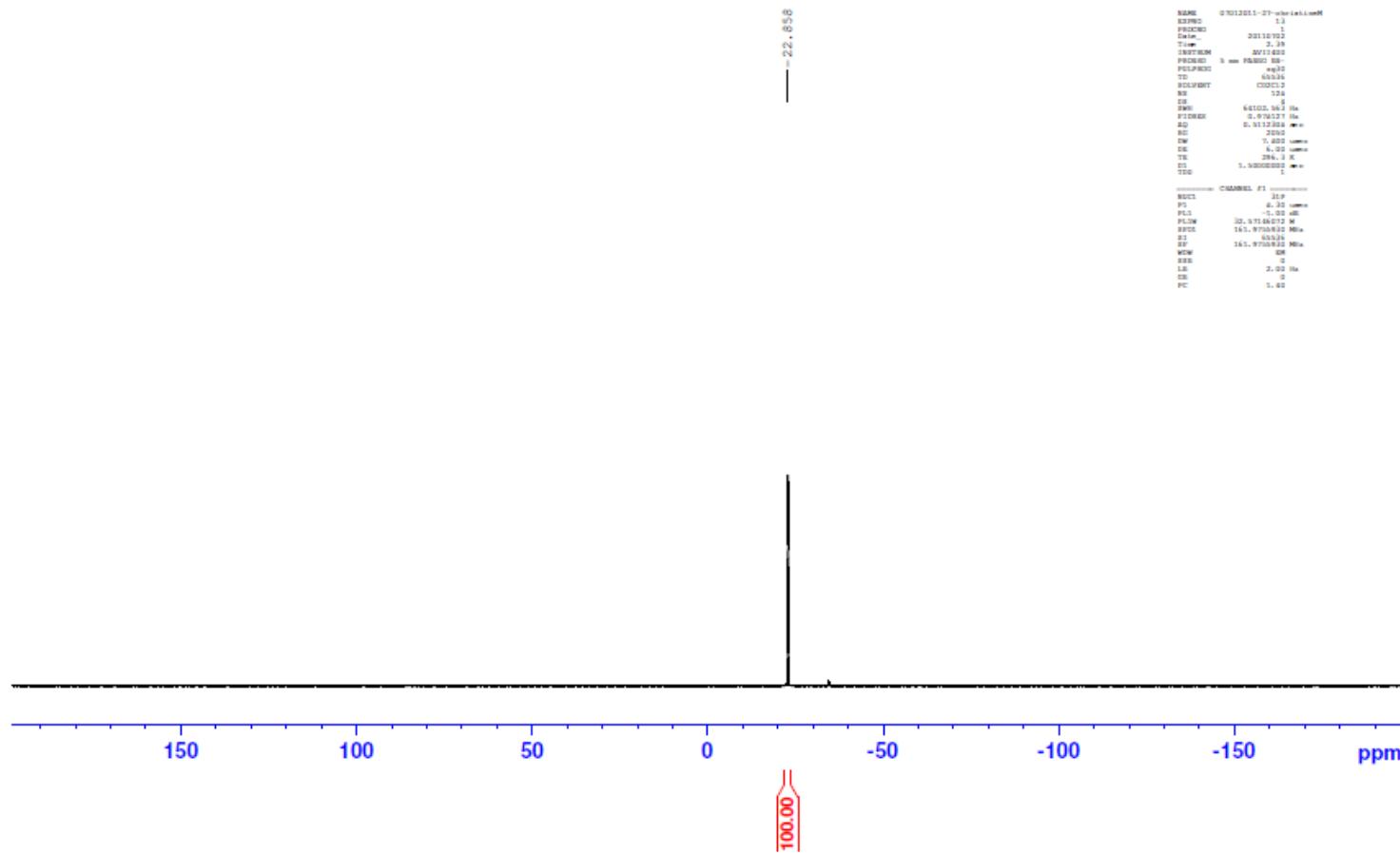
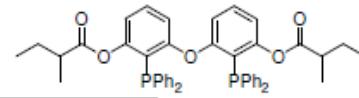


CC2036

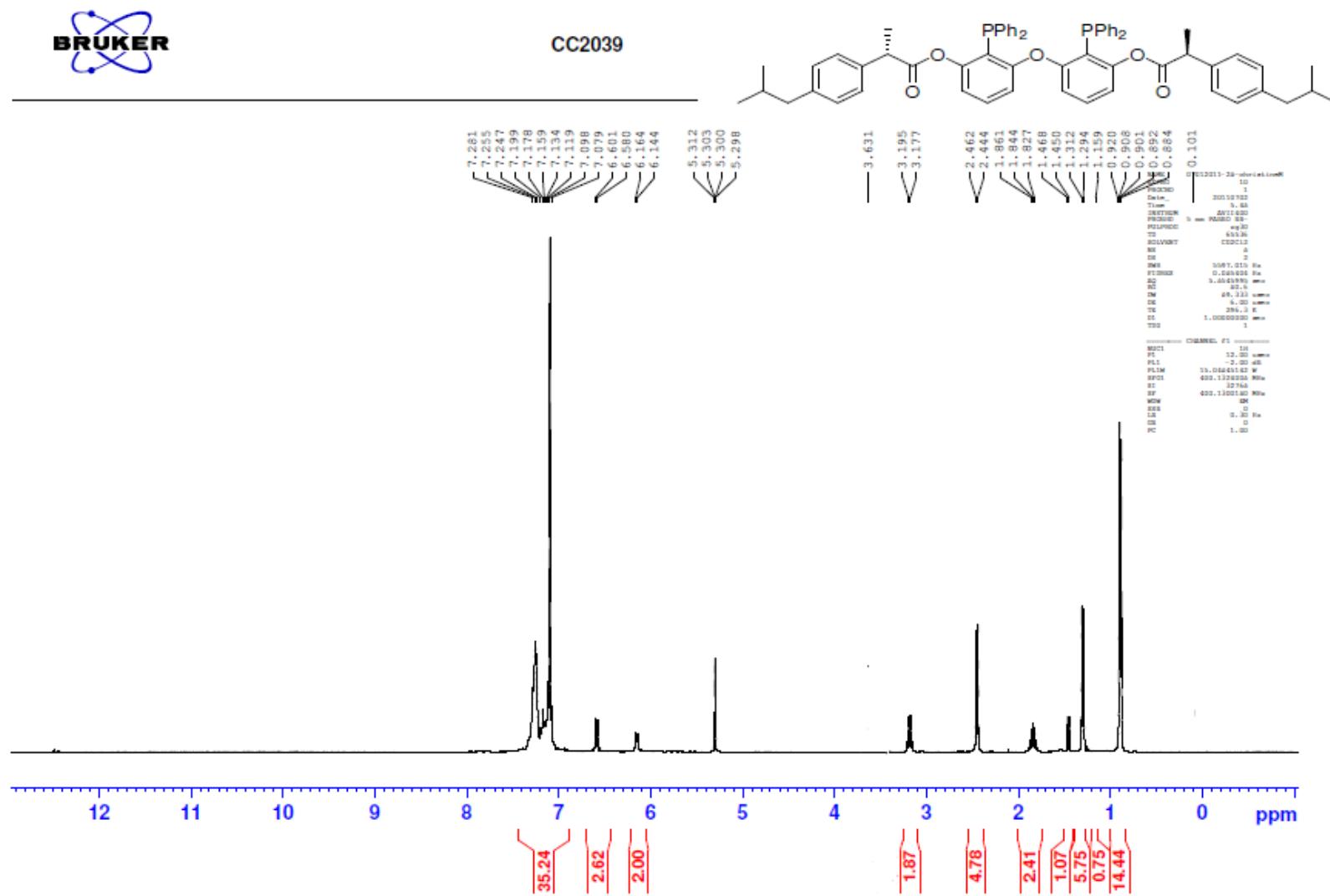




CC2036



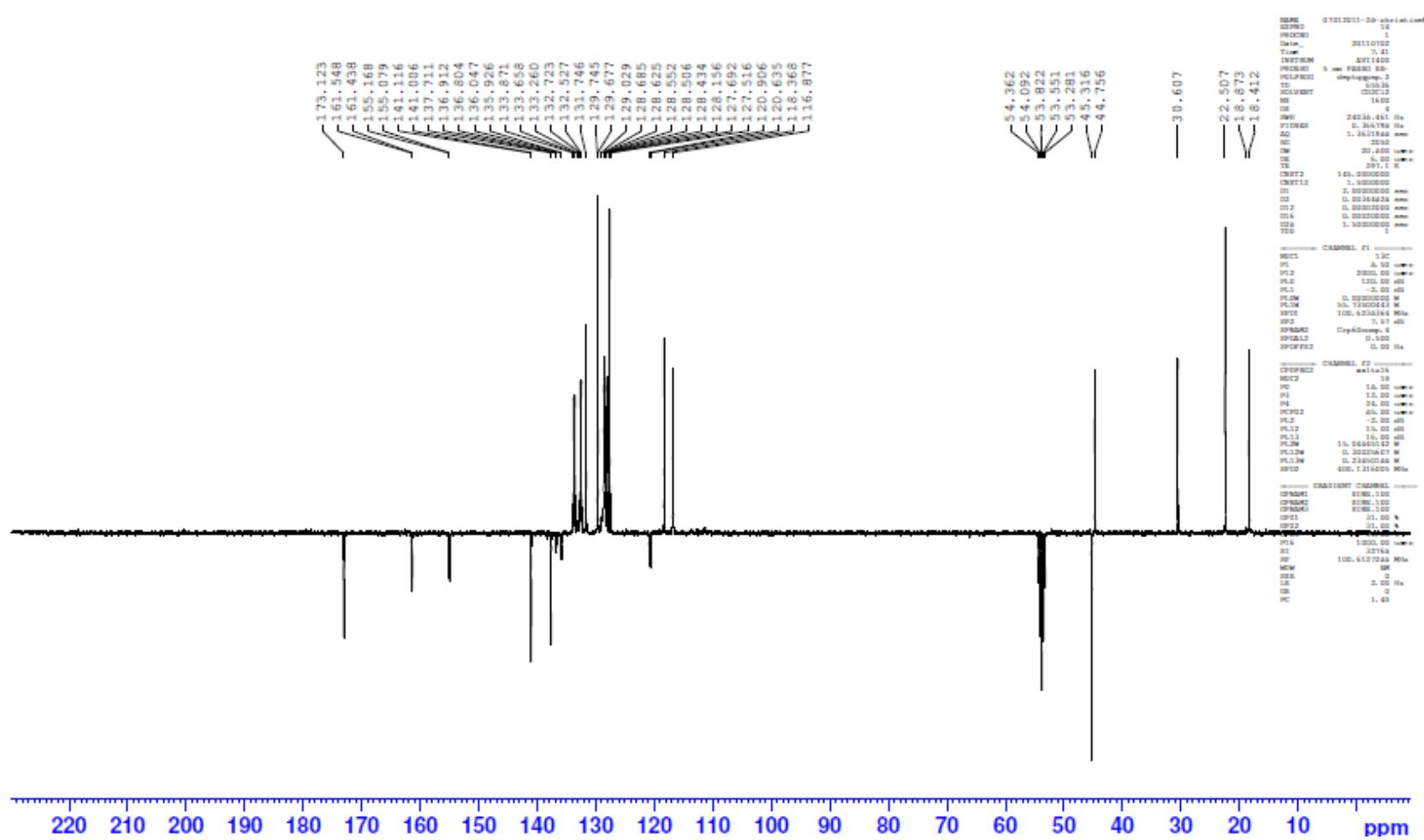
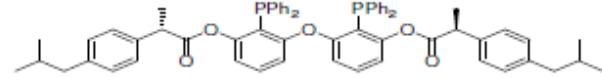
## 9- Compound 17c



**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)

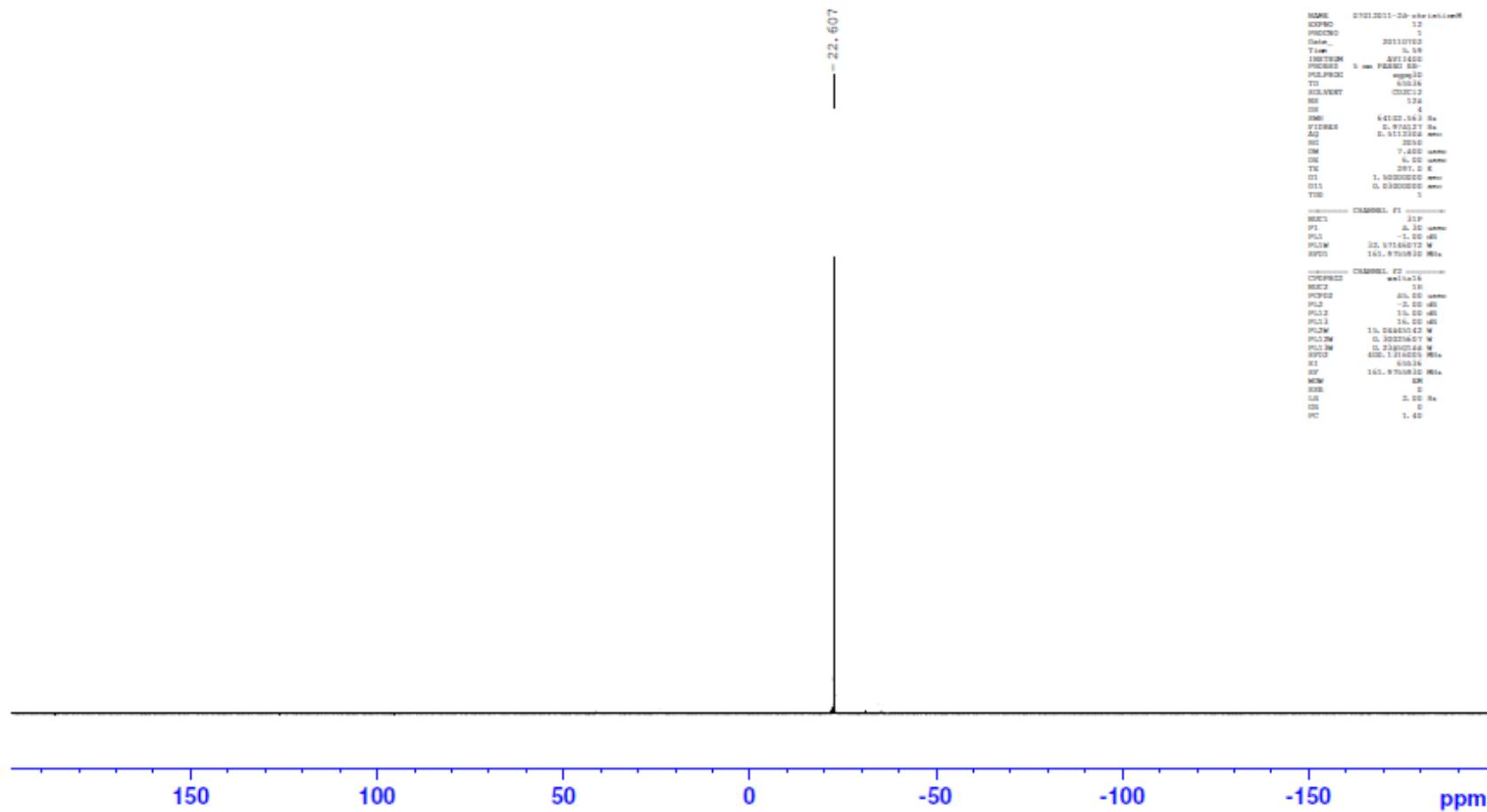
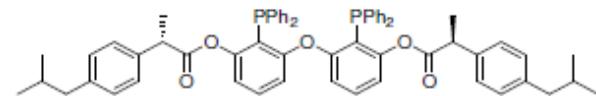


Figure S26  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of compound 17c (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

10- Compound 17d

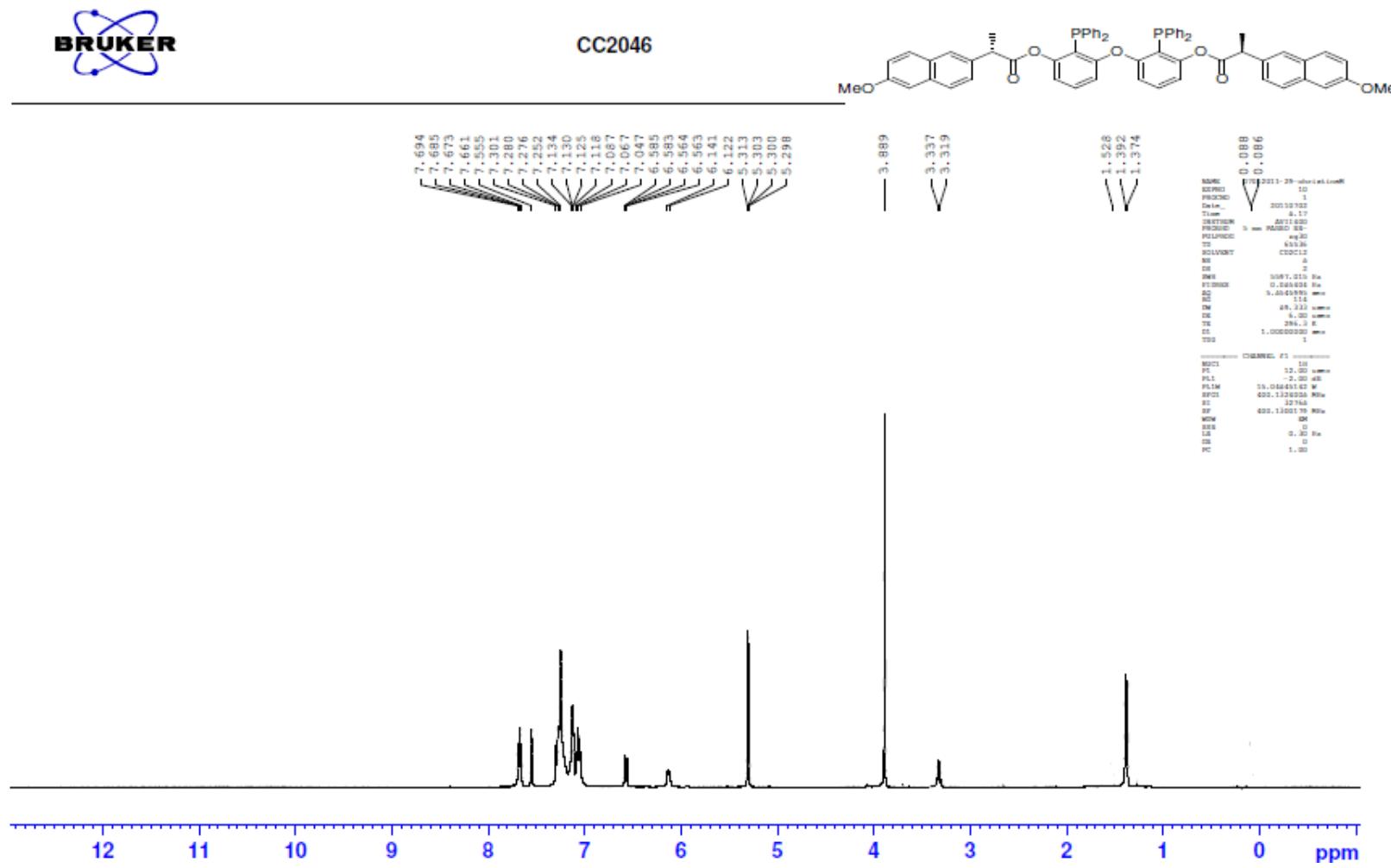
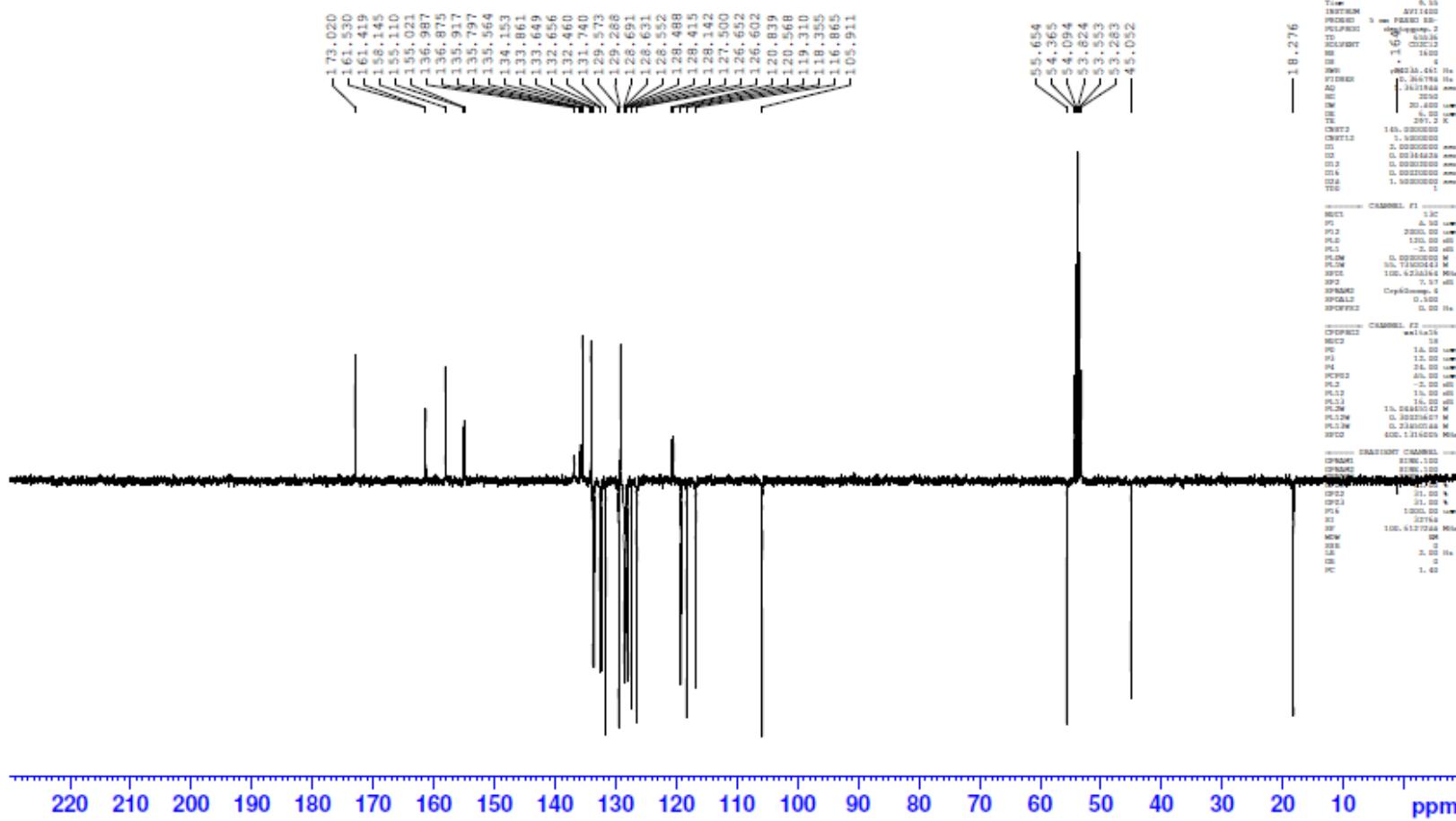
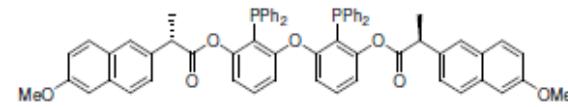


Figure S27    <sup>1</sup>H NMR spectrum of compound 17c (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)



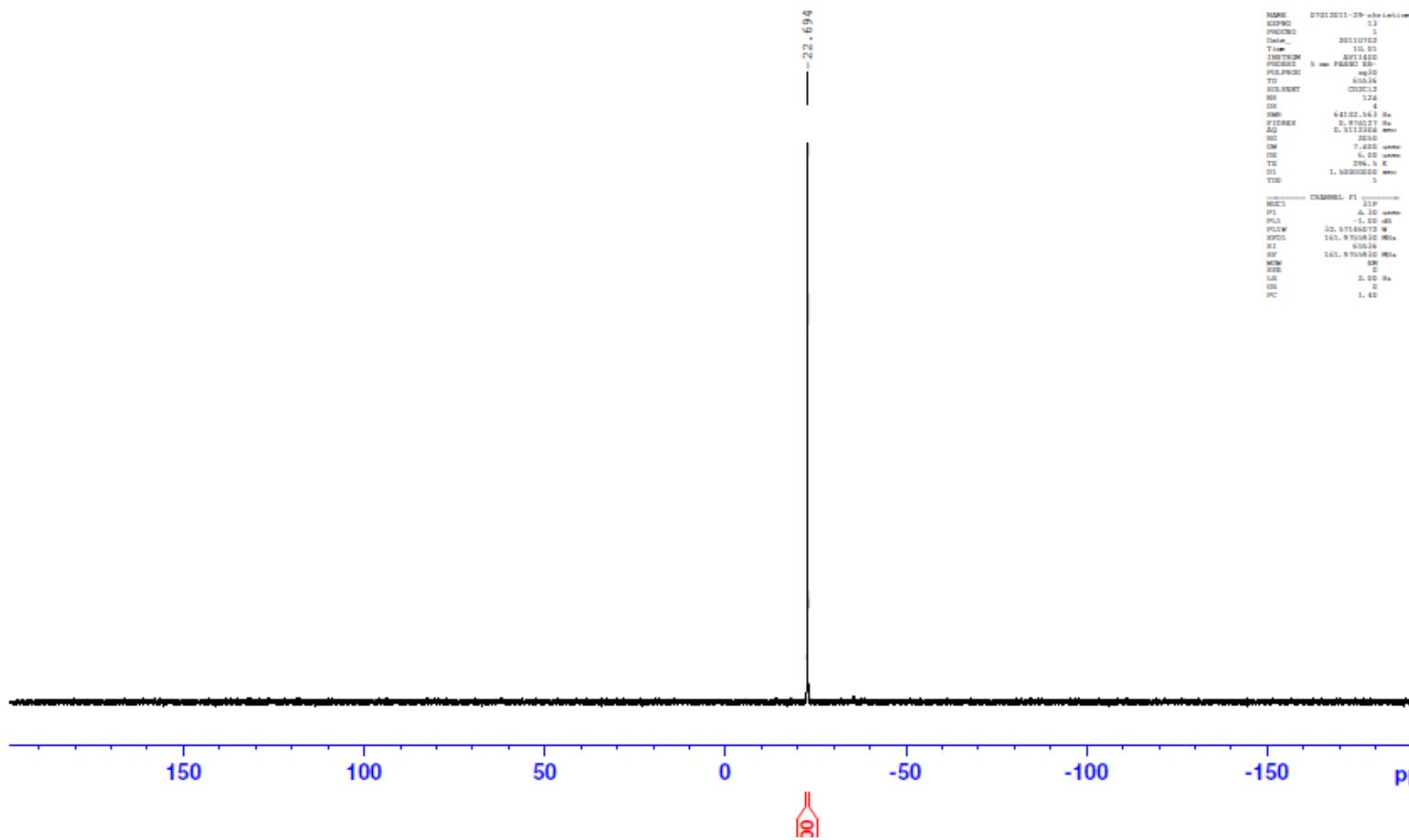
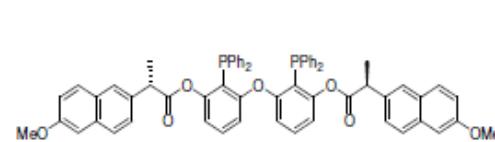
CC2046



**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

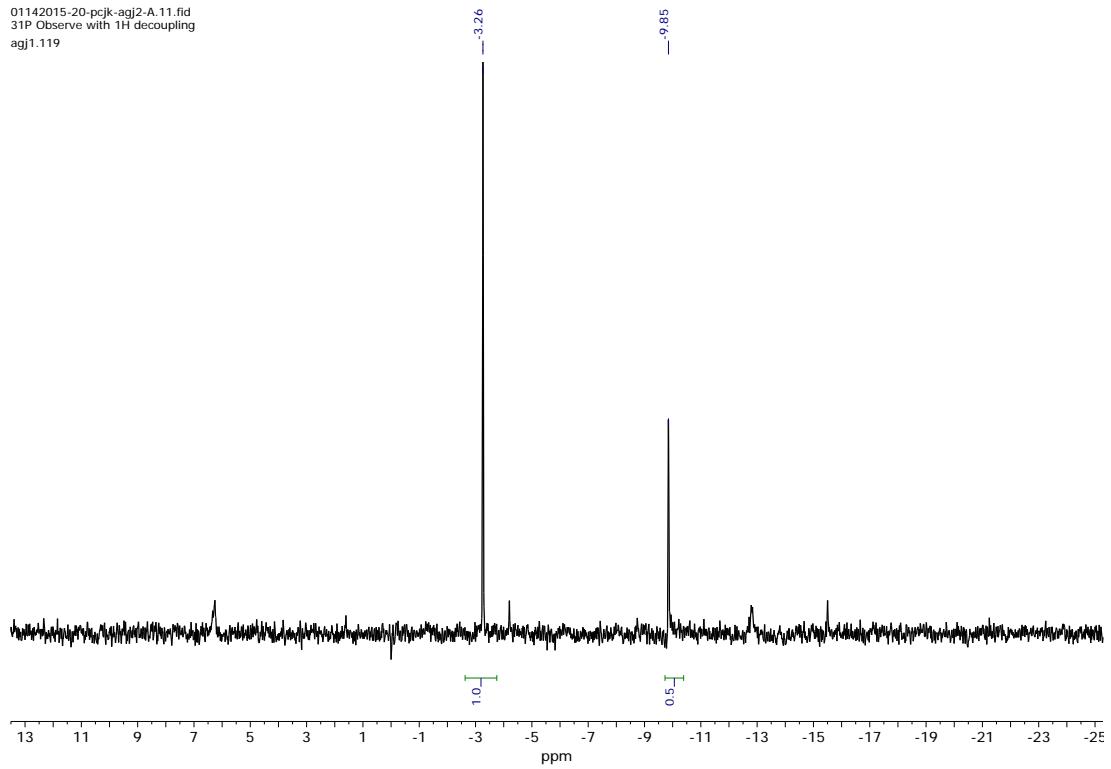
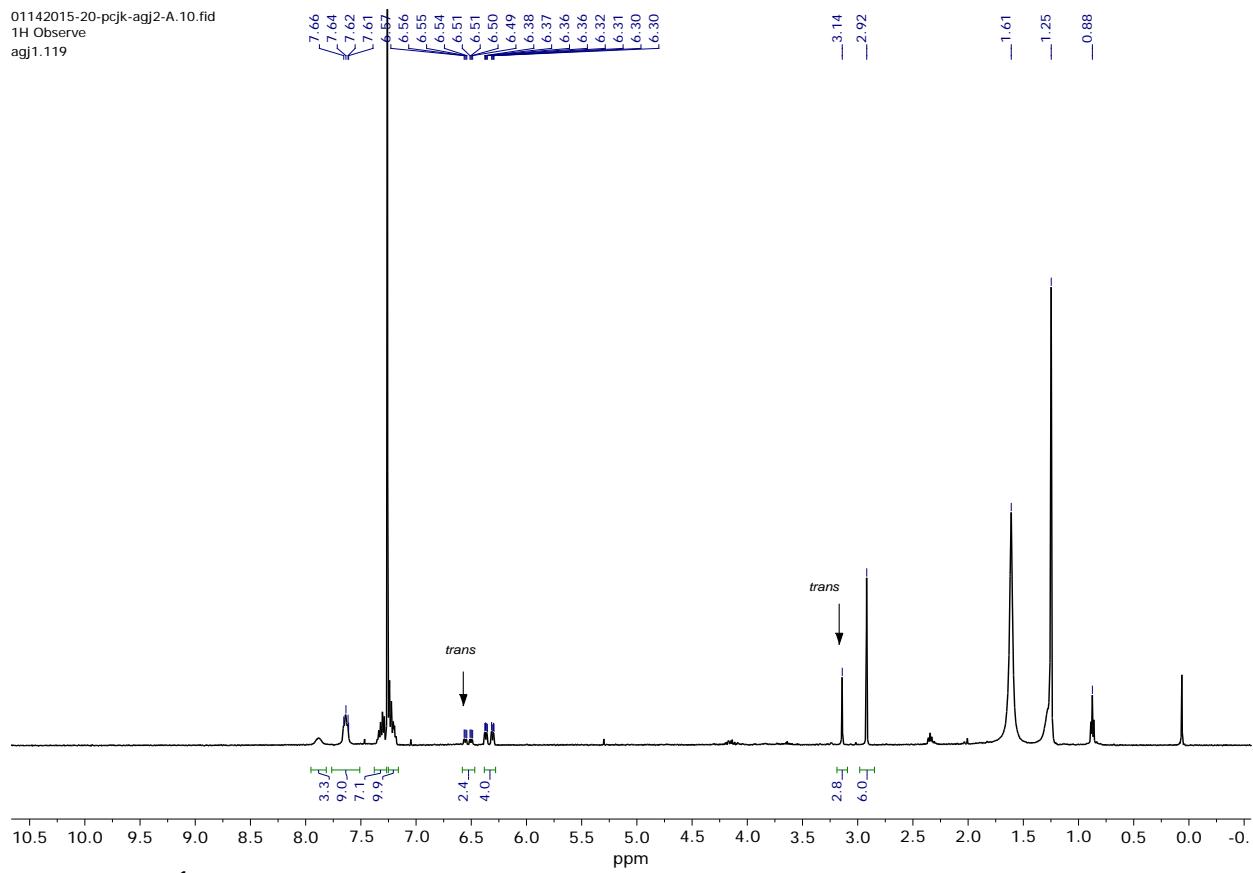
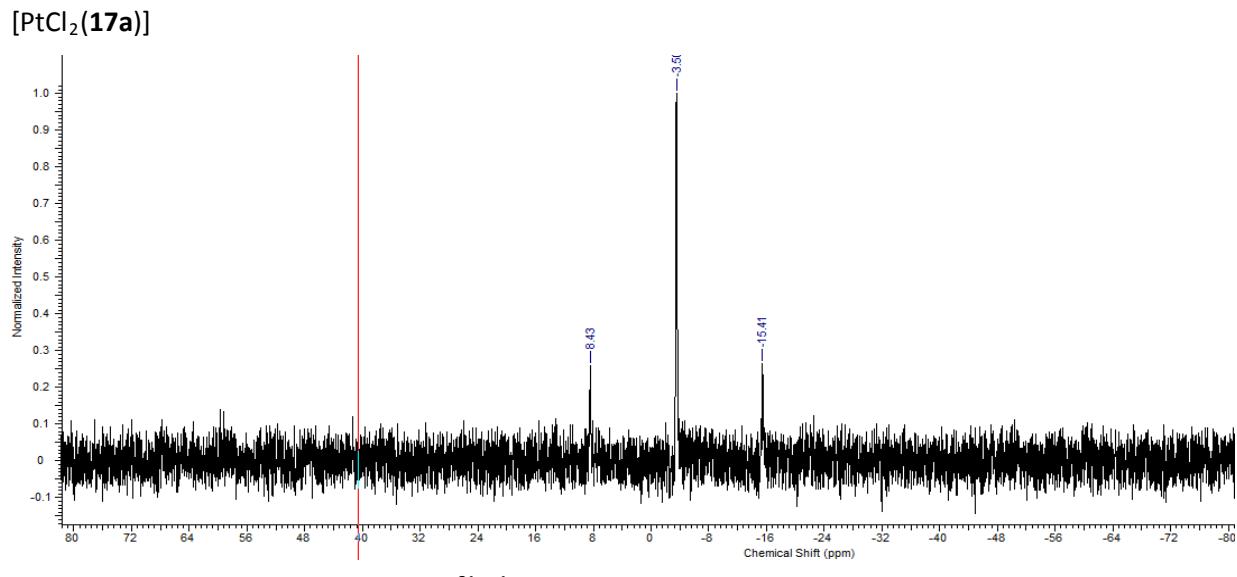


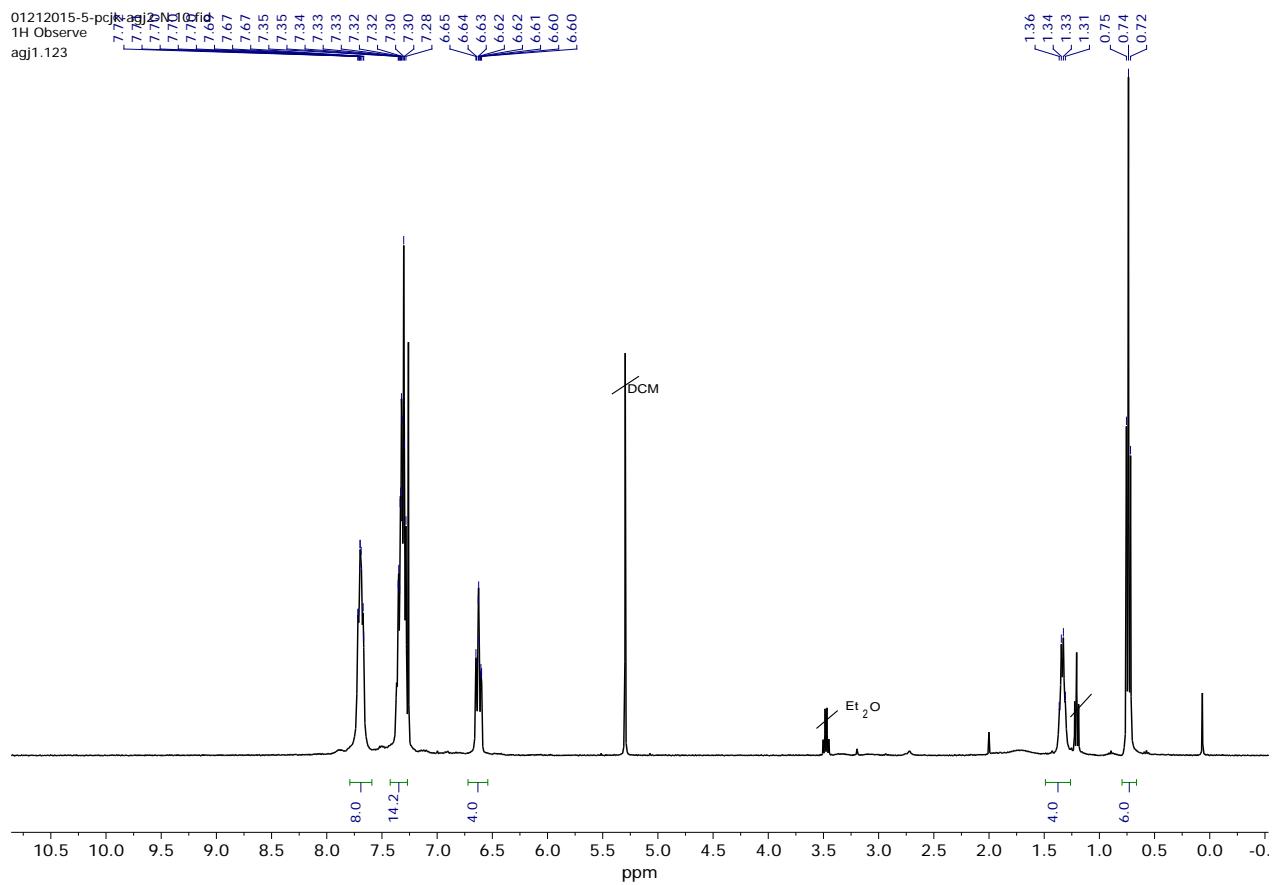
Figure S30: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(15) (202 MHz, CDCl<sub>3</sub>)



**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)]

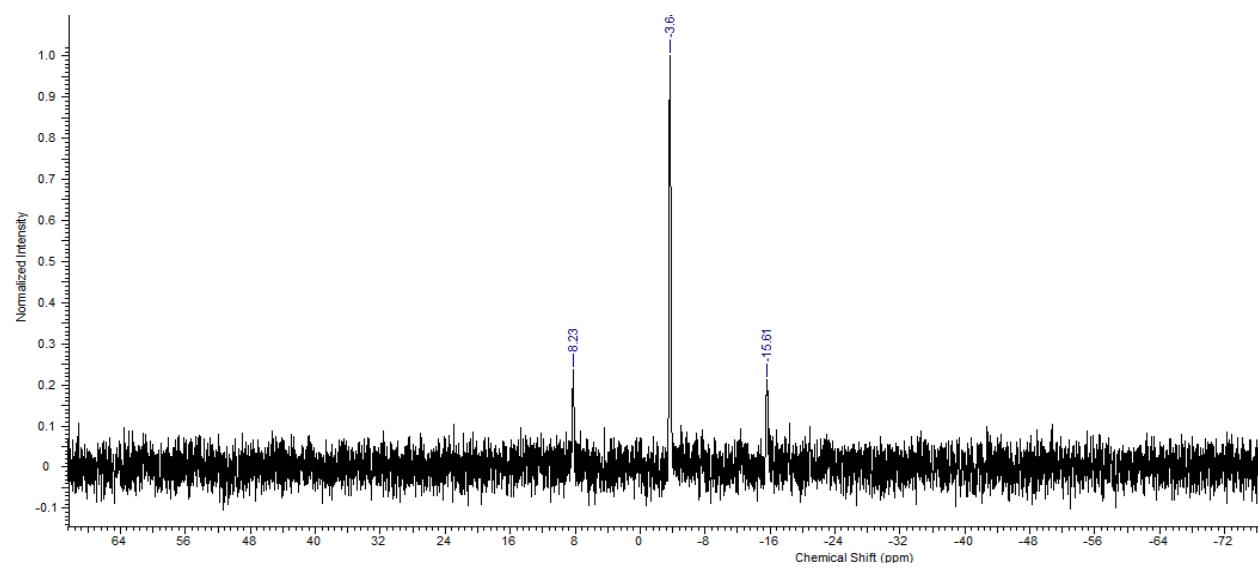


Figure S34: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(17b) (162 MHz, CDCl<sub>3</sub>)

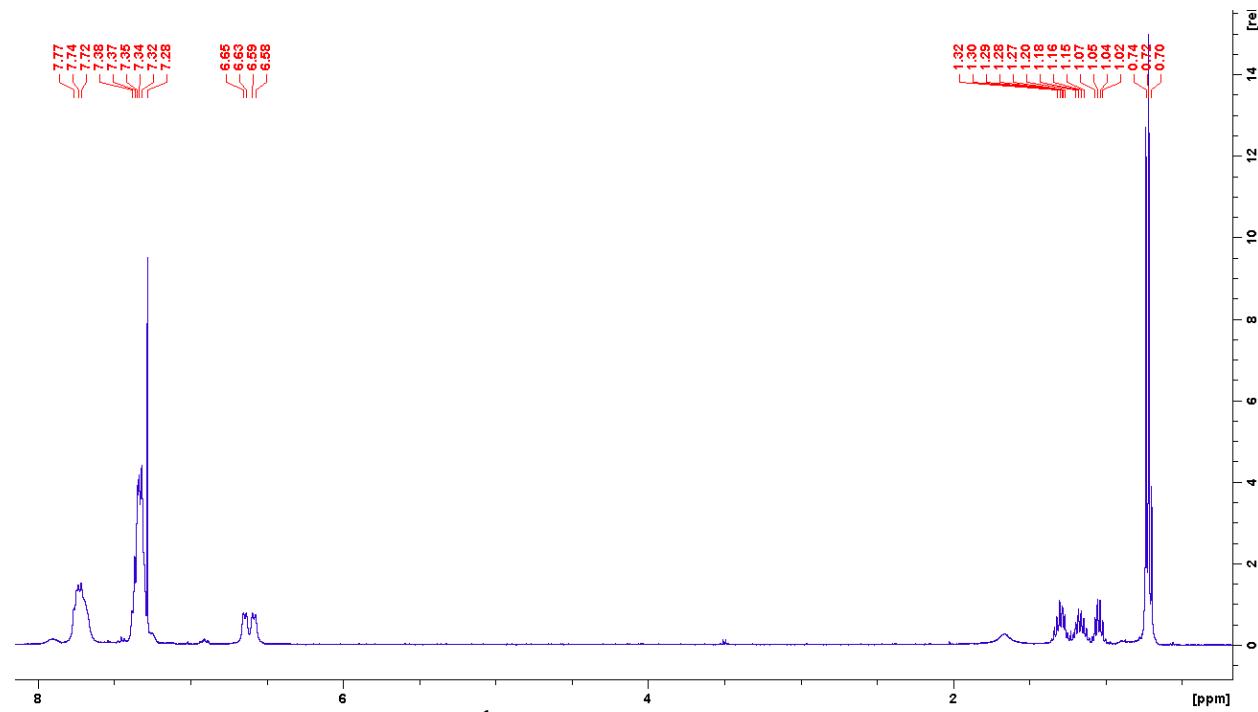


Figure S35: <sup>1</sup>H NMR of PtCl<sub>2</sub>(17b) (400 MHz, CDCl<sub>3</sub>)

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

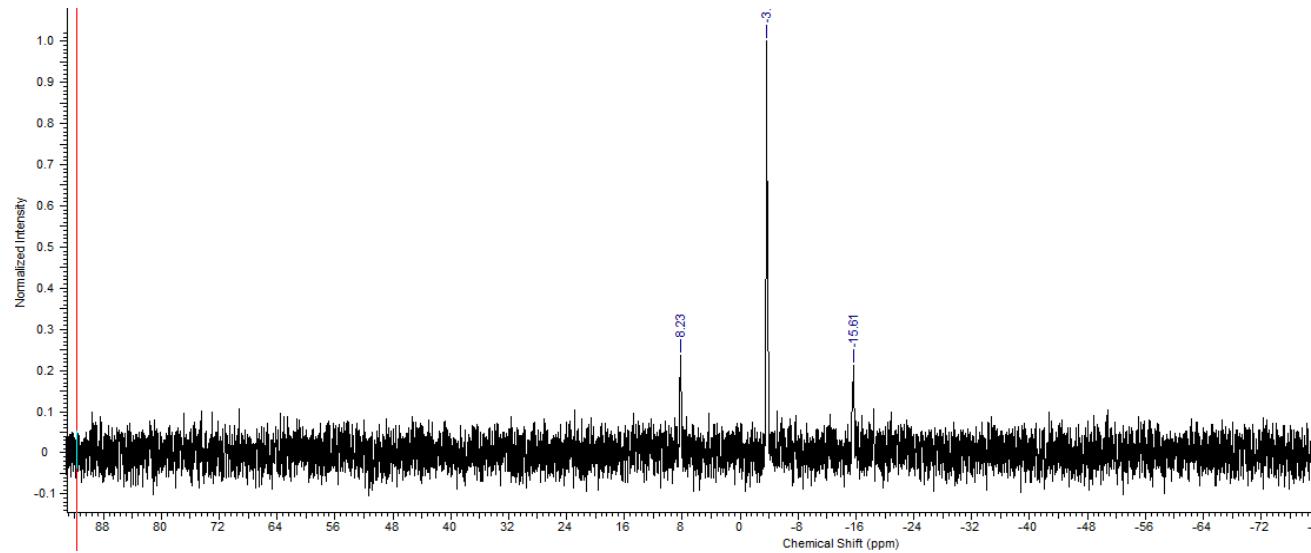


Figure S36: <sup>31</sup>P{<sup>1</sup>H} NMR of PtCl<sub>2</sub>(17c) (162 MHz, CDCl<sub>3</sub>)

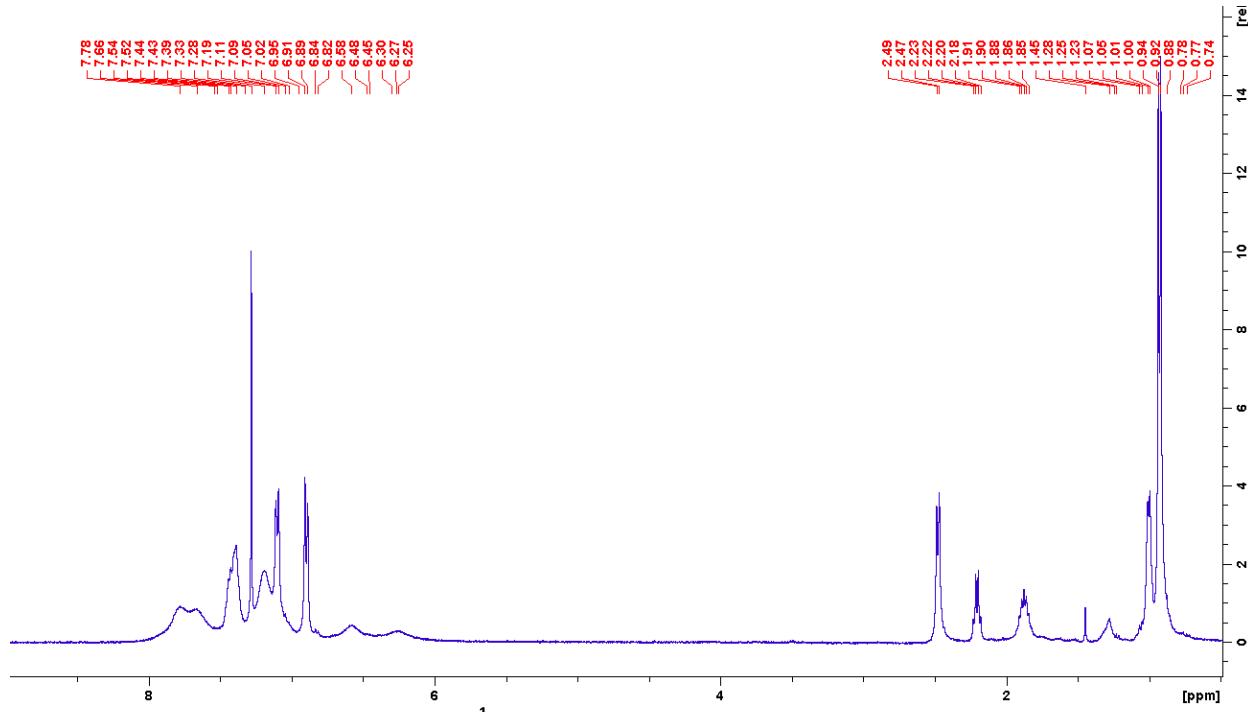


Figure S37: <sup>1</sup>H NMR of PtCl<sub>2</sub>(17c) (400 MHz, CDCl<sub>3</sub>)

## 12- Phosphine selenide compounds

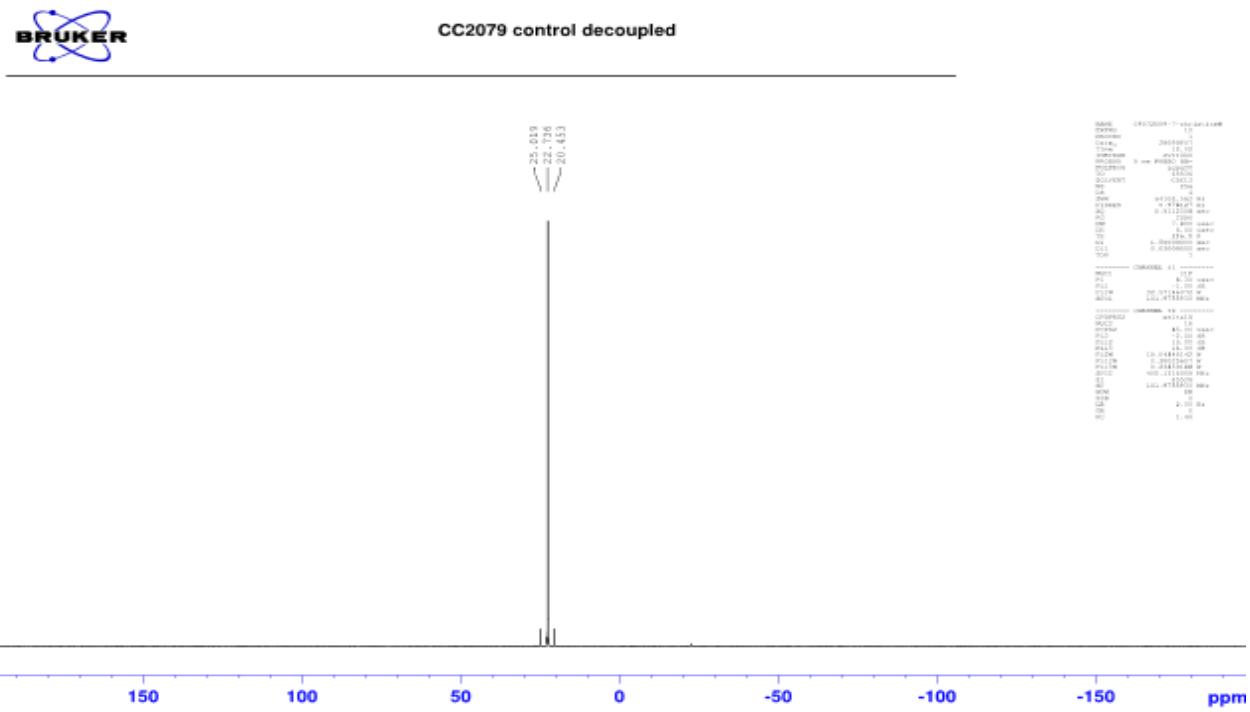
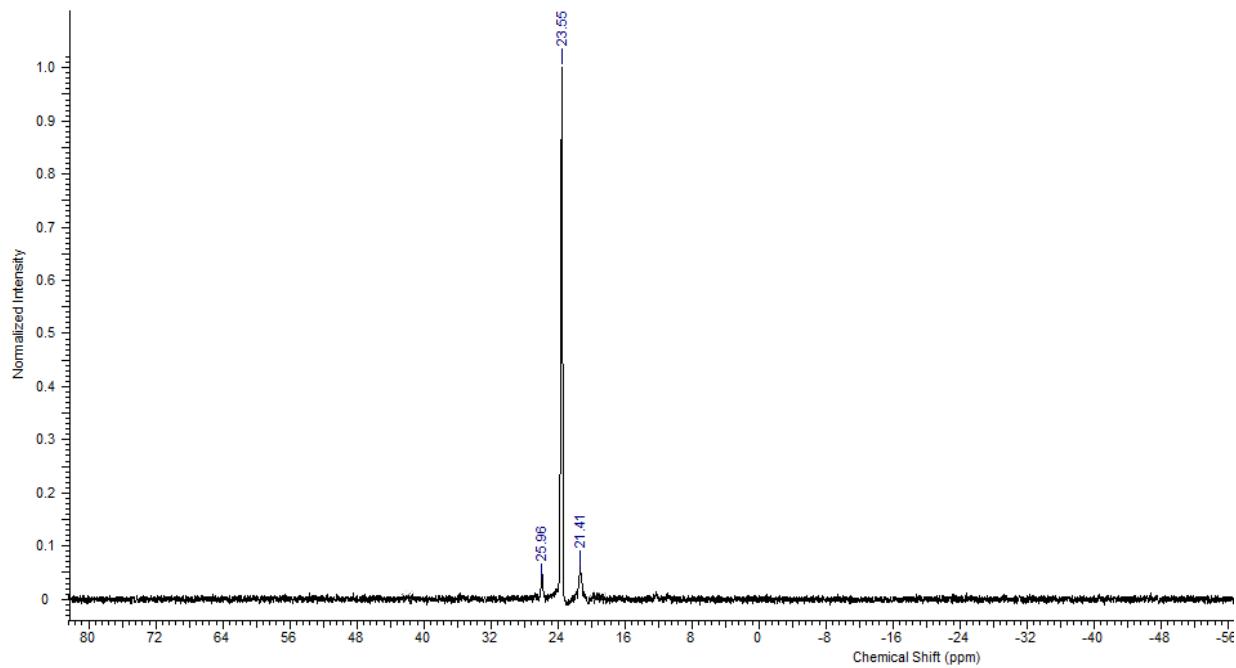
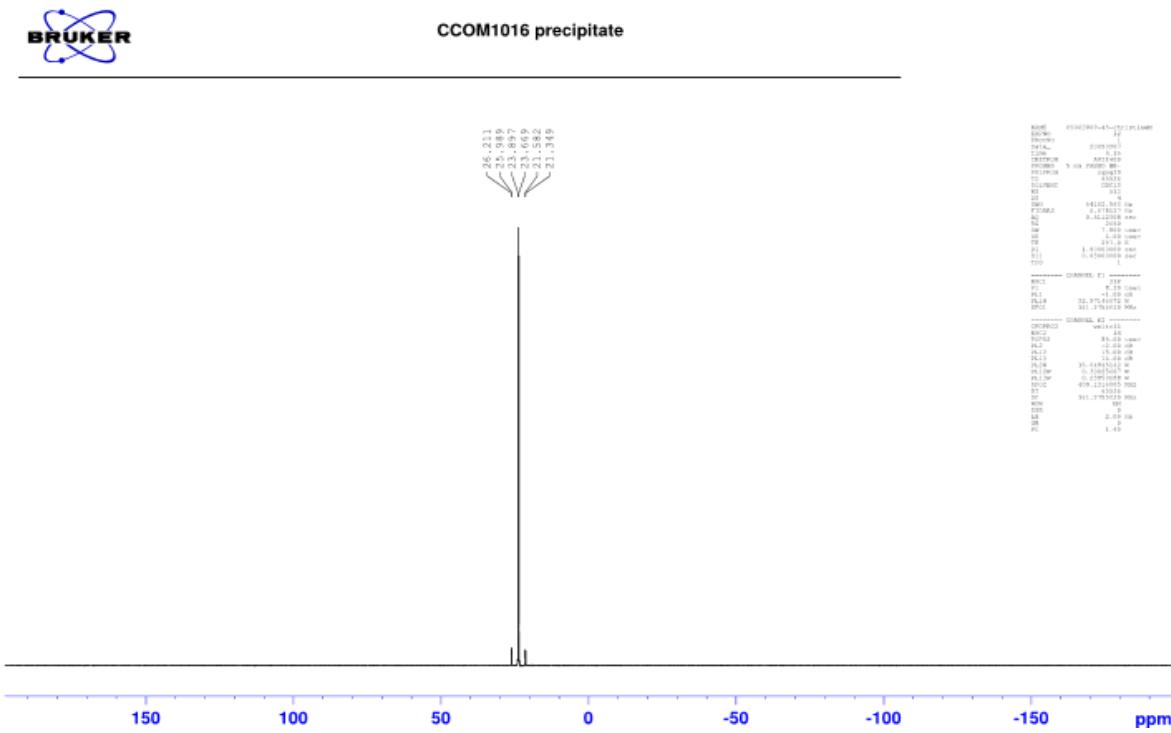
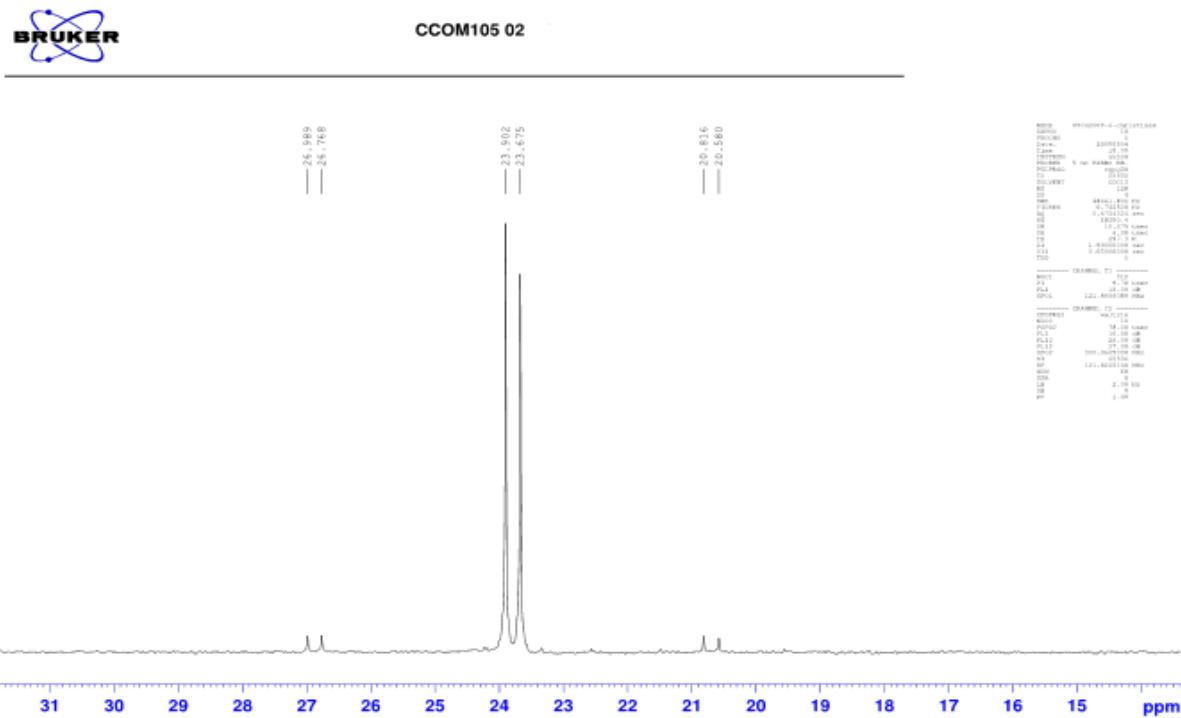


Figure S38      $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of diselenide of 15 (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



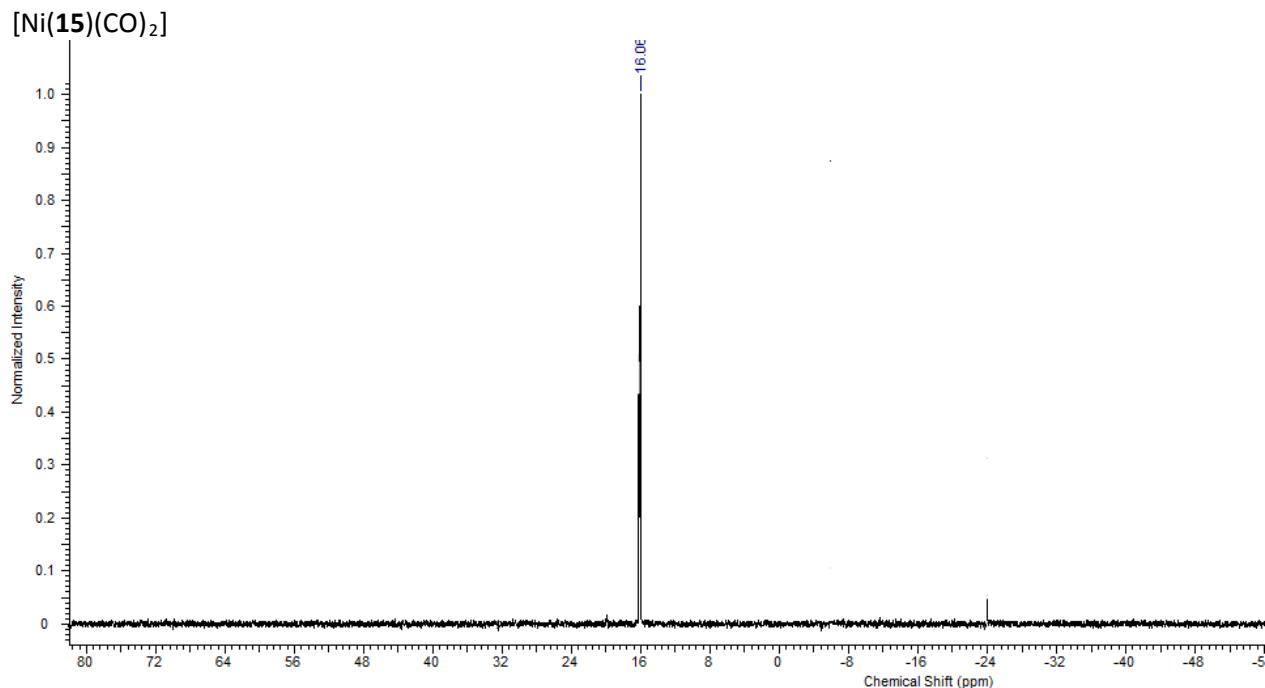
**Figure S39**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of diselenide of **17a** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



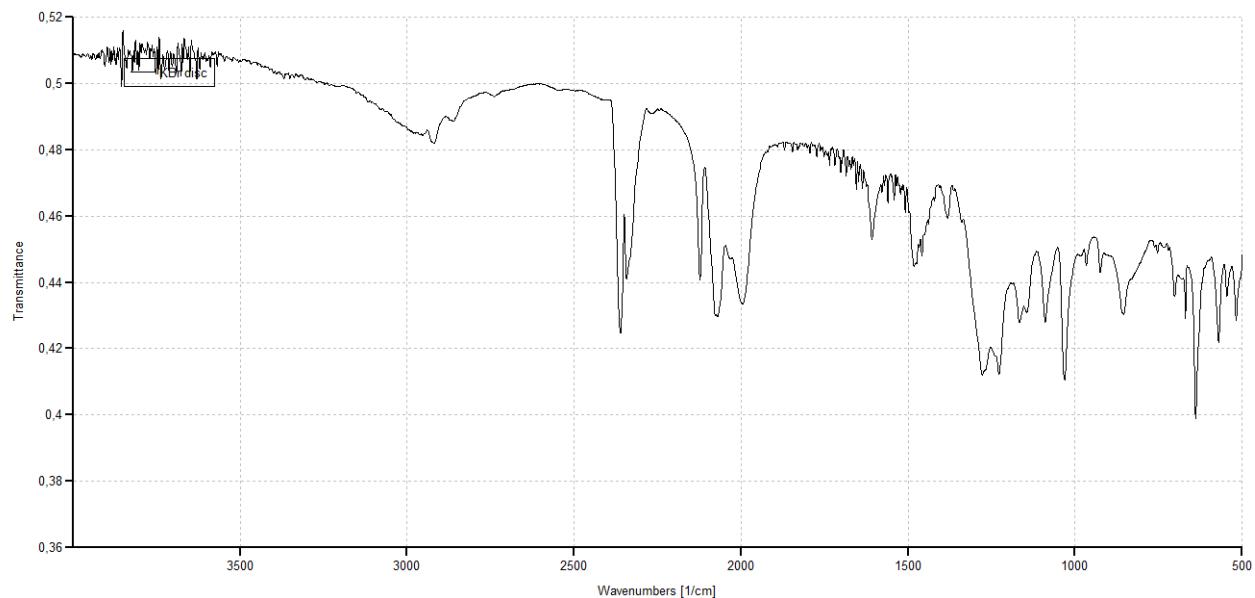


**Figure S41**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of diselenide of **17c** (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)

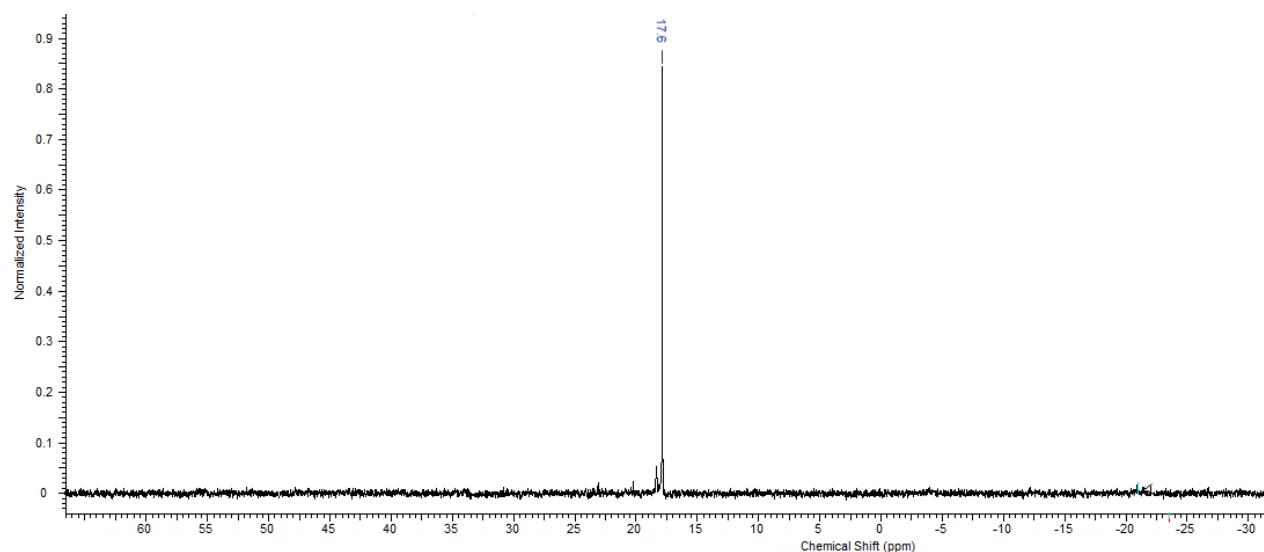
### 13- Nickel complexes



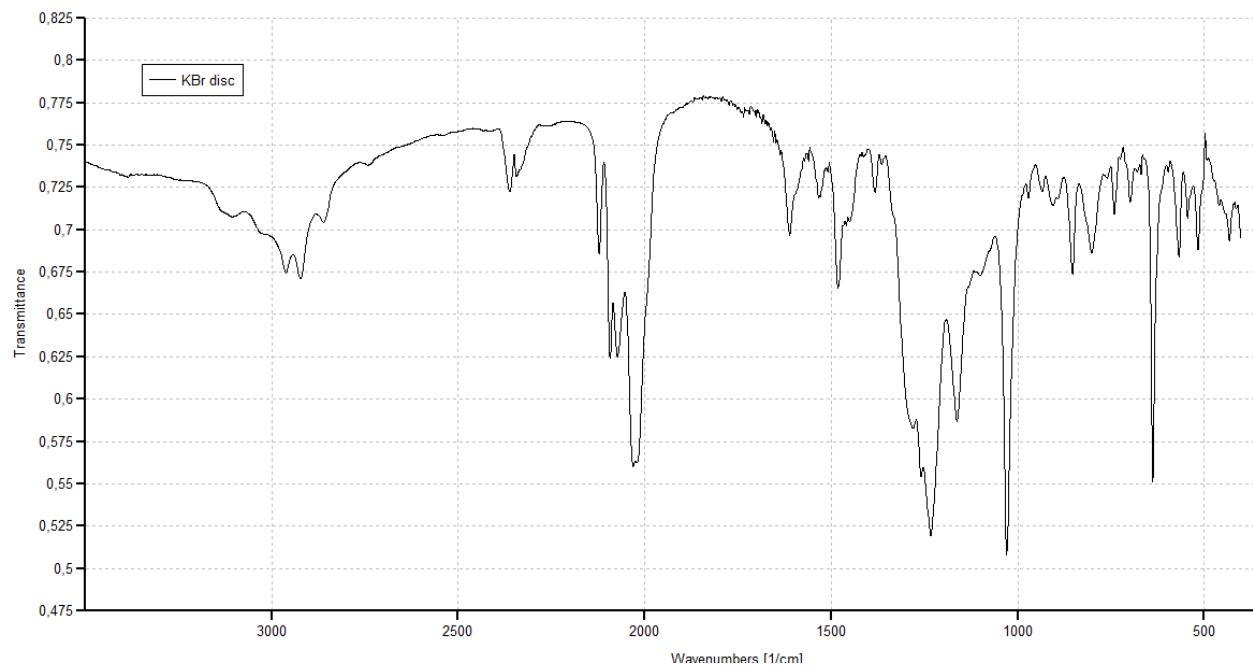
**Figure S42**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(15)(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



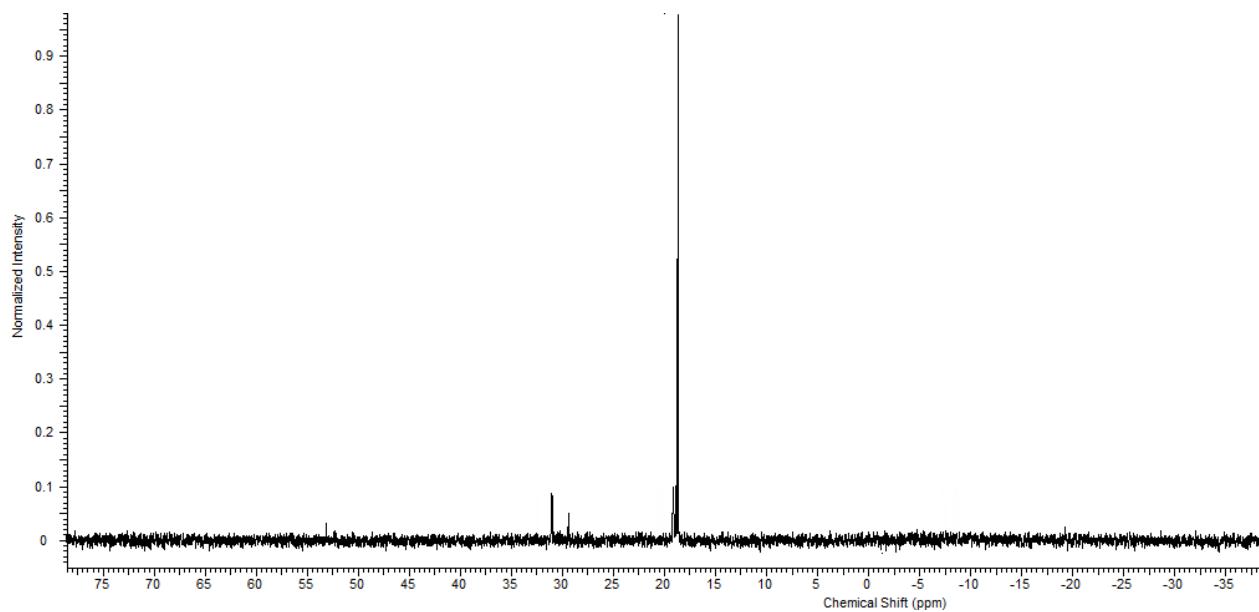
**Figure S43** IR spectrum of  $[\text{Ni}(15)(\text{CO})_2]$  (KBr)



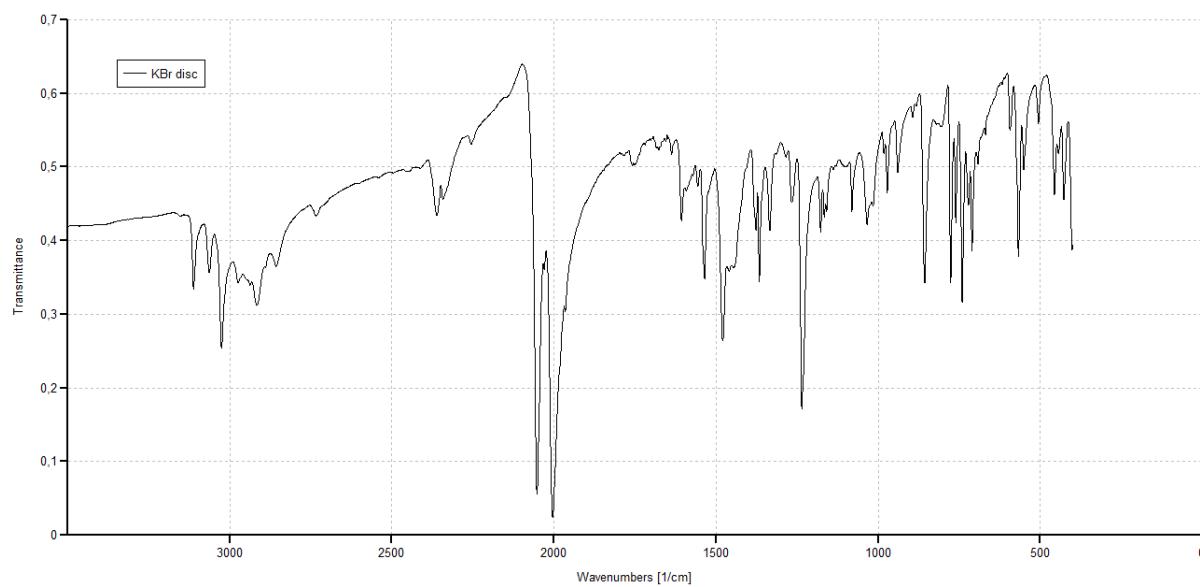
**Figure S44**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{a})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



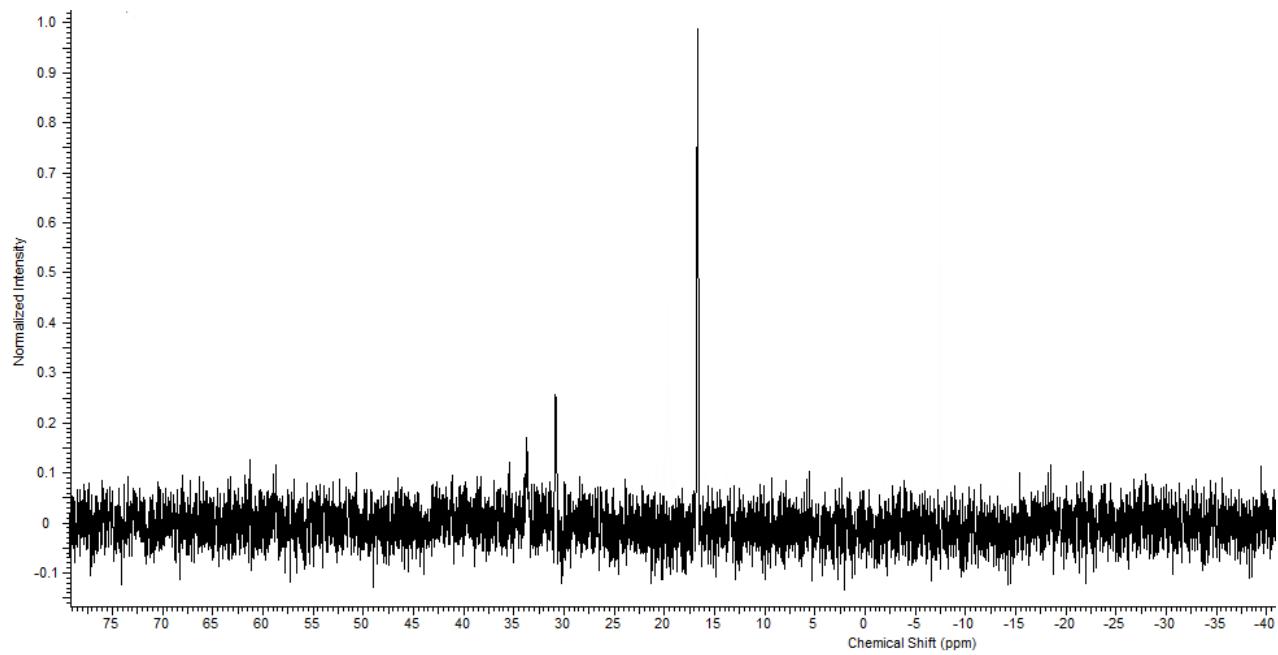
**Figure S45** IR spectrum of  $[\text{Ni}(17\text{a})(\text{CO})_2]$  (KBr)



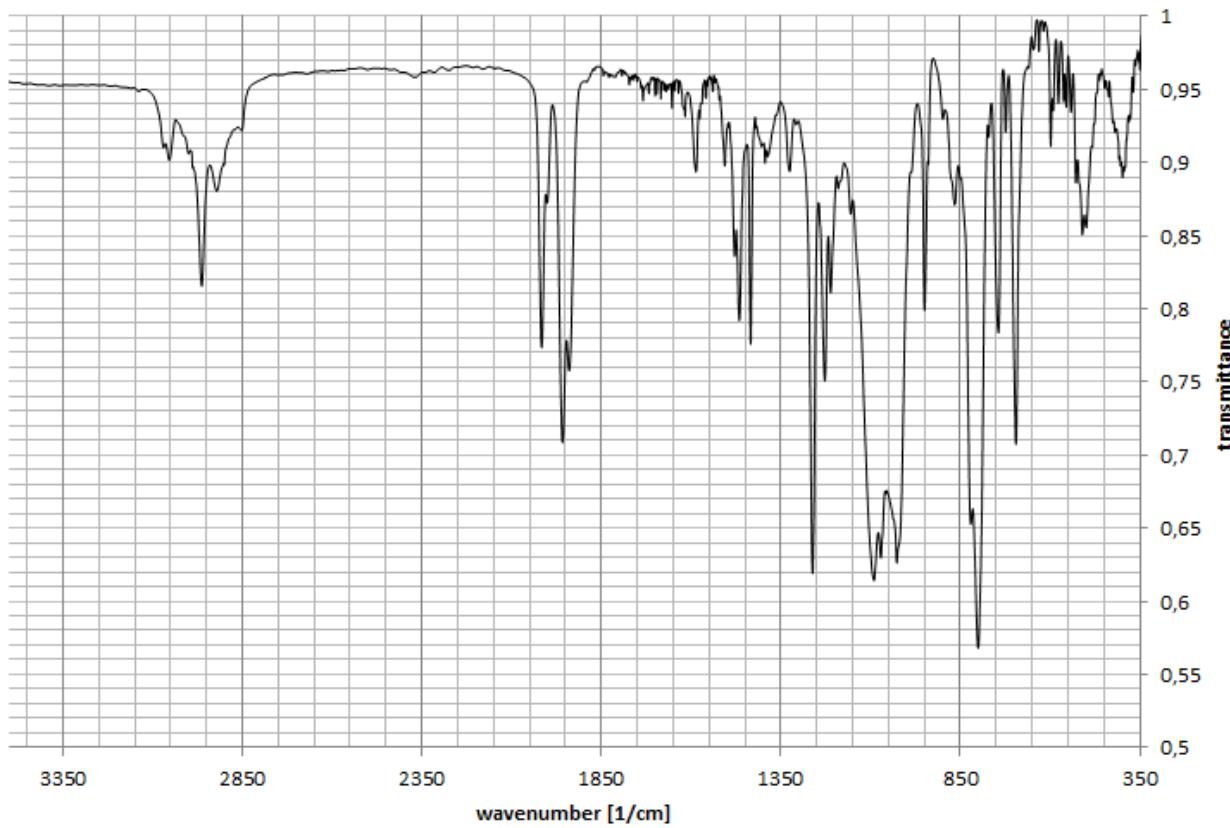
**Figure S46**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{b})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



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

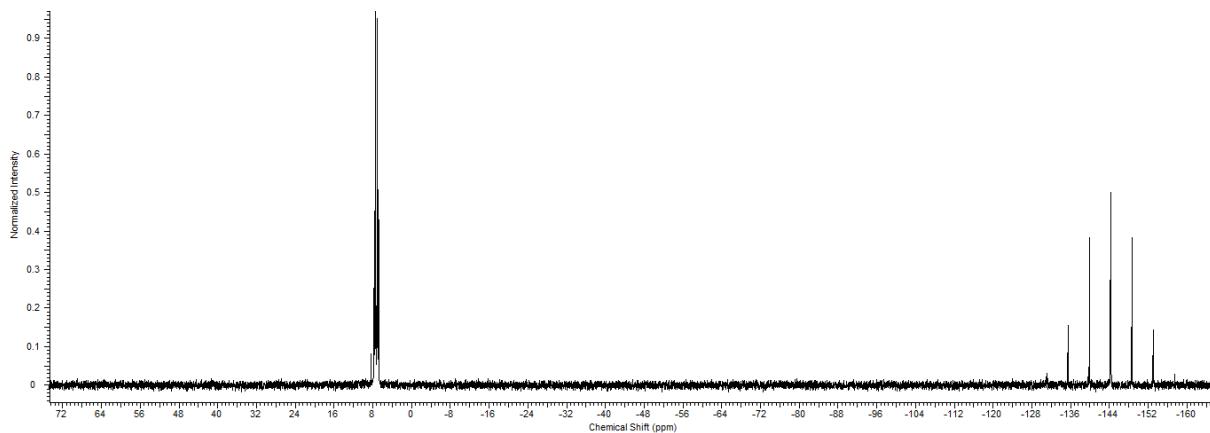


**Figure S48**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Ni}(17\text{c})(\text{CO})_2]$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



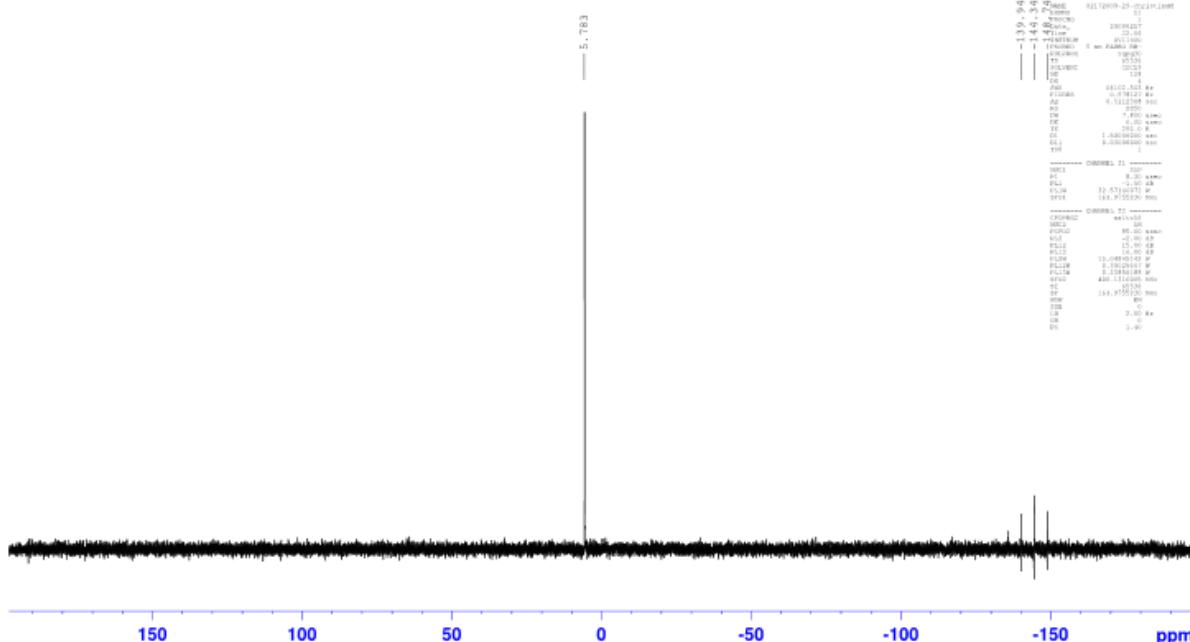
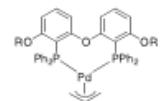
**Figure S49**      IR spectrum of  $[\text{Ni}(17\text{c})(\text{CO})_2]$  (KBr)

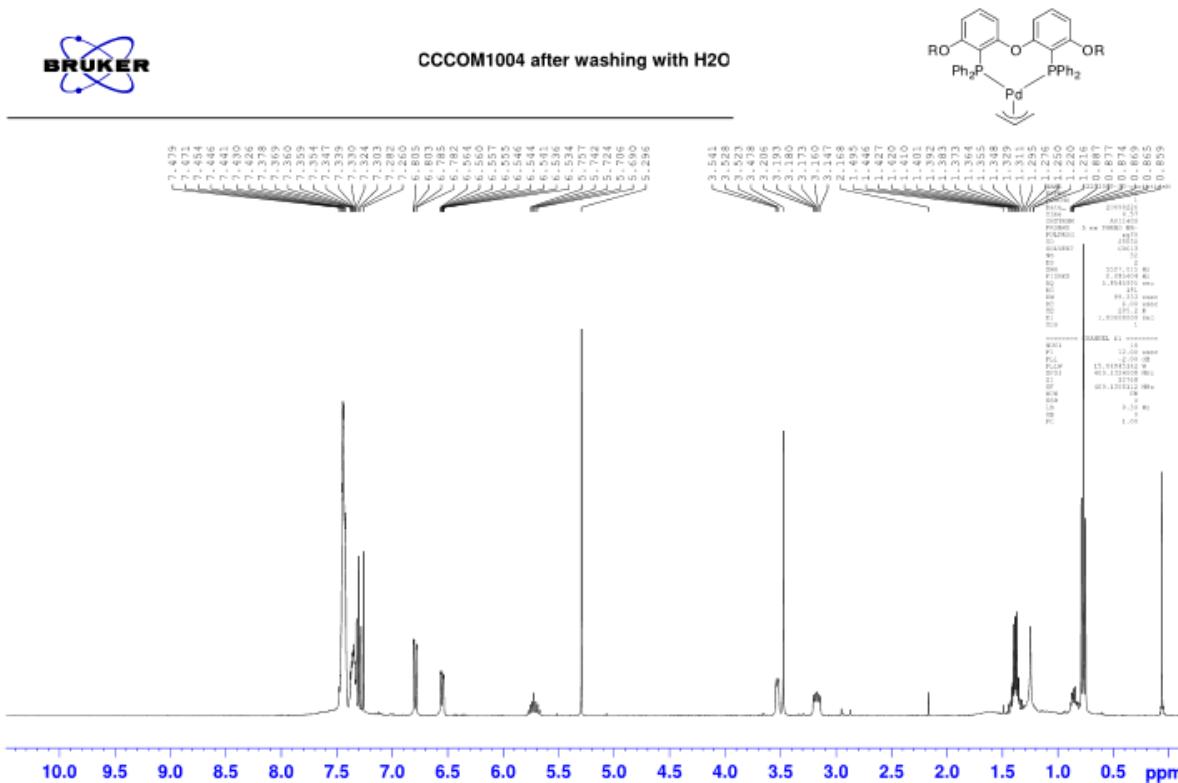
#### 14- Palladium complexes



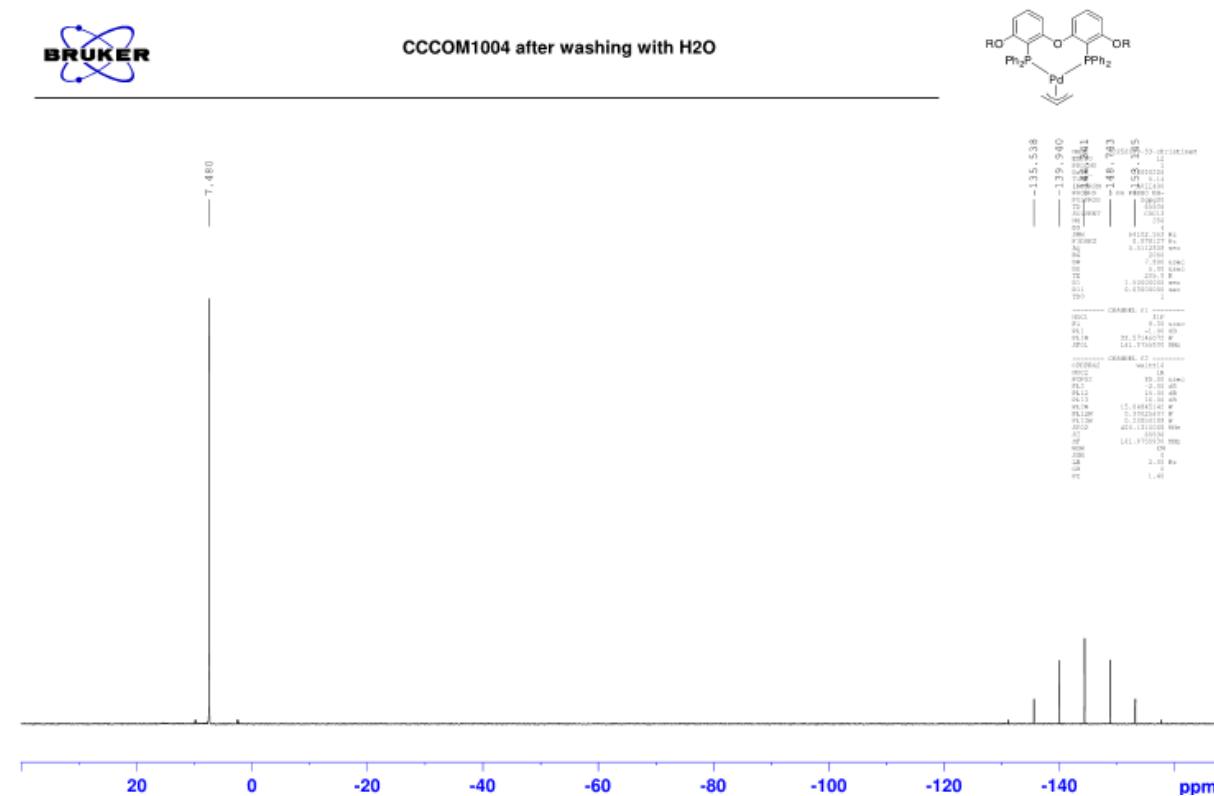
**Figure S50**       $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(14)]^+$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



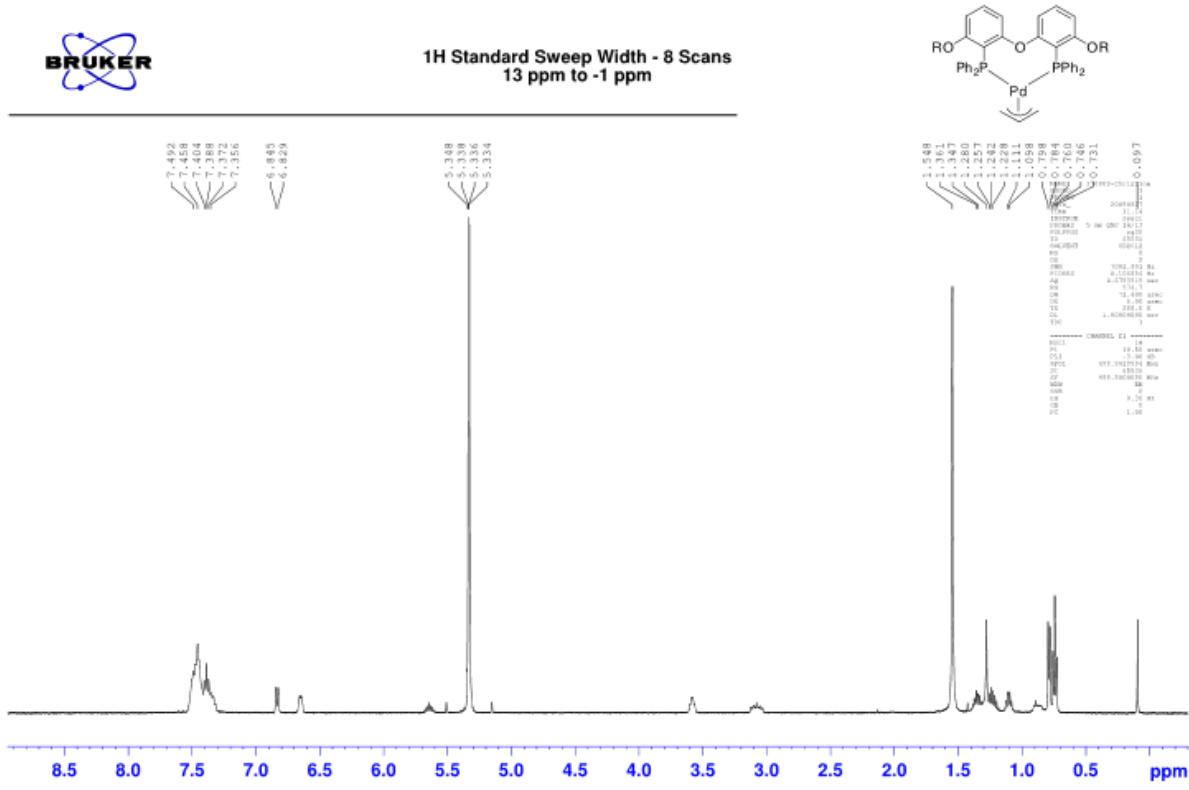
CCCOM1001 after H<sub>2</sub>O washing



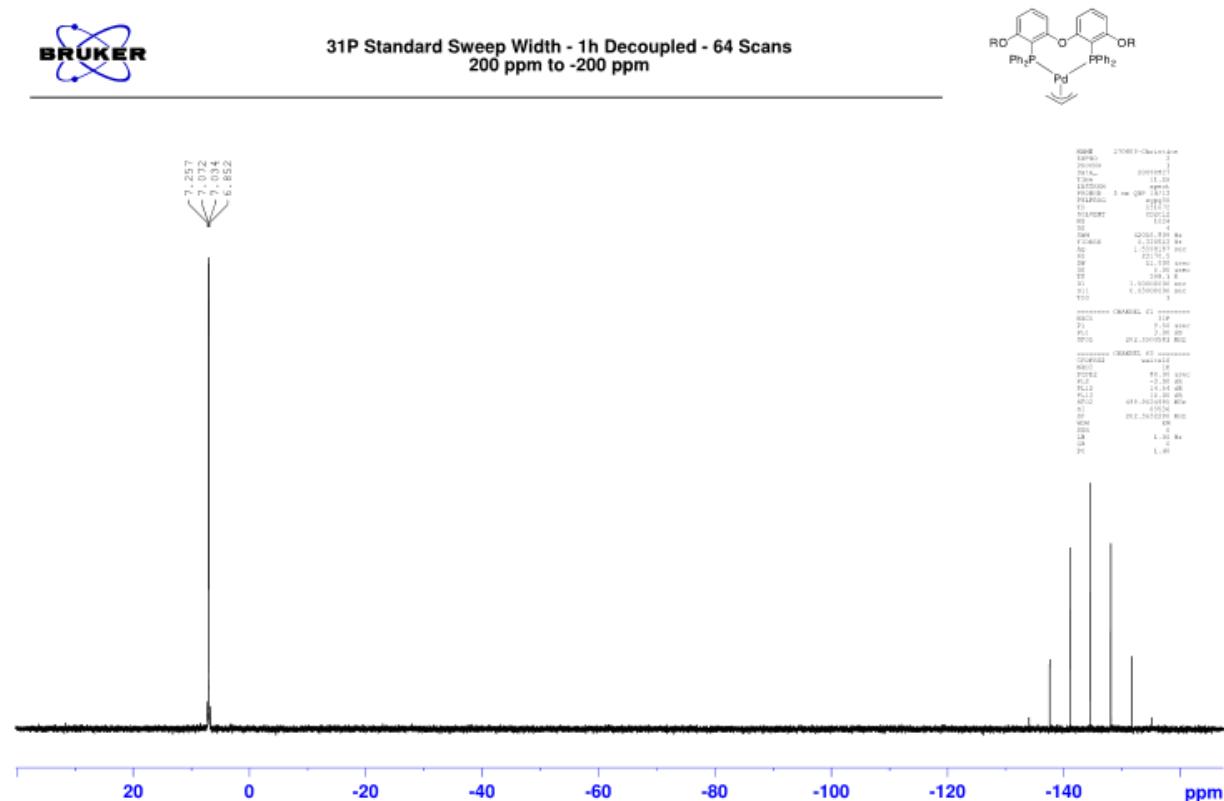
**Figure S55**  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{a})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



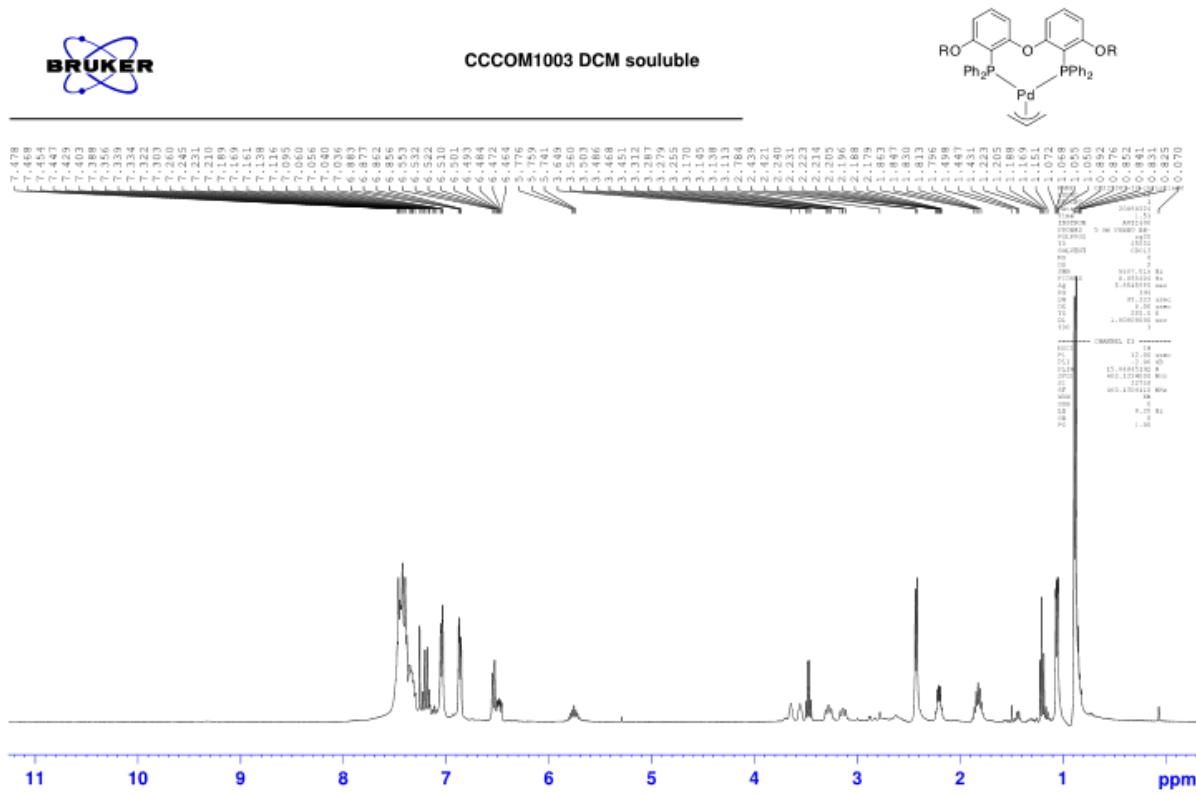
**Figure S56**  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{a})]^\ddagger$  (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



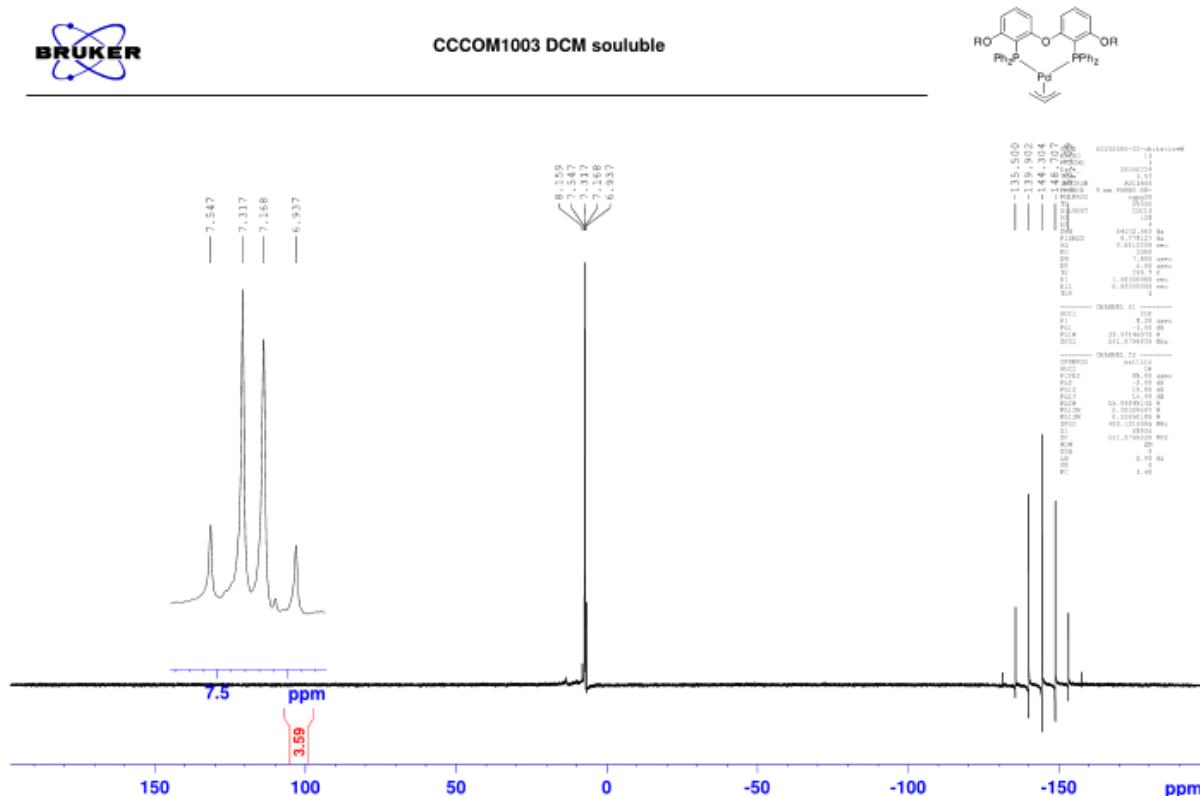
**Figure S57**  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{b})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



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



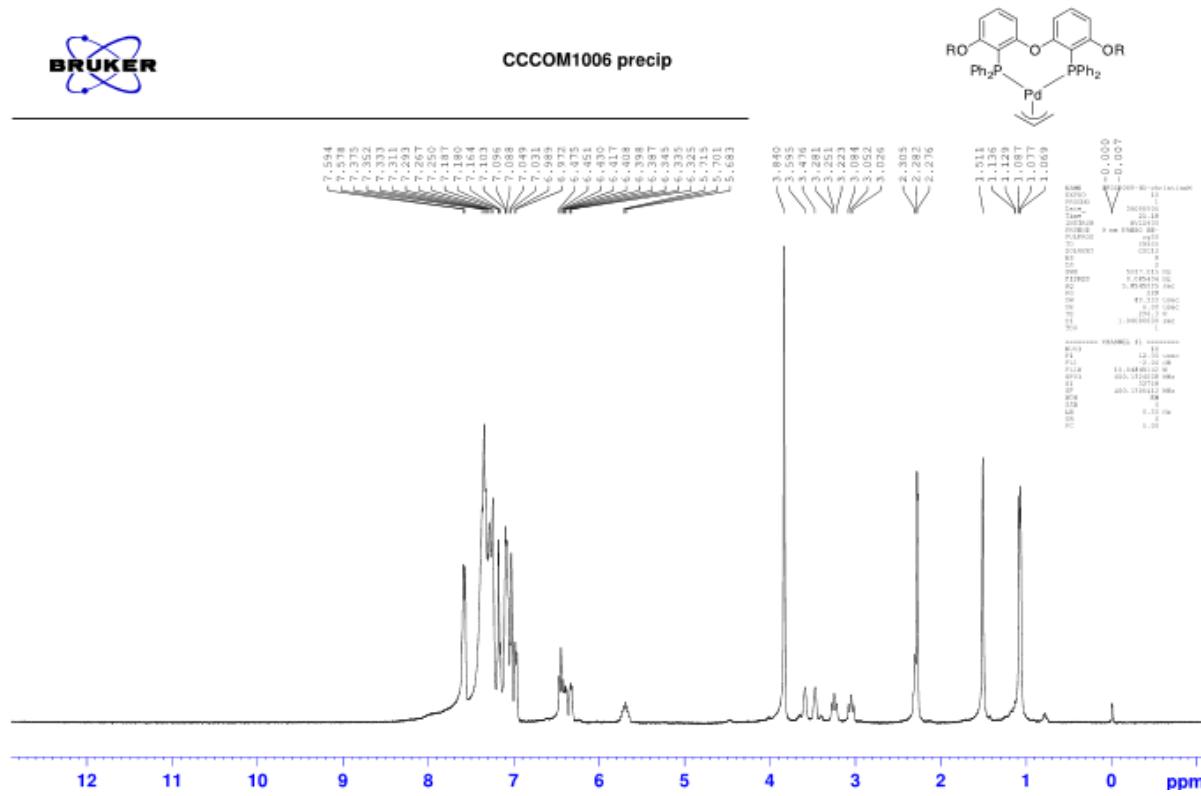
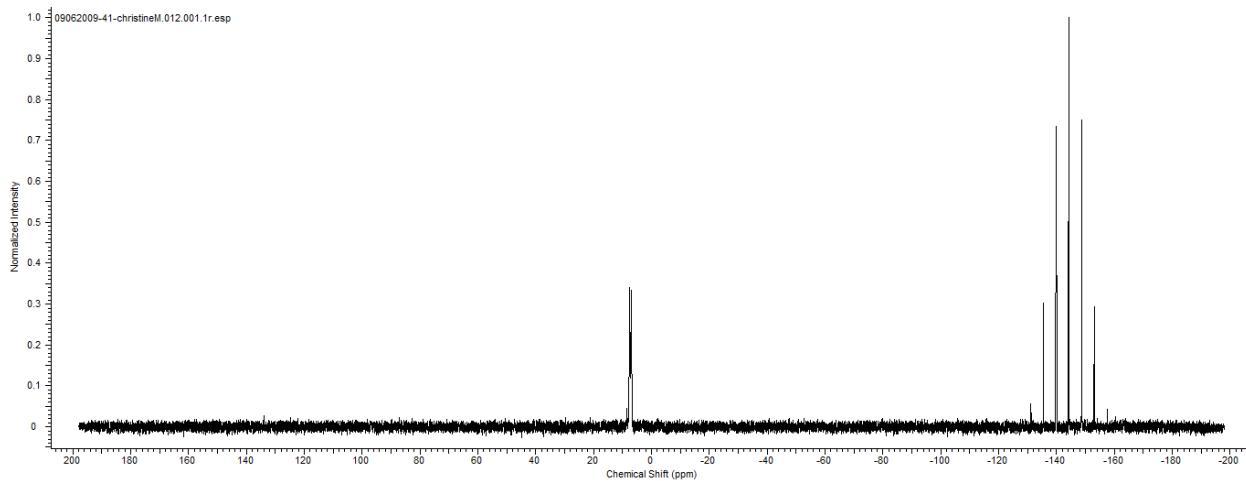
**Figure S59**  $^1\text{H}$  NMR spectrum of  $[\text{Pd}(\eta^3\text{-allyl})(17\text{c})]^+$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 297 K)



**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)



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Figure S61      <sup>1</sup>H NMR spectrum of [Pd(η<sup>3</sup>-allyl)(17d)]<sup>+</sup> (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)Figure S62      <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [Pd(η<sup>3</sup>-allyl)(17d)]<sup>+</sup> (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K)